Paint and Coating Testing Manual

15th Edition of the Gardner-Sward Handbook

Joseph V. Koleske
Editor

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Paint and Coating Testing Manual

Fifteenth Edition of the Gardner-Sward Handbook

Joseph V. Koleske, EDITOR

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Introduction

PAST TO PRESENT

The previous edition of this manual, the 14th, described in detail the changes that took place in the coating industry from the early 1970s to the early- to mid-1990s. Published in 1995, the 14th edition classified powder coating, radiation-cured coatings, and higher-solids coatings as new, with a potentially reasonable growth curve. It noted that at the time, all liquid coatings were at higher solids content (lower volatile organic solvent content) than in the 1960s when Rule 66 came into being. Powder coating and radiation curing were sufficiently new enough that chapters related to testing them were not included in the manual. High-solids development still struggled with the difficulties of decreasing molecular weight for low viscosity purposes and achieving the low molecular weight with functionality on all molecules that quality coatings require. However, the solids level has increased in solvent-based coatings and achievements have been realized in decreasing volatile organic content (VOC).

Since that time, powder coating has exploded. Today the technology is well established, has a significant share of the coatings market, is internationally accepted, and has a strong technical society that aids in future growth. To illustrate the widespread acceptance of powder coatings, one merely needs to look at advertisements. Outdoor metal furniture advertisements, for example, proudly include words that imply quality and durability—that is to say, "powder-coated finishes."

Of course, such furniture certainly is not the only commercial outlet for powder coatings. Applications include lighting fixtures, tubing and aerosol cans, automobile and bicycle wheels, rebars, store fixtures, agriculture and construction materials, and on and on. Initially, colors and color changeovers were considered to be a major obstacle to powder coating development, but today a broad variety of colors is available, including many metallic and special effect finishes with abrasion resistance, brilliance, and overall high quality. Powder coating provides quality, economy in manufacturing space, increased production, energy usage reduction, and other facets important to product development and sales in today's marketplace.

As with powder coating, radiation curing of coatings with either ultraviolet or electron beam radiation is no longer a new process. This technology also has been experiencing strong growth since the last edition of this manual. It is the technology in which, through an *in situ* means, a low viscosity liquid system is converted into a polymeric film or coating directly on a substrate that can be varied in nature—i.e., metal, wood, plastic, composite structures, etc. In effect, the originally liquid system is instantaneously converted into the final high molecular weight, cross-linked coating. Radiation curing of liquid systems is not limited to coatings, and it is growing in the printing ink and adhesive areas. It is considered to be "green" technology, is well established in the marketplace, has garnered a significant portion of the total coatings market, has a strong technical society dedicated to it, and is internationally accepted.

Radiation-curing technology has many facets that will ensure future growth. Harbourne[1] has pointed out that over and above the usual advantages behind ultraviolet radiation curing technology—energy conservation, usage efficiency, and environmental conservation—its driving force is the fact that the UV process has enabled production and development of products that could not have been achieved with earlier existing technologies. Such products include flexible electronics for energy storage and circuit development, polymeric solar cells, printable electronics, medical devices, touch screens, optical films, and on and on. In the area of solar energy, highly efficient organic photovoltaic cells are being developed that are thinner and lighter in weight with significantly decreased production costs. Such cells are used in emergency power generation, lighting, and outdoor power generation. New smart materials with self-healing properties will provide overall cost savings through high value-added finishes on a variety of substrates. Solvent-based, high-solids coating systems continue to be developed. Such coatings have markedly decreased volatile organic content and provide high quality coatings and reduced environmental damage.

FUTURE

As described above, powder and radiation-cured coatings have been experiencing excellent growth over the past decade or so, with each technology growing on its own merits. More recently, a combination of the two technologies—UV–Curable Powder Coatings—has very good growth potential. New opportunities for the combination are due to the same benefits mentioned above—economic, environmental, process, energy savings, and increased productivity.[2] The combination is meeting the less expensive, more rapid, and high quality challenges required by the demanding customers of today. The coatings are being used on medium-density fiberboard, plastics and other heat sensitive substrates, composites, and preassembled parts including completed items. Preassembled items often contain a number of different materials such as electronic components, gaskets, rubber seals, and the like--all of which are heat sensitive in nature. The ability to coat and cure such combinations with systems based on the combined technologies results in less thermal damage to the sensitive materials and thus greater efficiency and productivity along with cost savings.

Nanotechnology is a field of emerging technology that may hold great promise in the future for the coatings, inks, and adhesives industry and certainly for a broad variety of other industries. Nanotechnology has broad implications

[1] Harbourne, A. D. P., "The Evolution of UV Photopolymerization in Global Industrial Manufacturing Markets and the Promising Outlook for the Future of the Technology," *The 31st International Congress on Imaging Science*, Beijing, China, pp. 013–015 (2010).

[2] Schwarb, Ryan and Knoblauch, Michael, "New Opportunities for UV-Curable Powder Coatings, " *Coatings World*, Volume 16, Number 5, pp 43-48 (May 2011).

for new products and there are multi- and interdisciplinary efforts in progress. The technology deals with science on the nano, or one billionth-size, scale. Nanometer "particles" are 0.000000001 meter or 0.001 of a micrometer in size. Within the technology, an assembler or molecular manufacturing technique is used to position molecules through chemical reaction or interaction into new products or existing products with enhanced properties. Although the term "nanotechnology" was initially used to define efforts conducted on a molecular scale, currently the term has taken on a loose connotation for anything that is very small where small means something that is most usually smaller than a micrometer. Many examples of nanometer-designed products exist and a few of these are given below.

Recently a plant was built of produce carbon nanotubes[3]. Such tubes in combination with aluminum result in new lightweight, high strength composite materials that have promise in the energy, electrical, and computer industries. In another area, a multilayered, polymeric nanocomposite has been devised and it is thought to have the potential to make a self-healing paint.[4] In this technology, emulsion polymerization processes are used to develop a polymeric product that is covered with a silica-based layer of nanoparticles. Nanocomposite coatings for fabrics have also been described[5]. These coatings improve gas barrier properties as well as enhance mechanical characteristics.

Another area that is receiving attention is additives for coating formulation. An additive that improves properties of water-based metal coatings has been described[6]. Although the additive is not chemically described, it is said to increase crosslink density and thereby various mechanical properties of cured films. An additive to accelerate the radiation-curing process is a small particle-sized version of nepheline syenite that is prepared by a micronizing process[7]. The micronized, ultra-fine form of this combination mineral—soda feldspar, potash feldspar, and nepheline--is said to enhance optical and physical performance in clear industrial and wood coatings. Properties such as gloss, hardness, and scratch resistance are altered in a desirable manner. Cure rate via double bond conversion was enhanced in the presence of these very small mineral particles.

TESTING

As listed in Table 1, ASTM International has developed several documents that are useful in the area of nanotechnology. Although the documents are not necessarily directly related to coatings and paints, they provide useful background for investigators in this field and, as is apparent, useful guides for laboratory efforts in the areas of terminology, particle handling, effect of nanoparticles on red blood cells, particle mobility through a graduated index, and other areas. In the future, it is expected that this area will further develop within ASTM International.

Joseph V. Koleske
Editor

TABLE 1—ASTM Standard Documents Related to Nanotechnology

ASTM Designation	Document Title
E2456-06	Terminology Relating to Nanotechnology
E2490-09	Standard Guide for Measurement of Particle Size Distribution of Nanomaterials in Suspension by Photon Correlation Spectroscopy (PCS)
E2524-08	Test Method for Analysis of Hemolytic Properties of Nanoparticles
E2525-08	Test Method for Evaluation of the Effect of Nanoparticulate Materials on the Formation of Mouse Granulocyte-Macrophage Colonies
E2526-08	Test Method for Evaluation of Cytotoxicity of Nanoparticulate Materials in Porcine Kidney Cells and Human Hepatocarcinoma Cells
E2530-06	Practice for Calibrating the Z-Magnification of an Atomic Force Microscope at Subnanometer Displacement Levels Using Si(III) Monatomic Steps
E2535-07	Guide for Handling Unbound Engineered Nanoscale Particles in Occupational Settings
E2578-07	Practice for Calculation of Mean Sizes/ Diameter and Standard Deviations of Particle Size Distributions
E2676-09	Practice for Tangible Property Mobility Index (MI)

[3] Anon, "Bayer MaterialScience Builds Carbon Nanotubes Plant," *Paint and Coatings Industry*, Volume 25, Number 11, p. 12 (Nov. 2009).
[4] Colver, Patrick J., Colard, Catheline A. L., and Bon, Stefan A. F., "Multilayered Nanocomposite Polymer Colloids Using Emulsion Polymerization Stabilized Solid Particles," *J. American Chemical Society*, Volume 150, No. 50, pp. 16850–16851 (2008).
[5] Eberts, Kenneth, Ou, Runquing, and Shah, Kunal, "Nanocomposite Coatings for High-Performance Fabrics," *Paint and Coatings Industry*, Volume 26, No. 4, pp. 32–36 (April 2010).
[6] Herold, Marc, Burgard, Detlef, Steingrover, Klaus, and Pilotek, Steffen, "A Nanoparticle-based Additive for the Improvement of Water-Based Metal Coatings," *Paint and Coatings Industry*, Volume 16, Number 8, pp. 24–27 (Aug. 2010).
[7] Van Remortel, Scott P. and Ratcliff, Robert E., "Ultrafine Nepheline Syenite as a Durable and Transparent Additive to Accelerate Radiation Cure," *Paint and Coating Industry*, Volume 27, Number 3, pp. 27–34 (Mar. 2011).

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Preface

For historical purposes, it is important to point out that at a January 1967 meeting of ASTM Committee D01 held in Washington, D.C., the American Society for Testing and Materials (ASTM International) accepted ownership of the *Gardner-Sward Handbook* from the Gardner Laboratory. It was through this laboratory that Dr. Henry A. Gardner published the previous twelve editions of the manual. Acceptance of this ownership gave ASTM an assumed responsibility for revising, editing, and publishing future editions of this well-known, respected manual. The undertaking was assigned to "Committee D01 on Paint and Related Coatings, Materials, and Applications." This committee established a permanent subcommittee, "D01.19 on Gardner-Sward Handbook," whose stated scope is delineated below. The 13th edition was published in 1972 as the *Paint Testing Manual* (STP 500) with Mr. G. G. Sward as editor and contributor. It was updated, expanded, and published in 1995 as the 14th edition, *Paint and Coating Testing Manual* (MNL 17) with Dr. Joseph V. Koleske as editor and contributor. The manual has served the industry well in the past by providing useful information that cannot be readily found elsewhere.

It has been about fifteen years since the 14th edition was published. Interest in the manual has been strong through the years. This new edition of the *Paint and Coating Testing Manual*, the *Fifteenth Edition of the Gardner-Sward Handbook* (MNL 17), has been updated and expanded.

The scope of the new edition is in keeping with the stated scope of Subcommittee D01.19:

> To provide technical, editorial, and general guidance for the preparation of the Fourteenth and subsequent editions of the *Gardner-Sward Handbook*. The handbook is intended for review of both new and experienced paint technologists and the past, present, and foreseeable trends in all kinds of testing within the scope of Committee D01. It supplements, but does not replace, the pertinent parts of the Society's Book of Standards. It describes, briefly and critically all Test Methods believed to have significance in the world of paint technology, whether or not these tests have been adopted officially by the Society.

Once again, in this new edition, ASTM standard test methods, procedures, and other documents are described in minimal detail, with the various volumes of the *ASTM Book of Standards* remaining the primary source of such information. An effort was made to include references in the absence of ASTM documents concerning industrial, national, international, and other society test methods. The new edition contains either new chapters, or the previous topics/chapters in rewritten/revised form. In a few cases, the previous edition was merely updated, attesting to either the quality of the earlier writing, the lack of development in the area, or the apparent waning of interest in the topic. A variety of modern topics have been included. New chapters have been added as, for example, "Measurement of Gonioapparent Colors," "Surfactants," "Powder Coating," and "Coalescing Aids." As in the previous edition, individual authors, experts in their particular fields, were given a great deal of freedom in expressing information about their topics, but all chapters were subjected to peer review by two colleagues. Thus, style and content presentation may widely vary, but efforts were made to have understandable syntax and thus readers should find the information useful and "easy" to read and put to use.

Manuals such at this one are prepared though a great deal of effort by the various authors and through the able assistance and behind-the-scenes concerted efforts of people such as Ms. Kathy Dernoga and Ms. Monica Siperko of ASTM International and Ms. Christine Urso, Ms. Barbara Carbonaro, Ms. Theresa Fucito, Ms. Patricia Mayhew, and Ms. Benita Hammer, of the American Institute of Physics, all of whom ensured that the manual was uniform in style and grammar and that manuscripts were submitted and processed in a timely fashion. The real unsung and unnamed contributors are the reviewers who gave encouragement to the various authors through constructive criticism, editorial information, and recommendations without deleteriously attempting to alter manuscripts from the author's intent. To all of these people, a heart-felt "thank you." Your talents have been utilized, you sacrificed much personal time, and you were patient with the numerous delays encountered on the road to making the manual a success.

Joseph V. Koleske
Editor

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Part 1: Regulations

1

Regulation of Volatile Organic Compound Emissions from Paints and Coatings

J. John Brezinski[1] and Ronald K. Litton[2]

INTRODUCTION

PRIOR TO THE 1960s, THE COATINGS INDUSTRY enjoyed a somewhat predictable regulatory and economic environment. The paint formulator selected solvents based on evaporation rate, solubility parameter, density, flammability, and, of course, cost. There was no apparent need to consider the relative photochemical reactivity of these materials, nor was there any appreciable incentive to reduce the solvent content of commercially acceptable coatings.

It was recognized that objectionable odors were released from some paints and coatings. Further, air emissions resulting from the evaporation of solvents during high-temperature processing of oils and resins caused occasional complaints from persons living near the coatings plant. The prevailing view of this period was summarized by Francis Scofield in his article in the 13th edition of the *Paint Testing Manual* entitled "Atmospheric Pollutants" [1].

> These "nuisance" types of pollution are a continuing problem but, in general, can be dealt with by dilution and dispersion of the objectionable materials to bring the concentration below a level that can be detected by the neighboring citizenry. Fortunately, most of the materials used by the paint industry are not toxic at concentrations significantly below the range at which they can be detected by the human nose, and sophisticated analytical procedures are rarely needed to deal with these "nuisance" problems.

Since the 1960s, societal concern about health and the environment has increased appreciably. Actions taken by federal and state legislative bodies have resulted in a steady avalanche of new laws and associated regulations that affect virtually all of the chemical industry. Some of the federal laws administered by the U.S. Environmental Protection Agency (EPA) that impact the coatings industry are shown in Table 1. They are designed to control the emission of pollutants to air, to water, and to soil.

In addition, among the new federal standards administered by the Occupational Safety and Health Administration are those that require manufacturers—including those making paints and coatings—to evaluate the hazards of products they make and to provide appropriate safety information to employees and users through the Material Safety Data Sheet (MSDS) and product labels:

- Hazard Communication Standard (HCS), 1983
- Occupational Exposure to Hazardous Chemicals in Laboratories, 1990

The discussion in this section will focus on the Clean Air Act and its amendments that, in the authors' opinions, have had (and will continue to have) the greatest impact on coatings. However, it should be noted that regulatory activities in specific regions of the United States (for example, the state of California and the Ozone Transportation Commission—that includes 12 states in the U.S. Northeast plus the District of Columbia) have resulted in the development of VOC emissions rulings (see section on "Other Important U.S. Regulatory Activities"), which are more stringent than those enacted through EPA. In addition, other regions of the world are developing or have already enacted regulations addressing the emissions of volatile organic compounds.

THE CLEAN AIR ACT AND AMENDMENTS

Photochemical Smog

A precipitating factor influencing the basis for selection of solvents for coatings in the 1960s and early 1970s was the recognition that solvents emitted to the atmosphere contributed to the growing "smog" problem, particularly in Southern California. The frequency of smog conditions in this area had increased steadily during the 1950s and 1960s as the number of automobiles, trucks, buses, and airplanes increased and as industrial development expanded with the accompanying growth of petroleum and chemical processing and power plant utilization.

Examples of Processes that Produce Hydrocarbons

- Petroleum production, refining, transport
- Internal combustion engines
- Natural processes—forests and plants (isoprene and terpenes)
- Surface coatings

The smog problem was (and still is) very acute in the Los Angeles air basin, an area uniquely situated in a series of plains that originate in the high mountains to the east. The basin enjoys predominantly sunny days with cool, moist air flowing with a light westerly wind most of the year. These factors cause a nearly permanent temperature inversion layer, trapping air emissions that combine to produce persistent and eye-irritating smog in the basin. A summer

[1] *Deceased, formerly of Hurricane, WV.*
[2] *Solvents Technical Service, Inc., 1015 Laurelwood Drive, Kingsport, TN 37660-8516.*

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TABLE 1—Federal Environmental Laws Administered by the U.S. Environmental Protection Agency.

Law	Abbreviation
Clean Air Act, 1970	CAA
Amendments of 1977	CAAA-77
Amendments of 1990	CAAA-90
Clean Water Act of 1972	CWA
Amendments of 1977	
Safe Drinking Water Act, 1974	SDWA
Toxic Substances Control Act, 1975	TSCA
Resource Conservation and Recovery Act, 1980	RCRA
Comprehensive Environmental Response Compensation and Liability Act, 1980	CERCLA (Superfund)
Superfund Amendments and Reauthorization Act, 1986	SARA
Title III, Emergency Planning and Community SARA, Title III Right-to-Know, 1986	

period in Los Angeles revealed that the use of organic solvents (for all purposes) accounted for about 18 % of the organic gases. About one half of the organic solvent emitted was attributed to the coatings industry, chiefly to the use in paint and coatings [1].

Based on the results of laboratory studies in "smog chambers," in which a mixture of a solvent and nitrogen oxide was exposed for 6 h to light approximately the intensity of noon sunlight, the solvents could be classified as "low" or "high" in photochemical reactivity related to the amount of peroxides and ozone produced. These studies formed the basis for the well-known Rule 66, an air pollution control regulation passed by the Los Angeles Air Pollution Control District. Rule 66 identifies an "approved" solvent as one that contains less than 20 % by volume of specific chemicals and is further limited to certain combinations of these chemicals. Thus, approved solvents can contain no more than designated amounts of the combinations shown in Table 2.

In effect, Rule 66 promoted the use of specific solvents such as aliphatic and naphthenic hydrocarbons, alcohols, esters, normal ketones, chlorinated hydrocarbons (except trichloroethylene), and nitroparaffins. Rule 66, superseded in 1976 by Rule 442, Usage of Solvents, by the California South Coast Air Quality Management District, was subsequently adopted by various other state jurisdictions.

VOC Definition

The U.S. EPA was created in 1970 by Congress as part of a plan to consolidate several federal environmental activities. Studies directed by EPA laboratories in Research Triangle Park, NC, of the photochemical reactivity of materials in a laboratory smog chamber revealed that when organic materials and nitrogen oxide were irradiated for periods of up to 36 h, even those solvents considered acceptable under Rule 66 reacted to form peroxides and ozone. Only a few materials showed negligible photochemical reactivity,

TABLE 2—Rule 66: Limits of Solvent Categories in Approved Mixtures.[a]

5 %	8 %	20 %
Hydrocarbons,	Aromatic	Ethylbenzene, branched
alcohols,	hydrocarbons	ketones, toluene, or
Aldehydes,	(W/8 C atoms)	trichloroethane
esters, ethers or		
ketones *having*		
an olefinic or		
Cycloolefinic		
Unsaturation		

[a] Calculated as the percent by volume of the total solvent.

among which were: methane, ethane, methylene chloride, 1,1,1-trichloroethane, and fluorinated compounds.

Since 1977, EPA has used the reactivity of ethane (based on a series of smog chamber experiments) as the benchmark for determining negligible reactivity. Compounds deemed less reactive than, or equally reactive to, ethane under the assumed conditions were classified as negligible. In contrast, compounds more reactive than ethane continued to be classified as reactive VOCs and were subject to appropriate control regulations.

These studies, which were prompted in part by the passage of the Clean Air Act of 1970, led to the conclusion that most organic compounds emitted to the atmosphere contribute to the formation of ozone. On this basis, EPA adopted as a regulatory objective the limit of essentially all volatile organic compounds emitted to the atmosphere from all sources, including paint and coatings applications [2].

EPA Regulatory Definition of VOC

The regulatory definition of volatile organic compounds (VOC) was revised by EPA as of November, 2004. A part of this definition is as follows:

40 CFR Part 51 Section 51.100 Definitions[3]

Volatile organic compounds (VOC) means any compound of carbon, excluding carbon monoxide, carbon dioxide, carbonic acid, metallic carbides or carbonates, and ammonium carbonate, which participates in atmospheric photochemical reactions

1. This includes any such organic compound other than those which have been determined to have negligible photochemical reactivity. The original list is: methane; ethane; methylene chloride (dichloromethane); 1,1,1-trichloroethane (methyl chloroform); 1,1,2-trichloro-1,2,2-trifluoroethane (CFC-113); trichlorofluoromethane (CFC-11); dichlorodifluoromethane (CFC-12); chlorodifluoromethane (CFC-22); trifluoromethane (HFC-23); 1,2-dichloro-1,1,2,2-tetrafluoroethane (CFC-114); chloropentafluoroethane (CFC-115); 1,1,1-trifluoro 2,2-dichloroethane (HCFC-123); 1,1,1,2-tetrafluoroethane (HF-134a); 1,1-dichloro 1-fluoroethane

[3] Code of Federal Regulations (CFR) Part 51; Requirements for Preparation, Adoption and Submittal of Implementation Plans, *Federal Register,* Volume 2, 1 July 2002, pp. 131–136.

(HCFC-141b); 1-chloro 1,1-difluoroethane (HCFC-142b); 2-chloro-1,1,1,2-tetrafluoroethane (HCFC-124); pentafluoroethane (HFC-125); 1,1,2,2-tetrafluoroethane (HFC-134); 1,1,1-trifluoroethane (HFC-143a); 1,1-difluoroethane (HFC-152a); parachlorobenzotrifluoride (PCBTF); cyclic, branched, or linear completely methylated siloxanes; acetone; perchloroethylene (tetrachloroethylene); 3,3-dichloro-1,1,1,2,2-pentafluoropropane (HCFC-225ca); 1,3-dichloro-1,1,2,2,3-pentafluoropropane (HCFC-225cb); 1,1,1,2,3,4,4,5,5,5-decafluoropentane (HFC 43-10mee); difluoromethane (HFC-32); ethylfluoride (HFC-161); 1,1,1,3,3,3-hexafluoropropane (HFC-236fa); 1,1,2,2,3-pentafluoropropane (HFC-245ca); 1,1,2,3,3-pentafluoropropane (HFC-245ea); 1,1,1,2,3-pentafluoropropane (HFC-245eb); 1,1,1,3,3-pentafluoropropane (HFC-245fa); 1,1,1,2, 3,3-hexafluoropropane (HFC-236ea) 1,1,1,3,3-pentafluorobutane (HFC-365mfc); chlorofluoromethane (HCFC-31);1 chloro-1-fluoroethane (HCFC-151a); 1,2-dichloro-1,1,2-trifluoroethane (HCFC-123a); 1,1,1,2,2,3,3,4,4-nonafluoro-4-methoxy-butane (C4F9OCH3);2-(difluoromethoxymethyl)-1,1,1,2,3,3,3-heptafluoropropane ((CF3)2CFCF2O CH3); 1-ethoxy-1,1,2,2,3,3,4,4,4-nonafluorobutane (C4F9OC2H5);2-(ethoxydifluoromethyl)-1,1,1,2,3,3,3-heptafluoropropane ((CF3)2CFCF2OC2H5); methyl acetate and perfluorocarbon compounds which fall into these classes:

i. Cyclic, branched, or linear, completely fluorinated alkanes;
ii. Cyclic, branched, or linear, completely fluorinated ethers with no unsaturations;
iii. Cyclic, branched, or linear, completely fluorinated tertiary amines with no unsaturations; and
iv. Sulfur-containing perfluorocarbons with no unsaturations and with sulfur bonds only to carbon and fluorine.

2. For purposes of determining compliance with emissions limits—VOC will be measured by the test methods in the approved State implementation plan (SIP) or 40 CFR part 60, Appendix A, as applicable. Where such a method also measures compounds with negligible photochemical reactivity, these negligibility-reactive compounds may be excluded as VOC if the amount of such compounds is accurately quantified and such exclusion is approved by the enforcement authority.
3. As a precondition to excluding these compounds as VOC or at any time thereafter, the enforcement authority may require an owner or operator to provide monitoring or testing methods and results demonstrating, to the satisfaction of the enforcement authority, the amount of negligibly-reactive compounds in the source's emissions.
4. For purposes of Federal enforcement for a specific source, EPA shall use the test methods specified in the applicable EPA-approved SIP in a permit issued pursuant to a program approved or promulgated under title V of the Act, or under 40 CFR part 51, subpart I or Appendix S, or under 40 CFR parts 52 or 60. EPA will not be bound by any State determination as to appropriate methods for testing or monitoring negligibly-reactive compounds if such determination is not reflected in any of the above provisions.
5. The following compound(s) are VOC for purposes of all recordkeeping, emissions reporting, photochemical dispersion modeling and inventory requirements which apply to VOC and shall be uniquely identified in emission reports, but are not VOC for the purpose of VOC emissions limitations or VOC content requirement:

t-butyl acetate

Note—The category of "VOC-exempt compounds" can be modified (i.e., add compounds to or delete them from the list) by EPA. Since the development of the initial list, numerous petitions requesting "VOC exemption" on specific compounds were submitted to EPA by various companies and trade associations. The petitions submitted requested that compound A be exempted from VOC control based on its low reactivity relative to ethane. As a result of those initiatives, several solvents were exempted by EPA. This list includes:

Methyl Formate (2004)
t-Butyl Acetate (2004)
Propylene Carbonate (2009)
Dimethyl Carbonate (2009)

The majority of VOC exempt solvents in the initial list were not useful in formulating coatings with good solubility and application characteristics. The delisting of acetone, parachlorobenzotrifluoride, volatile methyl siloxanes (VMS), and methyl acetate in the mid-late '90s (coupled with the recent delisting of the 4 aforementioned solvents) has provided coatings formulators with greater latitude in developing lower VOC coatings.

States may also have their own list of VOC-exempt compounds. Although state lists are often modeled after EPA definition, users of coating products should confirm that a solvent deemed VOC exempt by the agency is classified similarly by the respective state.

Metrics for Defining "Negligible Photochemical Reactivity"

In an effort to define chemicals as having "negligible photochemical reactivity" (and, therefore, exempt from VOC regulations) EPA designated ethane as the benchmark for separating reactive from negligibly reactive compounds under the assumed conditions. Prior to 1994, EPA had only granted VOC exemptions based on the metric known as the k_{OH} value. This value represents the molar rate constant for reactions between the given compound and the OH radical in the air. If the k_{OH} value of a compound is less than ethane, the compound may be less reactive than ethane and may be declared to be "negligibly reactive."

In the mid-1990s, in response to a petition for VOC exemption, EPA used another type of comparison to ethane based on the ozone forming potential of other reactions of the compound in addition to the initial reaction with the OH radical. This method was based on the concept of maximum incremental reactivity (MIR). The MIR values are usually expressed either as grams of ozone formed per mole of VOC (molar basis) or as grams of ozone formed per gram of VOC (mass basis). Both metrics were used to exempt two compounds in the 1990s.

Thus, since 1997, EPA has considered three different metrics to compare the reactivity of a specific compound to that of ethane:

1. the reaction rate constant with the hydroxyl radical (known as k_{OH})
2. MIR expressed as reactivity per gram basis
3. MIR expressed as reactivity per mole basis

Even though much debate and critique has ensued on the merits of a mass versus mole comparison, in "Interim Guidance on Control of Volatile Organic Compounds in Ozone State Implementation Plans" published on September 13, 2005 (70FR 54046), EPA stated:

> "A comparison to ethane on a mass basis strikes the right balance between a threshold that is low enough to capture compounds that significantly affect ozone concentrations and a threshold that is high enough to exempt compounds that may usefully substitute for more highly reactive compounds.... When reviewing compounds that have been suggested for VOC exempt status, EPA will continue to compare them to ethane using k_{OH} expressed on a molar basis and MIR values expressed on a mass basis."

The MIR values (both by mole and mass) are developed measures of photochemical reactivity derived from a computer-based photochemical model. This concept, which demonstrates that VOCs have different reactivity, i.e., different ozone-forming potential, is now shaping revised ozone control strategies at both the federal and state levels (view section on "Alternative Concept for Controlling Ozone Formation").

VOC and Ozone Formation

The understanding of "photochemical smog" and its contribution to the formation of ground level ozone has increased dramatically since the days of Rule 66. Basically, VOCs react with oxides of nitrogen (NO_X) in the presence of heat and sunlight to form ground level. However, the interrelationship of VOCs and NO_X in ozone formation is a complex series of reactions. One suggested pathway is depicted below [3].

$$NO_2 + \text{Sunlight} \rightarrow NO + O$$
$$O + O_2 \rightarrow O_3$$
$$O_3 + NO \rightarrow NO_2 + O_2$$
$$\text{VOCs} + \text{Sunlight} \rightarrow \text{Radicals}$$
$$NO + \text{Radicals} \rightarrow NO_2$$

Primary Sources of NO_x: On-road mobile sources, electricity generating units, and nonroad mobile sources.

Other articles have been published on factors affecting photochemical ozone formation and the potential of a given compound to contribute to ozone formation in the troposphere (lower atmosphere) [4,5].

In addition to the concentration of NO_2 and available sunlight in the atmosphere, ozone formation is also affected by temperature, humidity, as well as the concentration and composition of other VOCs present in the atmosphere. Also, substantial biogenic (natural) VOCs released from trees and other green plants can impact ozone formation at ground level.

Considerable interest has developed recently in the consideration of individual solvent photochemical reactivity in state, federal, and international programs related to air quality control (see section on "New Concept for Controlling Ozone Formation").

Other VOC Definitions

The U.S. EPA defines a category of VOC-exempt compounds (as described in the section on "EPA Regulatory Definition of VOC"). However, for many consumer products (i.e., floor polishes, glass cleaners, automotive rubbing or polishing compounds, etc.), EPA has determined that low volatility compounds may also be exempted from regulations as VOCs. These include solvents:

> Having a vapor pressure (VP) < 0.1 mm Hg at 20°C; or
> Consisting of > 12 carbon atoms, if the VP is unknown; or
> Having a MP > 20°C, and which does not sublime (i.e., does not change directly from solid into a gas without melting), if the VP is unknown.

Currently, there is no explicit LVP (low vapor pressure) exemption for products used in paints and coatings. Thus, some LVP products are regulated as VOCs in coatings but not when used in consumer products.

Lastly, a wide disparity in the definition of a VOC exists across countries. A product classified as a non-VOC in the Unites States does not automatically receive the same classification in Europe. For example, the criteria for the EU eco-labeling scheme is that a VOC is "any organic compound with, at normal conditions for pressure, a boiling point (or initial boiling point) lower than or equal to 250°C" [ref—Official Journal 39 (L4), 6 January (1996)]. Thus, coalescing aids for latex paints with a boiling point (BP) >250°C would not be a VOC under the EU eco-labeling definition. Other countries are becoming more proactive in developing rules and definitions addressing VOC issues.

The Ozone Standard

The Clean Air Act of 1970 targeted six criteria pollutants for control: carbon monoxide, lead, nitrogen dioxide, ozone, particulates, and sulfur dioxide. Criteria pollutants are those for which criteria were issued by EPA. These documents include national ambient air quality standards (NAAQS) for each criteria pollutant—levels that protect against adverse effects to health and to plants and materials [6]. These criteria documents and standards were to be reviewed every 5 years and if necessary, revised to assure that the standards provided adequate health protection. Criteria pollutants are measured using a network of monitors nationwide. Standards for ozone and nitrogen oxides are:

Ozone: In July 1997, the U.S. EPA revised its NAAQS for ground-level ozone and particulate matter. The complete standards appeared in the July 18, 1997, edition of the *Federal Register* (pp. 38652–38896). The EPA began phasing out and replacing the previous 1-hour standard (last revised in 1979) with a new 8-hour standard. The new standard would be 0.08 ppm measured over 8 hours, replacing the old standard of 0.12 ppm measured over 1 h. In establishing the 8-hour standard, the EPA defined the new standard as a "concentration based" form, and it called for measuring the 3-year average of the annual 4th-highest daily maximum 8-hour ozone concentration.

On June 20, 2007, the EPA administrator signed proposed revisions to the NAAQS for ozone. The end result of the proposal was the 8-hour "primary" standard for O_3 set at 0.075 ppm in the March, 2008 final rule.

On January 6, 2010, the EPA proposed to strengthen the NAAQS for ozone. This provision proposed that the 8-h "primary" standard for ozone be set at a lower level within the range of 0.060–0.070 ppm. This action would provide increased protection for children and other "at risk" populations against the adverse health effects related to ozone exposure. According to the publication "Ozone Air Quality

Standards: EPA's Proposed January 2010 Revisions" (following public hearings and comments)—a final rule was scheduled to be issued by August 31, 2010.

The Clean Air Act requires that the EPA set a standard based on the need to protect public health "with an adequate margin of safety." For policy guidance, timelines, recent actions, etc., on the new ozone standard, see the following: www.epa.gov/air/ozonepollution/.

Note—Primary standards set limits to protect public health, including the "health" of sensitive populations such as asthmatics, children, and the elderly.

The implementation of a new ozone standard is of vital interest to the paint industry since the CAAA-90 specifically identifies paint and coatings for various controls for VOC emission reductions, one precursor for ozone formation. Under the new standard, there could be additional ozone nonattainment areas that will increase the need for compliant coating technology.

Nitrogen Dioxide: The nitrogen dioxide concentration in the atmosphere cannot exceed 0.053 ppm as the annual arithmetic mean concentration. In 2010, the EPA supplemented the existing annual standard for NO_2 by establishing new short-time standard based on the 3-year average of the 98th percentile of the yearly distribution of 1-hour daily maximum. EPA set the level of this new standard at 100 ppb. Final rule is listed at: http://www.regulations.gov.

As of February, 2010, there are no areas in the United States that are designated as nonattainment of the NO_x, NAAQS. Although no change has occurred in NAAQS for nitrogen dioxide, decreasing NO_x emissions [various nitrogen compounds like nitrogen dioxide (NO_2) and nitric oxide (NO)] are receiving more attention from the EPA in an effort to minimize ground level ozone, which is formed when NO_x and VOCs react in the presence of heat and sunlight. This is an important shift in strategy for controlling ozone formation since it recognizes that in geographical regions in which the ratio of VOCs to NO_x is high ("NO_x -limited conditions"), additional reductions in VOC emissions will have a minimal impact on air quality.

CONTROL OF VOC EMISSIONS FROM COATINGS

The Clean Air Act addresses air pollution emanating from both existing sources and that from future new plant construction or significant modification of existing sources. States with areas that did not comply with the ozone standard were given primary responsibility to develop appropriate regulations for existing sources to meet the time schedule for compliance specified by Congress. The plan outlines the measures that the state will take in order to improve air quality.

The Federal EPA was assigned oversight responsibility for the state programs that were described in "State Implementation Plans" (SIPs). The plan outlines the measures that the state will take in order to improve air quality. No SIP can mandate weaker pollution controls than those established by the EPA. The SIP is reviewed by the EPA and if deemed unacceptable, the EPA must prepare one for it. For example, failure by a state to submit an adequate SIP can result in restrictions on federal highway funds.

Control Technique Guidelines

In 1977, the Agency issued the first of a series of guidance documents for the states related to various industrial coating operations or end-use categories. These documents, called "Control Technique Guidelines (CTG) Series, Control of Volatile Organic Emissions from Stationary Sources," include recommended VOC emission limits, based on the EPA's assessment of Reasonably Available Control Technology (RACT): the limits are expressed as pounds of VOC per gallon of coating (minus water), as applied. The EPA has defined RACT as the lowest emission limit that a source can meet by the application of control technology that is reasonably available considering technological and economic feasibility.

The Clean Air Act Amendments of 1977 directed that states had to revise their implementation plans for areas out of compliance with the national ozone standard. The revised SIPs were to include sufficient control of VOC emissions from stationary sources (buildings, structures, facilities, and installations), such controls to incorporate the RACT limits for coatings operations for which a CTG was published.

Note—CTGs are not federal regulations. However, they do provide federally prescribed control measures to be incorporated as a part of approved SIPs.

Under the CAAA-90, the EPA scheduled issuance of CTG documents for 29 categories of VOC sources, which covered a variety of surface coating operations. Section 183 of the amended act also requires that the EPA issue CTGs for an additional number of surface coatings processes by 1993. In addition, the EPA planned to integrate HAP (Hazardous Air Pollutant) rulemaking with VOC requirements under 183 (e).

For the industry source categories, the approach to reduce VOC emissions has been for applicators to either adopt an alternate coating technology (high-solids, waterborne, powder, UV cure), or install engineering controls (carbon adsorption, incineration, etc.).

NEW SOURCE PERFORMANCE STANDARDS

The control of VOC emissions from new coatings plants and from significant modifications of existing plants was addressed by the EPA in a series of New Source Performance Standards (NSPS), the first of which issued in 1980. These mandatory standards, which apply uniformly to all parts of the country, define the emission sources more narrowly and impose a tighter level of emission control than that for related existing sources. Facilities that are constructed, modified, or reconstructed after the NPSP was proposed by the EPA are subject to NSPS.

The VOC limits defined in the NSPS, expressed as kilograms of VOC per liter of applied solids, are based on the best demonstrated technology (BDT) for the specific coating operation. The NSPS requirements can be found in the Code of Federal Regulations at Title 40 (Protection of Environment), Part 60 (Standards of Performance for New Stationary Sources): http://ecfr.gpoaccess.gov/cgi/tZtext/text-idx?sid=474f779beade290997e4611971d078f4&c=ecfr&tpl=/ecfrbrowse/Title40/40tab_02.tpl.

The emission limits in both the CTG and NSPS documents, in the majority of cases, focus on restricting the VOC content per unit of coating or of coating solids applied in the operation, rather than placing a ceiling on individual plant emissions. The responsibility for establishing emission limits for particular plants, if appropriate, was left to the states [7].

TABLE 3—Clean Air Act Amendments—1990 major source identification based on VOC I emissions; limits for area classifications

Ozone Nonattainment Area Classification	VOC Emission Limit, tons/year
Marginal or moderate	100
Serious	50
Severe	25
Extreme	10

DETERMINATION OF VOC CONTENT

EPA Federal Reference Method 24

The procedures specified by the federal EPA for testing paint products for compliance with VOC limits are described in Federal Reference Method 24: Determination of Volatile Matter Content, Density, Volume Solids, and Weight Solids of Surface Coatings [8]. This standard employs several ASTM test standards, including those shown in Table 3. In addition, Reference Method 24A: Determination of Volatile Matter Content and Density of Publication Rotogravure Inks and Related Publication Rotogravure Coatings incorporates these ASTM standards. These two documents provide the framework for referencing these ASTM standards in determining VOC levels under regulation.

Method D2369 is a key procedure of Federal Method 24. Since 1980, several important revisions have been made in this standard to make it compatible with revisions in Method 24, including the addition in 1990 of instructions for testing multicomponent coatings and the deletion of sections dealing with testing at shorter times. The revised version of Federal Reference Method 24 is also included in the *ASTM Manual on Determination of Volatile Organic Compound* (*VOC*) *Content in Paints, Inks, and Related Coating Products,* 2nd ed., 1993 [9].

Substantial revisions were also made in ASTM D3960, Practice for Determining Volatile Organic Compound (VOC) Content of Paints and Related Coatings, a standard developed in ASTM Subcommittee D01.21 to provide a guide for the calculation of VOC and to establish a base for the investigation in ASTM of the precision of VOC content determination. The definitions and symbols used in D3960 are those adopted by the EPA and included in the Agency document "Procedures for Certifying Quantity of Volatile Organic Compounds Emitted by Paint, Ink and Other Coatings" that was published in 1984 [10].

Studies and discussions in ASTM Subcommittee D01.21 that led to the modification and improvements of ASTM standards referenced in Federal Method 24 and in ASTM Practice D3960 were conducted with the cooperation of EPA personnel of the Office of Air Quality Standards Development at Research Triangle Park, NC.

EPA Method 24 was designed to be used for measuring the VOC content of all coatings that are intended for either ambient or baking film conditions. However, that method was not applicable to ultraviolet (UV) radiation-cured coatings. Therefore, the method was subsequently amended to incorporate ASTM Method D5403-93, which does contain those procedures. The test methods in D5403 determine the weight percent volatile content of paint, coatings, and inks that are designed to be cured by exposure to ultraviolet light or to a beam of accelerated electrons. After radiation cure, the specimens are baked at 110±5°C for 60 min.

The general expression for calculating VOC content [ASTM D5201-05a (2010) Standard Practice for Calculating Formulation Physical Constants of Paint (Physical Constants of Paint and Coatings)] is available from ASTM International at the following link: http://www.astm.org/Standards/D5201.htm.

The expression "VOC" includes all organic emissions from a coating, not just the solvent in a coating. These emissions can include volatile additives, by-products of the cure reaction, etc. "Formulation" VOC content may or may not be an acceptable means for compliance, depending on the specific wording of the applicable regulation. It would be acceptable if the same VOC content is obtained when tested using EPA Method 24.

The EPA would have preferred to limit VOC emissions in the CTG on the basis of the unit volume of coating solids applied. However, the general expression for calculating VOC content in which VOC content is defined as mass per unit volume of coating less water and less exempt solvent was necessary as no acceptable consensus procedure was available for determining the volume percent nonvolatile content. In a presentation in Copenhagen in 1990, James C. Berry of the U.S. EPA stated: "Though certainly less than ideal, the major attraction is that the expression permits the determination of compliance from the analysis of a coating sample obtained during a plant inspection. In the simplest case, these units require only one volumetric and one gravimetric measurement" [7].

The measurement of low VOC content waterborne coatings (e.g., architectural) using EPA Reference Method 24 was found to be unreliable (confirmed by industry round-robin lab trials). Studies demonstrated that the error in VOC measurements in waterborne coatings was inversely proportional to the VOC content of the coating (i.e., the lower the VOC content, the poorer the precision to be expected). As industry moved toward lower VOC coatings for compliance purposes, it was prudent that a more reliable test method be found that more accurately quantified VOC content in waterborne coatings. After much stakeholder corroboration, the following test was developed: ASTM D6886-03 "Speciation of the Volatile Organic Compounds (VOCs) in Low VOC content Waterborne Air-Dry Coatings by Gas Chromatography," ASTM International. The method was designed primarily for the analysis of waterborne coatings in which the material VOC content is <5 wt %. Presently, ASTM D6686-03 is being revised (ASTM WK24436) to include VOC analysis of a wider range of materials.

OTHER VOC-RELATED METHODS AND STUDIES

ASTM development activity on other VOC-related standards continues to expand. Some standards have not been approved as yet by the Federal EPA for use in demonstration of compliance with VOC emission control regulations. Use of any of these standards to demonstrate compliance should be coordinated with appropriate regulatory agencies. Document summaries on all ASTM standard test methods are located at: http://www.astm.org.

Additional information on ASTM test methods and the EPA's surface coating rules are available at: http://www.epa.gov/ttn/atw/coat/common/coatingscalc.html.

Supplementary Information

Further information about the development, significance, and limitations of these VOC-related ASTM standards as well as about the use of ASTM standards for the demonstration of compliance with VOC emission control regulations is available in the ASTM *Manual on Determination of Volatile Organic Compounds in Paints, Inks, and Related Coating Products* [9]. Attachments in the second edition of this manual include the 1992 revision of Federal Reference Number 24 and a publication from EPA's Emission Standards Division titled "Procedure for Certifying Quantity of Volatile Organic Compounds Emitted by Paint, Ink and Other Coatings" [10]. Included in the latter publication are "VOC Data Sheets," applicable to coatings "as supplied" by the manufacturer and for coatings "as applied" by the user. The form used for "as supplied" coatings is patterned after a recommendation of the American Coatings Association (ACA). Other resources include other chapters from the *Paint and Coating Testing Manual.*

CLEAN AIR ACT AMENDMENTS OF 1990

The Clean Air Act Amendments of 1990 defined a comprehensive long-term approach "to achieve and maintain a healthy environment while supporting a strong and sustainable economic growth and sound energy policy."[4] A major impetus for these amendments was the continued inability of a number of heavily populated urban areas to meet the requirements of the national ambient air quality standards for ozone and carbon monoxide.

Among the specific issues addressed in the Act were: control of ozone in the atmosphere; control of hazardous air pollutants (HAPs); reduction of acid rain; and the protection of ozone in the stratosphere.

Features of the Act that have had a major impact on the coatings industry include:

Title I—Ozone Control in the Atmosphere

Title I specifically directed the EPA to develop control technique guidelines and maximum achievable control technology (MACT) standards for aerospace coatings and for shipbuilding coatings and repair. The EPA was also directed to prepare new control technique guidelines for additional coatings uses that included:

- Auto body refinishing
- Plastic parts (business machines)
- Plastic parts (others)
- Offset lithography
- Wood furniture

In 1997, the Coatings and Consumers Product Group of the U.S. EPA began the development of additional CTGs for a series of new surface coatings and for some of the categories, national rules. This coordinated rule development was an effort by the agency to ensure consistency in the rule developments within the surface coatings industries and composite operations (collectively known as the "Coatings and Composites Coordinated Rule (CCCR)." Coupled with this effort was the development of National Emission Standards for Hazardous Air Pollutants (NESHAPs) under section 112 of the CAA (see following section "Title III—Air Toxics Program"). The EPA involved a wide variety of industry stakeholders in the rule-making process in order to expedite the promulgation of rules and to make the process more cost effective for both the agency and industry. Extensive information on the current status of the Coatings and Composite Coordinated Rule Development is available at: http://www.epa.gov/ttn/uatw/coat/coat.html.

While coating formulators worked under established CTG and SIP guidelines, the CAAA-1990 (Section 183e) also required the EPA to conduct a study of the role of VOC emissions from consumer and commercial products (including that from aerosols) in ozone formation. This led to the development of national rules addressing VOC emissions from AIM (architectural and industrial maintenance) coatings and consumer products. The national AIM rule was finalized on Sept. 9, 1998. Details of the rule are available at: http://www.epa.gov/ttnatw01/183e/aim/aimpg.html.

This rule was directed at area sources, a collection of similar emission units within a geographical area. Therefore, engineering controls were generally not an option for coatings applied to structures in the fields. Thus, it was necessary that the applied coating meet the specified VOC content in the rule. Several states, including California and other northeastern states (OTC), have introduced rules regulating VOC emissions from AIM coatings. Typically, these are more stringent than the existing EPA national AIM rule (see subsequent section "Other Important U.S. Regulatory Activities").

National Rules for Consumer Products were promulgated in 1998. The regulation was designed to control VOC emissions from household consumer products, such as floor polishes, personal care, etc. Details of the rule are available at: http://www.epa.gov/ttn/atw/183e/cp/cppg.html.

In the CAAA-90, ozone nonattainment areas were placed in five classifications (marginal, moderate, serious, severe, and extreme) based on the mid-1991 ozone level and compliance with the national ozone standard by specific years is mandated in the law. In addition, a Northeast Ozone Transport Region was created, consisting of all states north of Virginia and east of Ohio.

Increasingly strict provisions, including further reduction of VOC emissions, were imposed on areas, the magnitude to be related to the severity of the ozone problem (i.e., the more severe the problem, the longer that Congress has provided for an area to reach attainment). Depending on the area classification, several or all of the following were required:

- Increased monitoring and more accurate VOC and NO_2 emission inventory
- Revision of state implementation plans to incorporate RACT limits from previous and future CTGs for all major stationary sources
- New source review and permits for new or modified stationary sources
- Reduced emission threshold levels for the definition of major stationary sources, ranging between 10 tons/year for severe classification areas to 100 for marginal or moderate areas
- Higher VOC emission offset requirements for new or modified sources

[4] U.S. EPA Office of Air and Radiation, "Implementation Principles for the Clean Air Amendments of 1990."

However, with the ongoing transition in the ozone standard, the agency had to designate and reclassify all nonattainment areas in the United States with respect to the latest standard. In the interim, the nonattainment area must demonstrate to EPA that they are making reasonable further progress toward improving their air quality.

Additional information as related to ozone compliance can be accessed at: http://www.epa.gov/air/ozonepollution/index.html.

Title III—Air Toxics Program

Before 1990, the EPA listed and regulated only eight HAPs as National Emission Standards for Hazardous Air Pollutants (NESHAP) under 40 CFR Part 61. The listed HAPs were based on risk findings and "Risk-Based" NESHAP were then developed to reduce the emissions of the designated pollutants. By the late 1980s, total HAP emissions remained largely uncontrolled.

Under Title III, the EPA is directed to evaluate and control the emission of air toxics (also known as hazardous air pollutants-HAPs) from major sources of air pollution. HAPs are materials known or suspected to cause cancer or other serious health problems, or to cause environmental and ecological effects. Originally 189 products and product categories (now 187) were identified in the Act, and the EPA has the authority to delete or add additional products to this list. Industry groups have petitioned the EPA to delist products (see following note). A list of the materials included on the HAP list can be found on the following website: http://www.epa.gov/ttn/atw/allabout.html.

Note—Three petitions were submitted by the American Chemistry Council (ACC) requesting that the EPA delist MEK, EB glycol ether, and MIBK from the HAP list.

The EPA issued a final rule on November 29, 2004, removing ethylene glycol monobutyl ether (EGBE) from the Clean Air Act list of Hazardous Air Pollutants (HAPs).

Later, on December 15, 2005, EPA issued a final rule removing Methyl Ethyl Ketone (MEK) from the list of Hazardous Air Pollutants (HAPs) under section 112(b) of the Clean Air Act.

In the Spring 2010 Semiannual Regulatory Agenda (SAN 4849, Sequence 688—Petition to Delist a Hazardous Air Pollutant from Section 112 of the Clean Air Act: Methyl Isobutyl Ketone (MIBK)), the EPA reported the following:

> "However, since the last submittal by the petitioner, a 2-year MIBK bio-assay by the National Toxicology Program (NTP) has been completed. A draft report of this study was reviewed by the NTP Board of Scientific Counselors Technical Reports Review Subcommittee, which accepted unanimously the conclusions in the report that there is some evidence of carcinogenic activity of MIBK. EPA has notified the petitioner that further review of the petition will require that the petitioner submit information regarding the relevance of the NTP study and a risk characterization for the human risk of cancer from MIBK exposures, which would include the derivation of a cancer unit risk estimate."

In a previous ruling (40 CFR Parts 63 and 302), low molecular weight EO glycol ethers such as 2-ethylhexyl ether have been excluded from the glycol ether category in the list of HAPs established by Section 112(b)(1) of the CAAA-1990.

The control of emissions of hazardous air pollutants was to be achieved through the promulgation of emission standards for facilities within an industry group (or source category) that emit these products. The initial list of categories of sources published by the EPA (57FR31576, July 16, 1992) included under *Surface Coatings Processes* those processes for which CTG or national rules have been issued or planned.

Under the "technology-based approach," the EPA was directed to develop MACT standards based on the best-performing existing sources and the current status of control technology. The MACT standards are based on emission levels already achieved by the best performing facilities. These emission levels define a baseline (often referred to as the "MACT floor"—typically the control achieved by the best 12 % controlled of existing facilities in the source category). Normally, the emission limit in a MACT standard is expressed as a per cent reduction in emissions or a concentration limit that regulated sources must achieve.

The legislation addresses the amount of HAPs emitted into the air—not the amount that may be used at a specific site. Thus, facility owners have flexibility in determining the most effective method to comply with the regulations. It should be noted that the standards do not apply to coatings that contain < 1 wt. % HAP content (cumulative total) or < 0.1 wt. % (if the HAP is a carcinogen). Thus, coatings that contain less than these de-minimis levels are considered to be HAP-free.

MACT standards apply to sources that are major emitters of HAPs. "Major" sources are defined as sources that emit or have the potential to emit 10 tons per year of any listed HAP, or 25 tons per year of a mixture of HAPs. New sources must comply immediately upon startup and existing sources within three years.

The Act directs that the health impact and economic factors be considered in defining appropriate MACT limits. The EPA must insure that MACT compliance is protecting public health and must establish residual risk standards within 9 years after promulgation of each MACT standard. If studies show excessive risk, EPA must enforce stricter standards.

Further, by the end of 1995 sufficient categories and sub-categories must be listed to ensure that 90 % of the area sources that emit the 30 most hazardous air pollutants are subjected to regulation. An "area source" is defined as any area that is not a major source, including structure, building or installation that emits or may emit HAPs.

A draft timetable for regulating the categories of sources of hazardous air pollutants was published by EPA in 1992 (57FR44147, 24 Sept. 1992). The Act established a schedule for promulgating MACT standards as follows:

1. By 11/15/92, not less than 40 categories.
2. By 11/15/94, 25 % of listed categories
3. By 11/15/97, another 25 % of listed categories
4. By 11/15/2000, all categories

EPA's published list of "source categories" contains numerous surface coating operations. By the end of 1994 HAP emission standards were due for the following surface coating processes: magnetic tapes, printing/publishing, shipbuilding and ship repair, and wood furniture. Once promulgated, each NESHAP is published as an individual Subpart to Title 40 Code of Federal Regulations (CFR) Part 63.

The EPA was required under Section 112 to complete promulgation of all MACT Standards by November 15, 2000. If that date was not met, then individual facilities within those categories must apply for case-by-case MACT determinations by May 15, 2002. This provision became known as the "MACT Hammer," and was intended to assure that the EPA would issue the designated NESHAPs on schedule.

Even though some NESHAPs were completed for surface coating categories prior to 2000, the promulgation of many of those standards was delayed. Additionally, the EPA was unable to meet the required deadline (May 15, 2002) for promulgating a NESHAP for any category of major sources. As a result, the agency promulgated a regulation on April 5, 2002, that would allow affected sources a pathway (two-part application procedure) to satisfy the requirements of Section 112(J). Environmental groups challenged the regulation in court and a settlement was issued giving states and industry guidance and new timelines on the permitting necessary for the remaining MACT rules that were not promulgated in the required time period. The status of the NESHAPs affecting coating processes can be found at several EPA websites: http://www.epa.gov/ttn/uatw/coat/coat.html and http://www.epa.gov/ttn/atw/mactfnlalph.html.

In addition to the federal HAP program, many states have their own air toxics program. These programs may include compounds not on the federal HAP list. One example is the California Air Toxics "Hot Spot" Information and Assessment Act. Thus, coatings users need to aware of state guidelines regulating air toxics as well.

Determination of HAP Content

The EPA's National Emission Standards for Hazardous Air Pollutants (NESHAP) for surface coatings specify that EPA Method 311 shall be used for determining the type/amount of volatile HAPs used in a coating (40 CFR Part 63 Appendix A). This method (gas chromatographic separation and quantification) applies only to HAPs that are included in the original coating as manufactured, not to those HAPs (methanol and formaldehyde) that may form as the coating cures.

This method is suitable for the determination of most compounds designated as HAPs by the EPA. Styrene, ethyl acrylate, and methyl methacrylate can be measured by ASTM D4827-93 or ASTM 4747-87. Formaldehyde can be measured by ASTM PS 9-94 or ASTM D1979-91. Toluene Diisocyanate (TDI) can be measured by ASTM D3432-89.

Issues remain over the precision of Method 311, particularly at very low HAP levels. Since no specific conditions (carrier gas, oven temperature, etc.) are given for the analysis in the test method, one single methodology may not be applicable for all HAPs in the formulation. Therefore, prior information on the volatile composition of the coating will aid in choosing the proper conditions for that analysis and ensure greater accuracy in the measurements. Certified Product Data Sheets (CPDS) from suppliers is one source of such information.

Title V—State Operating Permit Program

The state operating permit program is considered by the EPA as a cornerstone of the CAAA-1990 amendments designed to ensure that the ozone nonattainment areas meet compliance deadlines. This program will impact many previously unregulated coatings manufacturers and users. The final rule for the operating permit program was issued in 1992 (57FR32250, 21 July 1992—codified at 40 CFR Part 70).

The operating permit program has been called the "air pollution equivalent" of the NPDES permit program of the Clean Water Act, under which operating permits are required of sources that discharge pollutants to water. In the program under Title V, all federal and state air pollution rules and regulations will be consolidated under a single document wherein the states are given authority to monitor and enforce the regulations. Sufficient funds will be available to the states from a minimum annual fee of $25 per ton (with the Consumer Price Index Adjustment) for each regulated pollutant emitted the fee to be assessed against all major sources.

Major sources required to have state operating permits include those that have the potential to emit [i.e., the maximum capacity of a stationary source to emit any air pollutant under its physical or operational design (taking into account federally-enforceable emission restrictions)] 10 tons or more per year of a single regulated hazardous air pollutant or 25 tons per year of a combination of hazardous air pollutants. These pollutants include those materials for which a national emission standard (NESHAP) has been established. Under Title V of CAAA-90, and the final rule on operating permit programs, the EPA is to approve (or disapprove) state permit programs within one year of receipt; the major sources must apply for the five-year permit within one year of the EPA's approval of the state program, and all permits must be issued and be legally binding by the end of 1997. In addition, federal requirements specify that renewal applications must be filed 18 months before current permit expires; state programs may stipulate a shorter time. Under the rule, states have the option of exempting all non major sources, with some exceptions, from requiring a permit for five years after the state permit program is approved by the EPA.

The characterization of a major source in ozone nonattainment areas is also based on the amount of volatile organic compounds emitted annually. The threshold amount is related to the area classification and sources in ozone nonattainment areas that emit above the designated amount of VOC shown in Table 3 are identified as major sources. These limits vary between 10 tons/year for the "extreme" classification to 100 tons/year for the "marginal or moderate" classification. For ozone transport regions (e.g., one is established in the Northeast), a threshold limit of 50 tons/year of VOC emissions applies.

The earlier amendments of the CAA had also established specific permitting requirements. Permits were required for a variety of sources, including new major sources of criteria pollutants, which must undergo a preconstruction review and permitting process in accordance to federal law and regulations. In nonattainment areas, the process is called "New Source Review" (NSR). Several rule requirements must currently be met before a new or expanded facility can obtain a permit to operate in a nonattainment area. The permit applicant must adopt the most stringent pollution controls as well as certify that other facilities under its control in the state are in compliance with the air pollution control requirements. Thirdly, the permit applicant must obtain sufficient surplus emission reductions to "offset" their net emission increases. The "offset" ratios for nonattainment areas are not a one-to-one

offset. The ratio is greater for areas with more severe ozone problems. EPA guidance on the use of emission offsets is available in 40 CFR Appendix S to Part 51.

In addition to the permitting requirements for major sources in nonattainment areas, EPA wanted to assure that areas (attainment) currently meeting the NAAQS maintain a healthy level of air quality. An attainment area is governed by the "Prevention of Significant Deterioration" (PSD) program, which requires the new source to obtain a preconstruction permit. Now under the CAAA-90, such sources must also obtain and maintain an operating permit. Since attainment is pollutant specific, an area may be nonattainment for one pollutant and attainment for others.

The permitting process is quite detailed and often requires the assistance of an environmental consultant and/or attorney. The "Minimum Operating Permit Application Requirements" are defined at 40 CFR 70.5. Likewise, the "Minimum Requirements for the Permit Content" are defined at 40 CFR70.6.

Title VI—Stratospheric Ozone Protection

The CAAA-1990 directs the EPA to protect the stratospheric ozone layer. Scientists found that certain chemicals, particularly chlorofluorocarbons (CFCs), were causing destruction of the ozone layer in the stratosphere. The EPA was directed to publish and periodically update a list of Class I and Class II substances. Class I must include at least 15 CFCs, three halons, carbon tetrachloride, and 1,1,1 trichloroethane. Class II must include at least 33 HCFCs. Other substances found to have harmful effects on the stratospheric ozone layer could be added to either list, depending on their ozone depleting potential. Class I ODS has a high potential for ozone depletion, whereas the propensity for ozone depletion for Class II ODS is lower. Once the substances are properly categorized, the production and use of the substances in each class is reduced according to a specific schedule in the Act.

The most significant feature of the program to protect ozone in the stratosphere was the staged phaseout of 1,1,1-trichloroethane (also known as methyl chloroform, or MCF), a material widely used in coatings and classified as a "VOC-exempt" solvent by the EPA. The rule specified a time schedule for manufacturers to gradually reduce their production of methyl chloroform and to completely phase out the chemical by 2002. However, in March 1993, following additional scientific findings, the EPA proposed rules to accelerate the phaseout CFCs, methyl chloroform and carbon tetrachloride to January 1, 1996. Additional rule information on the accelerated phase out schedule for Class I substances can be found at: http://www.epa.gov/ozone/title6/phaseout/accfact.html.

In conjunction with Title VI of the CAAA-1990, an international effort to protect the stratospheric ozone layer was already in effect. A multinational agreement known as the Montreal Protocol was originally signed in 1997 and substantially amended in 1990 and 1992. In November of 1992, the parties of the Montreal protocol agreed to accelerate the phaseout of CFCs, methyl chloroform and carbon tetrachloride to January 1, 1996, in developed countries. Developing countries could continue to produce and purchase CFCs and carbon tetrachloride for use until 2010 and methyl chloroform until 2015. More information on this protocol and phase out schedules can be located at: http://www.unep.org/ozone/index.asp.

Section 612 of the CAA requires the EPA to establish a program to determine acceptable substitutes for the ODS listed in both Class I and II. On March 18, 1994, the EPA published the Final Rulemaking (59FR 13044), which provides the process for administering the SNAP (Significant New Alternatives Policy). Substitutes are reviewed on the basis of ozone depletion potential, global warming potential, toxicity, flammability and exposure potential. Lists of acceptable and unacceptable substitutes will be updated periodically in the *Federal Register*. The present list of substitutes for ozone-depleting substances is available at: http://www.epa.gov/ozone/snap/lists

Title VII—Enforcement

In addition to the requirements for enhanced monitoring, the EPA is granted broad new authority to impose penalties and substantial fines for various actions, including: violations of the SIP; violation of some of the operating permit provisions; and false statements in records, monitoring data, and reports. Also included are provisions for field citations by inspectors, which can lead to a substantial per-day-per-violation fine against a facility.

Criminal penalties are also built into the CAAA-1990 as well. "Any person" who knowingly violates the act can receive fines as well as imprisonment. This is true also if an individual fails to file or maintain records as required or negligently releases any air toxics that causes harm danger.

OTHER IMPORTANT U.S. REGULATORY ACTIVITIES

In the United States, other organizations besides the EPA are developing more stringent VOC levels for paints and coatings. The two primary ones are the South Coast Air Quality Management District (SCAQMD) with a myriad of regulations in effect; and the Ozone Transport Commission (OTC), with regulations that affect 13 Northeastern and Mid-Atlantic states.

In 1998, the SCAQMD passed AIM Coating Rule 1113, imposing severe VOC limits on AIM coatings sold in its district. In most categories, the VOC limits for AIM products were more stringent than the federal standards. Subsequent revisions (enforcing even more stringent VOC limits for AIM paints) were challenged by industry representatives and trade associations. Current information on Rule 1113 is available from the district's website: http://www.aqmd.gov.

Outside of California, the OTC developed model rules of control measures for a number of source categories, including AIM. The AIM Model Rule was developed for the OTC northeastern states based on California's Suggested Control Measure (SCM) for VOC limits for AIM coating applications. More information on OTC AIM Coatings Rule Development can be located at: http://www.otcair.org/.

In addition to the organizations listed above, another regional cooperation for working together on regional air problems was established in 1989 by the states of Illinois, Indiana, Michigan, and Wisconsin. This was known as the Lake Michigan Air Directors Consortium (LADCO). The state of Ohio joined LADCO in 2004. See the following website for further details: http://www.ladco.org/.

ALTERNATIVE CONCEPT FOR CONTROLLING OZONE FORMATION

Background

When the EPA developed its original VOC control policy for ozone formation, its general approach was based upon the control of total VOC emissions by mass, without distinguishing individual species of VOC (except those that were deemed "negligibly reactive"). And, collected emission data from earlier years appeared to confirm that this approach was relatively successfully. Specifically, the EPA estimated that emissions from man-made sources nationwide declined by 54 % from 1970 to 2003 even though population, vehicle miles traveled and gross domestic product rose 39 %, 155 % and 176 %, respectively [11].

Ongoing science led to a better understanding of how ozone forms and the rate of ozone formation in the atmosphere. Thus, questions were raised by various stakeholders about the current VOC policy for ozone control. For example, are other regulatory methods, such as a VOC reactivity scale, more effective for controlling ozone formation? And, if so, will and how does the EPA include a "reactivity" option in its current VOC policy?

Historical Perspective on Reactivity Concept

The continued research on photochemical reactivity led many to believe that a reactivity-based approach for reducing VOC emissions would be more effective (especially in areas requiring more aggressive VOC control) than the current mass-based approach. Reactivity is a measure of how much a volatile organic compound contributes to the photochemical formation of ozone. It is a property of the compound as well as the environment in which the compound is formed. Therefore, the reactivity of a specific VOC varies with ambient conditions, VOC:NOx ratios, the identity of other VOCs in the atmosphere, and the time interval of interest. Thus, assigning a value to the reactivity of a specific VOC and developing a ranking scale or method for regulatory purposes would require an extensive research effort.

Research over the last several decades led to the ultimate development of a concept known as "incremental reactivity" which enables one to assess relative atmospheric reactivity differences in VOCs. As early as 1952, it was noted that different organic compounds vary in their potential to form ozone [12]. Subsequent work in the late 1970s and early 1980s [13,14] led to the development of reactivity scales. Correspondingly in the 1970s, the EPA recognized the variability of the ozone-forming potential of different VOCs and created an extensive two-class reactivity bin ("negligibly reactive" and "reactive").

In the late 1980s, Dr. William P.L. Carter at the University of California Riverside [15], funded by the California Air Resources Board (CARB), investigated 18 methods of ranking the reactivity of individual VOCs. Subsequently, Dr. Carter and coworkers at Statewide Air Pollution Research Center (SAPRC) and later continuing at the College of Engineering Center for Environmental Research and Technology (CE-CERT) at the University of California at Riverside (UCR) studied further incremental reactivities using smog chambers and computer modeling. Three scales were suggested for further consideration:

1. Maximum Incremental Reactivity (MIR)
2. Maximum Ozone Incremental Reactivity (MOIR)
3. Equal Benefit Incremental Reactivity (EBIR)

Following further investigations, Dr. Carter concluded that the MIR scale was the most appropriate for regulatory purposes [16] and is now the most common measure of incremental reactivity in the United States. MIR is defined as a measure of the average ozone yield of VOCs derived by adjusting the NO_x emissions in 39 base case urban scenarios to yield the highest incremental reactivity of the base ROG mixture, where ROG is reactive organic gas. Using this methodology, each VOC is assigned an individual reactivity value. MIR values for hundreds of organic compounds have been determined and continue to be revised. IR values, including MIR values for coating solvents, can be downloaded from Dr. Carter's website: http:/www.engr.ucr.edu/~carter/SAPRC/saprc07.pdf.

Note—File is large—refer to Appendix B—Mechanism and Reactivity Listings for Individual VOCs. This report is a completely updated version of the SAPRC-99 chemical mechanism, designated SAPRC-07 that provides updates to MIR values and other ozone reactivity scales for over 1,100 types of VOCs.

Many other scientists [17–20] and stakeholders have been active in the past two decades in advancing the science of the reactivity concept. One such effort has been the work of R. G. Derwent [21,22] and coworkers in Europe who created a reactivity scale known as POCP (Photochemical Ozone Creation Potential). This scale incorporated the meteorological conditions prevalent in Europe. In December 2008, Derwent reported in a presentation at the Atmospheric Chemical Mechanisms Conference that the two chemical mechanisms [SAPRC-07 and MCMv3.1 (Master Chemical Mechanism)] appear to have generated consistent reactivity scales (MRI and POCP), respectively, under California conditions.

Note—The stated references [3–5,12–22] are only samples of the comprehensive literature available on "atmospheric chemistry." Refer to section "Regulatory Information" for more guidance on locating information on VOC reactivity.

A major contributor to the development of an improved scientific basis for reactivity-related regulatory policies has been RRWG (Reactivity Research Work Group) that was sponsored by NARSTO (formerly known as the North American Research on Tropospheric Ozone) http://www.narsto.org.

The RRWG was organized in 1998 to bring together multiple stakeholders (government, industry and academia) actively interested in assessing future policies germane to the reactivity of organic compounds emitted to ambient air. Prior to its formation, the most advanced VOC reactivity potential regulations had been implemented by California for the purpose of controlling emissions from automobiles.

The RRWG organized and continues to commission research efforts on VOC reactivity under various environmental scenarios. The ongoing research has not only led to a significantly better understanding of VOC reactivity under a variety of environmental conditions but has helped address policy-relevant science issues. The recent progress in atmospheric science as it relates to ozone formation has encouraged all stakeholders and their belief that future regulatory approaches using VOC reactivity metrics will be realized.

AEROSOL COATINGS REGULATIONS (ARB)

On Sept. 13, 2005, the EPA approved California Air Resource Board's (CARB) SIP for ozone control,[5] including a reactivity-based approach to reduce ozone formation from aerosol coatings. This regulation mandates that formulators of aerosol products must meet reactivity-based limits and encourages reductions of higher reactivity VOCs. In this regulation (using the MIR concept) the product-weighted reactivity of the volatiles are controlled rather than the total mass of VOC that is emitted. Thus far, it appears that the implementation and "workability" of this rule has not been problematic [23]. The details of the process by which CARB estimates "ozone equivalent" VOC reductions are located at: http://www.arb.ca.gov/regact/conspro/aerocoat/aerocoat.htm.

In late 2008, the EPA also approved a National (reactivity-based) Volatile Organic Compound Emission Standards for Aerosol Coatings: http://www.epa.gov/EPA-AIR/2008/March/Day-24/a5589.htm.

EPA and CARB believe that the new aerosol rules will create additional incentives for formulators to use solvents with relatively low contribution to ozone formation. By doing so, it will be possible to achieve more ozone reductions than through traditional VOC mass-based regulations.

SHAPING FUTURE REACTIVITY POLICY

As the science of reactivity continues to evolve, policymakers will be even better equipped for assessing the feasibility of using reactivity-based standards. As stated in the "Aerosol Coating" section, the EPA has already been proactive in employing reactivity-based regulations at both the state and federal levels.

The EPA continues to review its Photochemical Reactivity Policy. There are many pathways to update and/or revise EPA's existing rule [24]. According to the NARSTO Review Panel Final Report on February 25, 2009:

> On September 13, 2005, U.S. EPA published in the Federal Register a Notice of Interim Guidance on SIP Development, in lieu of a more formal Advance Notice of Public Policy (ANPR). The interim guidance "encourages States to consider recent scientific information on the photochemical reactivity of volatile organic compounds" and "summarizes recent scientific findings" but "does not change any existing rules." The guidance is available on EPA website at: http://www.epa.gov/ttn/oarpg/t1/memoranda/27601interimguidvoc.pdf and http://www.epa.gov/ttncaaa1/t1/meta/m27601.html. It encourages the states to incorporate reactivity features into their individual State Implementation Plans.

The EPA believes that traditional mass-based VOC control measures continue to be effective tools for minimizing VOC contributions to ozone nonattainment problems in many situations. However, as demonstrated by the recent aerosol rulings, the EPA also believes that it is possible to use reactivity-based limits to exceed what is achievable with mass-based limits in a specific source category. Is the aerosol coatings scenario viable for other source categories?

[5] 70FR 53930, September 13, 2005: Final Rule: Revisions to the California State Implementation Plans and Revision to the Definition of Volatile Organic Compounds (VOC)—Removal of VOC Exemptions For California's Aerosol Coatings Products Reactivity-Based Regulation.

Given the current unified effort of all stakeholders involved with reactivity science, it is believed that a pathway forward on VOC reactivity and how it may be incorporated into the development of ozone control will be expanded. And, when evidence supports that a reactivity-based regulation for a category is more effective than mass-based in ozone reduction benefits, then the current regulation should be reviewed for revision.

SCENARIO FOR THE NEXT DECADE

CAAA-1990 and the myriad of new federal and state regulations associated with implementation of this comprehensive law have had a major impact on the coatings industry. And, challenges still remain for essentially all coating operations: the level of new or stricter VOC emission limits for coating operations (both federal and state); and the time, manpower, and cost associated with complying with the many new regulations associated with the amendments.

Other issues such as NO_x reduction strategy, global harmonization of VOC definition, and the expanded use of the incremental reactivity concept can potentially impact coating formulators. Regardless of the regulatory issue, coating formulators must remain informed about changing environmental regulations.

The paint market will continue to globalize, which will require increased monitoring of developments in VOC reduction programs in other countries. Important to the coating formulators will not only be regulations germane to a specific region but other labeling initiatives (i.e., EU Eco Label, Green-label certification, LEED, etc.), specifying coatings with lower VOC content.

As in the decades of 1970 through 1990, the new millennium will continue to offer opportunities for raw material suppliers to develop and provide environmentally acceptable materials to paint formulators. This, in turn, will facilitate the development of new or modified coatings with reduced VOC/HAP content. Continued attention to the improvement of coating processes and to the use of abatement equipment for emission control during the application of coatings (when feasible) will be ongoing. Ultimately, the challenge for the paint chemist is to develop cost-effective products that are tailored to meet or exceed the performance and environmental requirements of the customer.

FINDING REGULATORY INFORMATION

EPA Sources

Federal environmental regulations, including those promulgated under the CAA, are published in the *Code of Federal Regulations* (CFR), a series of books that are generally available on the internet as well as in major libraries and law libraries. These regulations as well as those of related state and local codes are also obtainable from the associated regulatory offices. Regulations of particular interest to the coatings industry can be found in subchapters of the *Code of Federal Regulations* (Table 4): http://www.epa.gov/ttn/.

Proposed regulations are published by the EPA in the *Federal Register*. Typically, a public (written) comment period of 30 to 90 days on the proposals is allowed, and often a public hearing is scheduled at which oral comments can be presented. The comments received are considered by the Agency in the development of a final regulation that is published in the *Federal Register* together with the regulation compliance date.

TABLE 4—Code of Federal Regulations Sub-chapter Topics

Sub-chapter	Subject	Parts
C	Air programs	50–87
	New source performance standards	60
D	Water programs	104–149
I	Solid waste	240–281
J	Superfund/right-to-know	300–372
N	Effluent guidelines and standards	401–471
R	Toxic substances control act	700–799

Questions relating to the interpretation, applicability, and compliance to air quality regulations may be addressed to the U.S. EPA regional offices or to the specific state regulating body responsible for air quality control. The EPA regional offices as well as satellite locations and laboratories can be accessed at: http://www.epa.gov/epahome/postal.htm.

The EPA maintains a comprehensive website with links to current regulatory and technical information germane to the CAA. The primary site for information on air quality issues, ozone depletion, air toxics, etc., is EPA's Office of Air and Radiation site, located at: http://www.epa.gov/oar/.

Other Sources

Among the industry trade organizations (list is not exhaustive) that provide information to their membership about pending regulations and guidance on compliance with finalized regulations are: America Chemistry Council (ACC), American Coatings Association (ACA), RadTech International North America, Chemical Coaters Association International (CCAI), Electrocoat Association (ECA), Paint Research Association (PRA), Steel Structures Painting Council (SSPC), Powder Coating Institute (PCI), Reactivity Research Work Group (RRWG), Chemical Specialty Products Association (CSPA), and European Solvents Industry Group (ESIG).

Several coatings journals publish excerpts from regulations and summary reviews. In addition, numerous universities have programs devoted to scientific advancements in coatings technology related to changes in air quality regulations.

Information regarding paint raw materials, coating technology, equipment, and environmental issues impacting the industry are also available through various trade shows and websites devoted to paints and coatings. Another valuable resource for environmental issues associated with the coatings industry is raw material manufacturers, especially solvent producers.

Note—the websites in this chapter were accessed on August 30, 2010.

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Part 2: Naturally Occurring Materials

2

Bituminous Coatings

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INTRODUCTION

General Overview

IN THE UNITED STATES, THE TERMS "BITUMINOUS" and "asphaltic" are often used interchangeably. In Europe, bitumen usually refers to the mixture of heavy hydrocarbons, free of inorganic impurities. Asphalt is often considered the impure form of the generic material [1]. For our purposes, the ASTM definitions will be used.

ASTM Standard Terminology Relating to Roofing, Waterproofing, and Bituminous Materials (D1079-09) [2] defines bitumen as either "(1) a class of amorphous, black or dark colored, (solid, semi-solid, or viscous) cementitious substances, natural or manufactured, composed principally of high molecular weight hydrocarbons, soluble in carbon disulfide, and found in asphalts, tars, pitches and asphaltites; or, (2) a generic term used to denote any material composed principally of bitumen."

Asphalt is similarly defined as "a dark brown to black cementitious material in which the predominating constituents are bitumens which occur in nature or are obtained in petroleum processing." While the term has historically implied the natural deposits (the Trinidad Lake asphalts on the Island of Trinidad or the Bermudez Lake, Venezuela, asphalts), most asphalt used in the United States today for coatings applications is from petroleum processing [3].

History and Background of Bitumens

As one of man's oldest engineering materials, the adhesive and waterproofing properties of bitumen have been known since the earliest days of civilization. The area between the Tigris and Euphrates rivers in Iraq, long believed to be "the cradle of civilization," contains the earliest deposits of asphalt and liquid petroleum. Early historical and biblical accounts tell of the use of asphalt in shipbuilding and foundation mortars. The Egyptians were known to have used asphalt in the mummification process; in fact, the part-Persian word for asphalt, "mumiya," is believed to be the origin of our word "mummy" [4].

The first asphalts produced in the United States were derived from California crude oils in the late 19th century. A straight run distillation, often without steam, was able to produce a good-quality material suitable for paving work. Most of this material was competing with foreign imports from the Lake Trinidad region on the Isle of Trinidad off the north coast of South America. In the early 20th century, Mexican asphalt obtained from Mexican crude oil was used extensively in the eastern United States and gained a reputation as a high-grade standard paving bitumen.

Today, asphalts are found throughout the world in several natural deposits of soft bituminous material or as hard glassy, black bitumen associated with certain rock formations or impregnating various limestone or sandstone-type formations. Additionally, asphalts are derived from colloidally dispersed asphalt hydrocarbons in crude petroleum. This leads to the classification of bitumens into the two following classes: (1) natural asphalts (bitumens) and (2) artificial or oil asphalts (petroleum asphalts)

The purity of bituminous materials is generally related to the degree that they are soluble in certain organic solvents. For years, the degree of solubility in carbon disulfide (CS_2) has been a typical method for determining the purity of natural asphalts. ASTM Standard Test Method for Bitumen Content [D4-86(2004)] formalizes this procedure with CS_2 solubility as the primary screening test. Most oil asphalts are generally greater than 99 % soluble in CS_2.

The natural asphalts can be further classified by the geographical region of their origin, as well as the extent to which impurities are present. For example, Trinidad, refined, of approximately 50 %–57 % bitumen; Cuban, refined, of 80 %–90 % purity; Bermudez, refined, of 85 %–92 % purity; and various rock asphalts, i.e., limestone, sandstone, tar sands, etc., with varying degrees of bitumen content.

A separate class of natural bitumens is the asphaltites. These are also called the solid bitumens and are asphalts without impurities (silts, clays, salts, etc.), although their degree of CS_2 solubility varies. Examples of these materials are Gilsonite, grahamite, glance pitch, or manjak, as well as harder materials that show no softening point, such as the pyrobitumens. The most important of these for coatings applications is Gilsonite.

Artificial bitumens have been classified into the three following major groups [5].

1. Oil or petroleum asphalts are soft to hard asphalts of high solubility in carbon disulfide (more than 99 %) and are classed as pure bitumens. They are obtained from the vacuum or steam distillation of crude oils containing high asphalt content. The distillation concentrates the colloidally dispersed asphalt into the "still bottoms" or "residuum" and is often a solid material. Precipitation methods are also used to recover asphalt from raw lubricating oils. This de-asphalting operation uses propane or other low-boiling hydrocarbons. The

[1] *DCA Coatings, Cleveland, OH*

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materials produced are the so-called asphaltic resins, with the hard, high asphaltene asphalts as the precipitate. Variations are made by controlling the propane stream. Oxidized or "blown" asphalts are obtained by blowing air at high temperatures through soft or liquid petroleum residues. This procedure can take semi-asphaltic materials of low purity and produce considerable amounts of bitumen. The resulting material is harder, with a higher softening point.

2. "Cracked" asphalts are also petroleum derivatives, but are obtained from by-products in oil-cracking processes. Residues are distilled to produce asphalt. They are variable in composition and may contain a certain amount of uncracked paraffinic material. These materials represent asphaltic hydrocarbons approximately intermediate in aromaticity between oil asphalts and the completely aromatic, highly condensed bitumens found in coal tars, water-gas tars, coal carbonization tars, and their pitches.
3. Coal tar, water-gas tars, and their pitches are derived from tars. ASTM D1079 defines tar as "a brown or black bituminous material, liquid or semi-solid in consistency, in which the predominating constituents are bitumens obtained … from the processing of coal, petroleum, oil-shale, wood, or other organic materials." The "free carbon" content, or other carbon disulfide insoluble matter, distinguishes coal tar from the asphaltites and oil asphalts. The latter are devoid of free carbon. Coal tars and their products are not included in the category of asphalt.

In the early 1960s, approximately 70 % of all oil asphalts were consumed by the road-paving industries with 20 % used in roofing. The solid bitumens and asphaltites of natural origin found their greatest consumption in lacquer, paint, and electrical insulation. Today, the paving industry is still the largest user of these materials, but the scope and area of specialty coatings has broadened considerably. In recent years, asphalts and other bitumens have become increasingly important as the cost of other natural and synthetic binders has continued to escalate. Their ability to act as adhesives with excellent moisture vapor transmission properties continues to result in new and varied uses.

Coating Types

The types of asphaltic or bituminous coatings available can be classified, in a large part, by the industry of use. Industries considered are as follows:

1. The paints and coatings industry, where bituminous coatings have been used to protect metal from the effects of water and oxygen degradation.
2. The roofing industry, where asphaltic coatings are used extensively to weatherproof buildings.
3. The construction industries, where concrete and mortar are waterproofed.
4. The paving industry, where the adhesive properties of asphalt as binder are put to good use in roads.

Specialty Paints and Coatings

Asphalt, coal tar, and other bitumens have been used in several specialty areas in the paint and coatings industry. The predominating use has been in the area of pipe coatings and automotive under-body coatings, although containment coatings are fast becoming a sizable market.

In pipe coatings, the base bitumen forms an interpenetrating network with a thermosetting resin to form an impervious barrier to groundwater and the effects of catastrophic rusting. On deep buried pipes or those set in concrete, the cost associated the use of an expensive binder is offset by the replacement costs involved. The thermoset resins most frequently used have been the epoxides. The bitumens used in these coatings have generally been the coal tars and pitches. This was primarily due to the compatibility of these highly aromatic materials with epoxy resins as well as the ease of working with a liquid material. The final film hardness is derived from the cross-linked epoxy network.

There has been a growing concern over the years with the toxicity of highly aromatic systems. The result has been that trade sales and light industrial coatings have moved away from coal tar or its pitches. Recently, the asphaltites and oil asphalts have been used in these types of coatings. The trend has been to use softer asphalts. Some form of compatibilizer has also been necessary to make these lower aromatic-content systems stable.

In automotive under-body rust proofing, bituminous coatings have found extensive use. These materials are modified with rubbery materials to give flexible coatings with excellent adhesion to metal parts. Many years ago, the predominant bitumen in use had been coal tar. Today, with the move away from highly aromatic products, petroleum asphalts are generally used. To use the harder bitumens such as asphaltites and petroleum asphalts, plasticizers are incorporated to soften and liquefy the bitumen. Originally these plasticizers were materials such as di-octyl phthalate (DOP) or butyl benzyl phthalate commonly found in other coatings applications. However, the toxicity of DOP has limited its use and items such as di-isodecyl and di-isononyl phthalates are being used instead. Aromatic processing oils were also used for this purpose but their toxicity has also limited their use. Natural and synthetic waxes are added to prevent chipping from road debris.

Given the severe penalties associated with contamination of groundwater, chemical and moisture-resistant coatings for containment dikes are being used more and more in the chemical process industry. Most state and local regulations require the use of a containment wall around every storage tank that may potentially rupture and contaminate the water table.

Coatings for this application have included coal tar epoxies and other coal tar/organic resin blends. Gilsonite-based resinous coatings have been widely used and, depending on the chemical nature of the contained material, petroleum asphalt urethanes and epoxides are available.

Additional areas where bitumens have shown applicability as specialty coatings have included the areas of sealing soil to minimize water penetration (pond liners, seepage control for levees and dams, and hazardous waste containment) as well as sound deadening on sheet metal and their use in binding other bituminous materials such as coal or lignite for pelletization.

Roof Coatings

In roof coatings, bitumens have been important raw materials since the turn of the century. Today, many commercial roofing systems use some form of asphalt or chemically modified asphalt in their construction. The application of

an asphalt or polymer-modified hot melt asphaltic material, followed by the application of a reinforcing membrane, is the basic construction of a modern built-up roof.

In some markets, the current industry trend has been away from the use of hot melt coatings, where a roofing kettle that heats the materials up to 450°F (232°C) to reach their application viscosity is required, and toward cold-applied systems. Here, the asphalt is usually modified with solvents, fillers, and thixotropes as well as various additives to result in a formulation that can be applied at ambient temperatures with good flow properties and that which will subsequently dry or cure into a weatherproofing membrane.

In these coatings, volatile solvents are varied to control cure times. In general, the solvents are either mineral spirits or naphthas. While asbestos was long a preferred additive for thixotropy and reinforcement, the hazards of working with and removing old installations with asbestos-containing materials have driven the products toward asbestos-free roofing materials. This has led to the use of cellulose, synthetic, and glass fibers as a partial replacement for asbestos. Bentonite and attapulgite clays are then used to obtain the required thixotropy. Today, the use of asbestos has been almost entirely eliminated in roofing.

The asphalt portion of these coatings usually consists of materials referred to as cutbacks. Various solvents are used to cut (solubilize) the asphalt, depending on the cure times required. The solvent predominantly used today is mineral spirits with a flash point of 104°F (40°C). Faster evaporating versions of these cutbacks have been used as primers for better substrate adhesion. These materials generally use faster aromatic solvents, including toluene, xylene, and the aromatic naphthas. The asphalt content varies from 30 % to 70 % by weight.

The preceding materials, while they can, in the strictest sense, be considered coatings, are actually closer to adhesives in performance; that is, these coatings are applied to hold the reinforcing membranes together. Although the last coat applied may be a flood coat of the adhesive coating, the roof is usually not left this way. Weathering characteristics are significantly improved when these roofs are gravel surfaced. This graveled surface blocks harmful ultraviolet (UV) radiation and serves to improve the fire resistance. The most common roof gravels are river-washed crushed stone, granite, and blast-furnace slag recovered from the iron ore reduction process and composed of silicates and aluminosilicates of lime [6]. Other materials, also available for this purpose, include a variety of small, synthetic, colored roofing granules, similar to those used on shingles.

From 400 to 600 lb (181–272 kg) of river-washed gravel per 100 ft^2 (9.29 m^2) of roof is used, or, if weight considerations are important, 50–60 lb (22.68–27.2 kg) of the smaller roofing granules can be used. The bituminous coating is then an adhesive for these gravels.

Due to weight limitations on existing roofs and costs associated with roof tear-offs and subsequent reroofing, current philosophy is to maintain the existing roof. When physically possible, restoration instead of replacement is very cost effective. This requires the use of coatings whose purpose is to repair damage to the roof and re-establish or maintain the weather-tight seal. After the repairs are complete, a reflective coating may be applied to act as a UV barrier and thermal reflector, or additional gravel added. Several different types of coatings have been available for each of these purposes.

Asphalt cutbacks and emulsions are the primary coating used for restoration. They are applied in heavy applications of 40–80 mm thick. This allows the coating to cover minor surface defects that are present on the old roof. Splits and cracks can be repaired by using these materials with either fiberglass or polyester reinforcements. A final application gives a reasonably watertight monolithic appearance.

Asphalt emulsions consist of two types. In one, the water is dispersed in the asphalt external phase. In the other, the asphalt is dispersed in a water external phase. The first are called water-in-oil (W/O) emulsions. The latter are oil-in-water (O/W) emulsions. Roofing emulsions are predominately water-in-oil emulsions. The oil-in-water emulsions are more widely used in the paving industry and will be discussed in more detail in that section.

The water-in-oil emulsions are produced from finely powdered clays, which act as dispersants for the water. Dispersing agents of this type show some affinity for water or are sufficiently hygroscopic to hold water and bring it into dispersion in the asphalt. The bentonite clays form extremely colloidal gelatinous mixtures and pastes with water and result in asphalt dispersions of very small particle size. These smooth buttery emulsions are very stable and can be fibered for reinforcement and modified with latex resins to obtain a degree of elasticity. Most commercial products are unmodified and yield a final coating possessing all the properties of a gelled asphalt after evaporation of the water. Several books are available that offer more detail in the area of emulsion technology [7–9].

Asphalt emulsions can be left untopcoated, but are frequently coated with reflective topcoats to help control rooftop temperatures. For several years, the major types of coatings for this application have been solvent-borne aluminum pigmented bituminous coatings. A wide variety of bitumens have been used, including asphalt, asphaltite, tar, and pitch. Their viscosity has generally been low with moderate levels of volatile solvents present. Most of the solvent-based aluminum bitumen paints in use today are asphalt vehicles made from petroleum asphalt cutbacks. Mineral spirits have been the predominately used solvent. The pigment used has been a leafing grade of aluminum paste. It is reported that some early formulations used cumerone indene resin to improve the leafing characteristics and act as an anti-bronzing agent. Bronzing occurs when low molecular weight residue migrates to the surface, staining the aluminum surface weeks to months after the film has cured, making it look brown and limiting its reflectivity. A level of 2.0 lb (0.91 kg) of aluminum paste is typically used per gallon in these coatings [10].

With the recent increase in environmental legislation and an increased awareness of health issues, alternatives to these solvent-borne coatings are beginning to find their place in the market. Specifically, asphalt emulsions of various solids are being used in conjunction with new aluminum pigment technology, which allows the manufacture of relatively stable waterborne versions [11,12]. These materials generally consist of petroleum asphalt emulsions that use organophosphate-treated leafing-aluminum pastes. The phosphate passivates the aluminum, giving it more stability on storage. The solids of such coatings vary from 25 %

to 50 % by weight. Additional modification similar to other emulsion systems is also used in these coatings.

Newer technologies to stabilize aluminum pigments in water have recently been introduced. Chemically bound chrome is used to passivate the aluminum [13]. While quite expensive, these products are finding use in the automotive industry. As their cost decreases, perhaps they will be available for the waterborne bituminous aluminum market.

Other technologies exist that are non-bituminous in composition. These coatings include elastomeric latexes, solvent and waterborne urethanes, epoxides, and alkyds. These are usually pigmented with titanium dioxide (TiO_2), aluminum or the newer infrared reflective pigments, to give thermally reflective coatings. These types will be discussed elsewhere in this manual.

Waterproofing Membranes

Bitumen-modified waterproofing membranes are used extensively in the construction industry. The most common substrate is poured or precast concrete or mortared "cinder block." Pre-stressed concrete in the foundations, walls, and roof decks of high-rise buildings is also a suitable candidate for these membranes. In the home construction and repair industries, cinder block foundations and concrete footers are commonly waterproofed with bitumen-modified polymeric coatings.

The bitumen of interest in these markets has predominately been coal tar pitch and petroleum asphalts. Waterproofing membranes are generally composed of bitumen in an elastomeric polymer matrix. The aromatic polyurethanes are frequently used for this purpose.

In coating structural steel and steel reinforcement bars, coal tar epoxies have been extensively used. Their composition and purpose is similar to that of pipe coatings used for the prevention of underground corrosion. Their composition can be modified to conform to a particular steel coatings application.

As in other markets, the use of aromatic coal tars is slowly being replaced by safer soft petroleum asphalts. Environmental issues aside, higher technology systems are beginning to be seen. Other types of coatings for rebar in the past five years have included fused epoxy powder coatings systems and polyethylene dip-coated systems. While much more expensive than bitumen-modified systems, their improved performance have made them of interest.

Coatings for Paving

The paving industry is probably the oldest using bitumen and its coatings. Asphalt cutbacks have also been known as "road oils." For years, these solvent cut materials were used to seal roads as well as coat aggregates for application to the road surface. Today, hot asphalt or cutback is used to prime new paving as well as to repair damaged or worn areas.

Today, most road coating uses asphalt emulsions. These are generally chemically stabilized emulsions. The emulsion is prepared beforehand and mixed with aggregate on site and is referred to as *chip* and *seal*. Hot asphalt is not required in this application, making it much easier than the use of hot mix paving, where the asphalt is heated to melting before application. In paving, oil-in-water emulsions predominate.

The oil-in-water emulsions are formed from the action of a chemical emulsifier, which can be anionic, cationic, or nonionic in nature. The anionic and cationic emulsifiers form an emulsion in which the dispersed phase shows a definite charge. These emulsions are said to "break" upon contact with a charged aggregate, yielding the exclusion of one phase from the other. The speed of break can be modified, yielding rapid, medium, or slow-setting emulsions. The cat-ionic versions are preferred because the coating formed does not re-emulsify. With anionic emulsifiers, break occurs when emulsions destabilize due to water loss on drying. One disadvantage of this is the possibility of re-emulsification in the early stages of cure. Once the coating has dried, water is no longer a problem.

Paving sealers are used to protect new or old asphalt driveways or parking lots. The sealers are generally coal tar in nature due to good resistance to gas and oil. Asphalt sealers can also be used, but must be latex or polymer modified to improve solvent resistance.

Other types of bituminous coatings used in the paving industry include slurry seals and microsurfacing, which uses latex or polymer-modified asphalts with fine aggregate filler as a surface treatment for repair of minor damage to roads. Coal tar is not used in this application because the resulting coating is too slippery. Tack coats consisting of asphalt cutbacks are also used when one layer of asphalt needs to be adhered to another.

IDENTIFICATION OF BITUMINOUS MATERIALS

This section will catalogue several test methods currently available through ASTM for characterization of bituminous paints and coatings. Many of these methods are familiar to the coatings chemist as standard paint-related tests found in Volumes 6.01 through 6.04 of the *Annual Book of ASTM Standards*. Several others are under the jurisdiction of Committee D8 on Roofing, Waterproofing, and Bituminous Materials. These methods appear in Volume 4.04 of the *Annual Book of ASTM Standards*.

Tests on Bituminous Materials

The following test methods are used to differentiate one type of bitumen from another. They also can distinguish mixtures of bitumens and their purity. As bitumens are considered pseudo-plastic materials, with no true melt point, softening point and penetration are the two major tests routinely performed to identify differences within grades of the different bitumen classes. Viscosities at elevated temperatures are also very important with several instruments and their methods listed.

In earlier editions of this manual, several tests were described that were in common use in 1972. Among the tests described were the solubility of bitumens in carbon disulfide (CS_2) to identify the purity of a bitumen sample, since by definition only CS_2 soluble matter is bitumen. Also listed were tests to determine the presence of asphalt and tar in suspected mixtures (the Oliensis Spot Test) and the characteristics of bituminous samples dispersed in solvent. These methods have since been incorporated into the *Annual Book of ASTM Standards* and will not be described in detail.

It is important to point out that each industry that uses bitumens has tended to develop its own series of common pertinent tests. Today most of those pertinent tests have been incorporated as ASTM standards. In addition to ASTM, other organizations have tried to compile these tests for their members' use. The Asphalt Institute, an international nonprofit organization sponsored by members of the

petroleum asphalt industry, also publishes a handbook that has evolved over the past 50 years as the standard reference work in the field of asphalt technology and construction, especially in the paving industry [14]. This reference book cites both ASTM test methods and, where applicable, American Association of State and Transportation Officials (AASHTO) counterparts to these methods. A large part of the manual is devoted to practical how-to information about how to use asphalt, as well as comprehensive data on asphalt technology, and is highly recommended.

Standard Specifications and Standard Test Methods for Bituminous Materials

D4-86(2004)	Standard Test Method for Bitumen Content
D5-06e1	Standard Test Method for Penetration of Bituminous Materials
D36-06	Standard Test Method for Softening Point of Bitumen (Ring-and-Ball apparatus)
D70-09e1	Standard Test Method for Specific Gravity and Density of Semi-Solid Bituminous Materials
D88-07	Standard Test Method For Saybolt Viscosity
D92-05a	Standard Test Method For Flash and Fire Points by Cleveland Open Cup
D95-05e1	Standard Test Method for Water Petroleum Products and Bituminous Materials by Distillation
D140/D140M-09	Standard Practice for Sampling Bituminous Materials
D529-04	Standard Practice for Enclosed Carbon Arc Exposures of Bituminous Materials
D1079-09	Standard Terminology Relating to Roofing, Waterproofing and Bituminous Materials
D1669-07	Standard Practice for Preparation of Test Panels for Accelerated and Outdoor Weathering of Bituminous Coatings
D1670-04	Standard Test Method for Failure End Point in Accelerated and Outdoor Weathering of Bituminous Materials
D4798/ D4798M-09	Standard Practice for Accelerated Weathering Test Conditions and Procedures for Bituminous Materials (Xenon-Arc Method)
D4799-08	Standard Practice for Accelerated Weathering Test Conditions and Procedures for Bituminous Materials (Fluorescent UV, Water Spray, and Condensation Method)
D4989-90a(2008)	Standard Test Method for Apparent Viscosity (Flow) of Roofing Bitumens Using the Parallel Plate Plastometer
E96/E96M-05	Standard Test Methods for Water Vapor Transmission of Materials
E102/E102M-93(2009)	Standard Test Method for Saybolt Furol Viscosity of Bituminous Materials at High Temperatures
E108-07a	Standard Test Methods for Fire Tests of Roof Coverings

Specifications and Test Methods for Asphalt

D71-94(2004)	Standard Test Method for Relative Density of Solid Pitch and Asphalt (Displacement Method)
D312-00(2006)	Standard Specification for Asphalt Used in Roofing
D449-03(2008)	Standard Specification for Asphalt Used in Dampproofing and Waterproofing
D1370-00(2007)	Standard Test Method for Contact Compatibility Between Asphaltic Materials (Oliensis Test)
D1856-09	Standard Test Method for Recovery of Asphalt from Solution Abson Method
D2042-09	Standard Test Method for Solubility of Asphalt Materials in Trichloroethylene
D2521-76(2008)	Standard Specification for Asphalt Used in Canal, Ditch, and Pond Lining
D2746-07	Standard Test Method for Staining Tendency of Asphalt (Stain Index)
D3461-97(2007)	Standard Test Method for Softening Point of Asphalts and Pitches (Mettler Cup-and-Ball Method)
D4402-06	Standard Test Method for Viscosity Determination of Asphalt at Elevated Temperatures Using a Rotational Viscometer

Specifications and Test Methods for Coal Tar, Pitches, and Highly Cracked Petroleum Products

D61-75(2004)	Standard Test Method for Softening Point of Pitches (Cube-in-Water Method)
D450-07	Standard Specification for Coal Tar Pitch Used in Roofing, Dampproofing, and Waterproofing
D2318-98(2008)	Standard Test Method for Quinoline-Insoluble (QI) Content of Tar and Pitch
D2319/D2319M-98(2008)e1	Standard Test Method for Softening Point of Pitch (Cube-in-Air Method)
D2320-98(2008)	Standard Test Method for Density (Relative Density) of Solid Pitch (Pycnometer Method)
D2415-98(2008)	Standard Test Method for Ash in Coal Tar and Pitch
D2416-84(2004)	Standard Test Method for Coking Value of Tar and Pitch (Modified Conradson)
D2764-99(2004)e1	Standard Test Method for Dimethylformamide-Insoluble (DMF-I) Content of Tar and Pitch
D2962-97(2007)	Standard Test Method for Calculating Volume-Temperature Correction for Coal-Tar Pitches

D3104-99(2005)	Standard Test Method for Softening Point of Pitches (Mettler Softening Point Method)
D4072-98(2008)	Standard Test Method for Toluene-Insoluble (TI) Content of Tar and Pitch
D4312-95a(2005)	Standard Test Method for Toluene-Insoluble (TI) Content of Tar and Pitch (Short Method)
D4616-95(2008)	Standard Test Method for Microscopical Analysis by Reflected Light and Determination of Mesophase in a Pitch
D4715-98(2008)e1	Standard Test Method for Coking Value of Tar and Pitch (Alcan)
D4746-98(2008)	Standard Test Method for Determination of Quinoline Insoluble (QI) Content in Tar and Pitch by Pressure Filtration
D4892-89(2009)	Standard Test Method for Density of Solid Pitch (Helium Pycnometer Method)
D4893-94(2004)	Standard Test Method for Determination of Pitch Volatility
D5018-89(2009)	Standard Test Method for Shear Viscosity of Coal Tar and Petroleum Pitches

TESTS AND SPECIFICATIONS FOR COATINGS

General Tests for Coatings

Several of the test methods familiar to the industrial paints and coatings chemist can also be used to characterize the performance and physical properties of bituminous coatings. The following methods can be found in Volume 3.02 and Volumes 6.01 through 6.04 of the *Annual Book of ASTM Standards*.

Tests and Specifications

B117-07a	Standard Test Method of Salt Spray (Fog) Testing
D522-93a(2008)	Standard Test Methods for Mandrel Bend Test of Attached Organic Coatings
D562-01(2005)	Standard Test Method for Consistency of Paints Measuring Kreb Unit (KU) Viscosity Using A Stormer-type Viscometer
D609-00(2006)	Standard Practice for Preparation of Cold-Rolled Steel Panels for Testing Paint, Varnish, Conversion Coatings and Related Coating Products
D610-08	Standard Test Method for Evaluating Degree of Rusting on Painted Steel Surfaces
D662-93(2005)	Standard Test Method for Evaluating Degree of Erosion of Exterior Paints
D714-02(2009)	Standard Test Method for Evaluating Degree of Blistering of Paints
D1212-91(2007)	Standard Test Method for Measurement of Wet Film Thickness of Organic Coatings
D1474-98(2008)	Standard Test Methods for the Indentation Hardness of Organic Coatings
D1475-98(2008)	Standard Test Method for Density of Paint, Varnish, Lacquer, and Related Products
D1640-03(2009)	Standard Test Methods for Drying, Curing, or Film Formation of Organic Coatings at Room Temperature
D1644-01(2006)	Standard Test Methods for Nonvolatile Content of Varnishes
D1654-08	Standard Test Method for Evaluation of Painted or Coated Specimens Subjected to Corrosive Environments
D1849-95(2008)	Standard Test Method for Package Stability of Paint
D2243-95(2008)	Standard Test Method for Freeze-Thaw Resistance of Water-Borne Coatings
D2247-02	Standard Practice for Testing Water Resistance of Coatings in 100 % Relative Humidity
D2369-07	Standard Test Methods for Volatile Content of Coatings
D2370-98(2002)	Standard Test Method for Tensile Properties of Organic Coatings
D2832-92(2005)	Standard Guide for Determining Volatile and Nonvolatile Content of Paint and Related Coatings
D3170-03(2007)	Standard Test Method for Chipping Resistance of Coatings
D3359-09	Standard Test Methods for Measuring Adhesion by Tape Test
D3960-05	Standard Practice for Determining Volatile Organic Compound (VOC) Content of Paints and Related Coatings
G6-07	Standard Test Method for Abrasion Resistance of Pipeline Coatings

Solvent-Thinned or Cut-Back Coatings

The following test methods relate specifically to solvent thinned or cut-back bituminous coatings such as those used for weatherproofing roofs or protecting metal structures and appurtenances. Although volatile organic content of coatings has become increasingly more important, leading to the greater use of emulsified bitumen, the sealing and waterproofing properties of straight asphalt have continued to make these types of coatings viable. This in turn has made their test methods pertinent.

General

D402-08	Standard Test Method for Distillation of Cut-Back Asphaltic (Bituminous) Products
D529-04	Standard Test Method for Enclosed Carbon Arc Exposures for Bituminous Materials
D3105-08	Standard Index of Methods for Testing Elastomeric and Plastomeric Roofing and Waterproofing Materials

Roof Coatings

D41-05	Standard Specification for Asphalt Primer Used in Roofing and Waterproofing
D43-00(2006)	Standard Specification for Creosote Primer Used in Roofing, Dampproofing and Waterproofing
D1227-95(2007)	Standard Specification for Emulsified Asphalt Used as a Protective Coating for Built-Up Roofing
D2823-05	Standard Specification for Asphalt Roof Coatings
D2824-06	Standard Specification for Aluminum-Pigmented Roof Coatings, Non-Fibered, Asbestos Fibered, and Fibered Without Asbestos
D4479-07	Standard Specification for Asphalt Roof Coatings-Asbestos Free
D5076-90(2006)	Standard Test Method for Measuring Voids in Roofing and Waterproofing Membranes

Waterproofing Membranes

D41-05	Standard Specification for Asphalt Primer Used in Roofing, Dampproofing and Waterproofing
D43-00(2006)	Standard for Creosote Primer Used in Roofing, Dampproofing and Waterproofing
D5076-90(2006)	Standard Test Method for Measuring Voids in Roofing and Waterproofing Membranes

Paving Sealers

D3320-00(2004)e1	Standard Specification for Emulsified Coal Tar Pitch (Mineral Colloid Type)
D3423-84(2003)	Standard Practice for Application of Emulsified Coal Tar Pitch (Mineral Colloid Type)
D4866-88(2003)e1	Standard Performance Specification for Coal Tar Pitch Emulsion Pavement Sealer Mix Formulations Containing Mineral Aggregates and Optional Polymeric Admixtures

Specialty Coatings

D41-05	Standard Specification for Primer Used in Roofing and Waterproofing
D43-00(2006)	Standard Specification for Creosote Primer Used in Roofing, Dampproofing and Waterproofing
D1187-97(2002)e1	Standard Specification for Asphalt-Base Emulsions for Use as Protective Coatings for Metal

Emulsion Coatings

General

D529-04	Standard Test Method for Enclosed Carbon Arc for Bituminous Materials
D1187-97(2002)e1	Standard Test Method for Asphalt-Base Emulsion for Use as Protective Coatings for Metal
D2939-03	Standard Test Method for Emulsified Bitumens Used as Protective Coatings

Clay Stabilized Emulsions

D1227-95(2007)	Standard Specification for Emulsified Asphalt Used as a Protective Coating for Roofing
D3320-00(2004)e1	Standard Specification for Emulsified Coal Tar Pitch (Mineral Colloid Type)

Anionic Emulsions

D1227-95(2007)	Standard Specification for Emulsified Asphalt Used as a Protective Coating for Roofing

Non-Ionic Emulsions

D1227-95(2007)	Standard Specification for Emulsified Asphalt Used as a Protective Coating for Roofing

Cationic Emulsions

D1227-95(2007)	Standard Specification for Emulsified Asphalt Used as a Protective Coating for Roofing

Resin Modified Bituminous Coatings

Synthetic Resins

D3468-99(2006)e1	Specification for Liquid-Applied Neoprene and Chlorosulfonated Polyethylene Used in Roofing and Waterproofing

WITHDRAWN SPECIFICATIONS AND TEST METHODS

The following specifications and test methods have been withdrawn by ASTM since the last printing of this book. The dedicated researcher may wish to investigate archived copies of these methods for the potential insight they bring to testing bituminous based coatings in general and asphalt in particular. D1328 is the only method for which an alternate method was established. The others were withdrawn the year specified.

D255-70	Method for Steam Distillation of Bituminous Protective Coatings—Withdrawn 2000—No Replacement
D466-42	Method of Testing Films Deposited from Bituminous Emulsions—Withdrawn 1991—No Replacement

D555-94(1999)	Standard Guide for Testing Drying Oils—Withdrawn 2007—No Replacement
D1328-86	Standard Test Method for Staining Properties of Asphalt—Withdrawn 1992—Replaced by D2746-97
D1540-82	Standard Test Method for Effect of Chemical Agents on Organic Finishes Used in the Transportation Industry—Withdrawn 1991—No Replacement
D1542-60	Standard Test Method for Qualitative Detection of Rosin in Varnishes—Withdrawn 1997—No Replacement
D2569-97(2002)	Standard Test Method for Distillation of Pitch—Withdrawn 2006—No Replacement
D2963-78	Standard Test Method for Testing Flow Table Consistency of Clay-Stabilized Asphalt Emulsions—Withdrawn 1997—No Replacement
D3805-85	Standard Practice for Application of Aluminum-Pigmented Asphalt Roof Coatings— Withdrawn 1996—No Replacement

CONCLUSION

Bituminous coatings are still used extensively today. The waterproofing and adhesive properties, coupled with the relatively inexpensive costs for most bituminous materials, continue to drive their many diverse industrial applications. The preceding information will give the reader an understanding of the chemistry and uses of bituminous coatings in industry and a realization that even several thousand years after their discovery and first use the usage of these bituminous raw materials as an engineering raw material is still growing.

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3

Cellulose Esters of Organic Acids

Jos S. de Wit[1] and Deep Bhattacharya[2]

INTRODUCTION

CELLULOSE ESTERS ARE BASED ON ONE OF THE most abundant naturally occurring biopolymers, namely cellulose. This polysaccharide represents a readily available, sustainable feedstock alternative to petroleum-based materials. Although a broad variety of cellulose esters can be made, this chapter only provides a general discussion on the commercially available organic acid esters of cellulose: cellulose acetate (CA), cellulose acetate propionate (CAP), and cellulose acetate butyrate (CAB).

Cellulose esters are the reaction product of combining organic acids and/or acid anhydrides with the hydroxyl groups found on the anhydroglucose repeating units of a cellulose molecule [1, 2]. In addition to esterification, several subsequent processing steps are required in the manufacture of cellulose esters including hydrolysis to obtain the desired residual hydroxyl level, filtration, precipitation, washing, dewatering, drying, and screening. Details about these and other manufacturing steps can be found at various places in the three volumes of Ott, Spurlin, and Grafflin [3]. The final product is a dry, free-flowing powder in most instances, although other physical forms can be produced when required.

Basic information about physical properties, solubility properties in various solvents and monomers, and compatibility properties of various cellulose esters is provided. Typical uses as well as selected new uses for cellulose esters are briefly discussed as a general guide to selecting these polymeric materials for a variety of applications.

TYPES OF CELLULOSE ESTERS

Three types of cellulose esters are commercially available, including CA, CAP, and CAB (Fig. 1). Table 1 shows the types of commercially available cellulose esters. Cellulose acetate butyrate is the most commonly used organic cellulose ester for coating applications.[3] Many types have been manufactured by varying acetyl/butyryl ratios, hydroxyl content and molecular weight to meet the requirements of the applications for which they were developed.

Cellulose acetates are the least soluble and least compatible of the cellulose esters, and they require strong solvents for dissolution. They have high glass transition temperatures and produce tough and hard films with excellent chemical resistance. CAPs have improved compatibility and solubility and are used in applications where low odor is required. CAB esters are used as binders in protective and decorative coatings for metal, wood, textiles, cloth, paper, plastic, human nail care, printing inks, trucks and buses, polarographic oxygen electrodes, solid rocket propellants, and leather. They provide excellent color and color retention, toughness, flexibility, flow control, as well as good weather resistance. All three products are available with a range of substituents and molecular weights that determine their solubility, compatibility, viscosity, and hardness. Recently, Yuan et al. [4] have investigated the permeability characteristics of cellulose acetate butyrate coating films and their importance as semipermeable membranes in osmotic drug delivery systems. Similar studies related to this end use include the use of CAB as a matrix tableting and/or taste masking material when combined with CA and hydroxypropyl cellulose [5–7]. A novel technique for forming very thick but wrinkle-free membranes that involves solvent-nonsolvent mixtures has been described [8]. Table 1 contains a listing of properties for commercial cellulose esters.

CAB esters are also useful as coatings additives where they can provide a significant performance edge. Frequently, these polymers are described as versatile problem solvers because cellulose esters provide qualities such as good flow and leveling, faster drying, sag resistance, viscosity control, intercoat adhesion, and metal flake orientation.

Cellulose esters are typically supplied as dry, free-flowing fine powders and they should be handled accordingly since any free-falling powder can generate static electricity. Proper precautions should be taken when handling the dry-powder cellulose esters.

FACTORS AFFECTING PERFORMANCE OF CELLULOSE ESTERS IN COATINGS

Performance attributes of cellulose esters are affected by the chemical composition and the molecular weight of the ester. The larger size and lower polarity of the propionyl or butyryl group on the molecule alters the packing density of the cellulose chains, causing them to spread farther apart and lowering the attraction between the neighboring units. In solution, these groups affect the configuration and conformation of the molecular chains and thus alter properties. The extent to which these factors occur depends on the degree of substitution (DS) and the particular substituents. DS is commonly used to quantify the number of hydroxyls per anhydroglucose unit groups being replaced by acyl

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[3] Although not discussed in this chapter, other cellulose derivatives are in commercial use. For example, cellulose nitrate is used as a lacquer in the furniture coating business and alkylene oxide derivatives of cellulose are used in thickening and other liquid flow altering areas (see Chapter 33 of this Manual).

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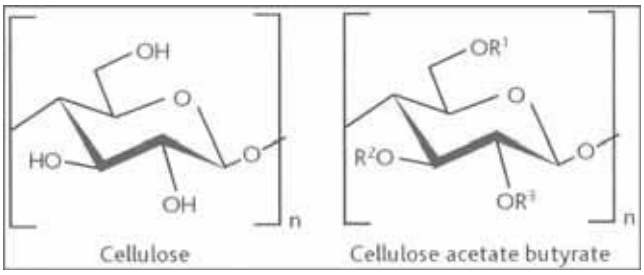

Fig. 1—Repeating unit in cellulose esters; R^1, R^2, R^3 = acetyl, butyryl, or H.

groups. The DS ranges from 0 (cellulose) to 3 (tri-esters). CABs are the most commonly used cellulose esters in coatings and are discussed in more detail below.

As the butyryl content increases, solubility, compatibility, flexibility, diluent tolerance, and moisture resistance are increased. Lower butyryl levels are associated with increased chemical and grease resistance, hardness, and melting range.

Most of the butyrates are manufactured with a hydroxyl content best suited for general applications (about 1.5 %), permitting good solubility, compatibility, and performance in coatings applications. Most CABs are soluble in esters, ke-tones, glycol ethers, glycol ether esters, blends of alcohols, and aromatic hydrocarbons, and they are quite tolerant of diluents such as aromatic hydrocarbons and alcohols. At levels around 5 %, solubility in lower molecular weight alcohols occurs. At higher hydroxyl levels, reactivity increases, providing cross-linking capability with amino and isocyanate resins. However, in non-cross-linking systems, higher levels decrease moisture resistance due to increased hydrophilicity.

When considering the hydroxyl functionality in the stoichiometry of a cross-linkable coating system, the following calculations may be useful:

TABLE 1—Typical properties[a]

Eastman™ Cellulose Ester	Viscosity[b] S	Viscosity[b] Poise	OH (%)	Melting range (°C)	T_g (°C)	Wt/Vol (lb/gal)	Wt/Vol (kg/L)	MW_n[c]	Comments
Cellulose acetate butyrate									
CAB-551-0.01	0.01	0.038	1.5	127–142	85	9.67	1.16	16 000	Butyryl level: flexibility, solubility, & compatibility
CAB-551-0.2	0.20	0.76	1.8	130–140	101	9.67	1.16	30 000	
CAB-553-0.4	0.30	1.14	4.8	150–160	136	10.00	1.20	20 000	
CAB-531-1	1.90	7.22	1.7	135–150	115	9.75	1.17	40 000	
CAB-500-5	5.00	19.00	1	165–175	96	9.83	1.18	57 000	
CAB-381-0.1	0.10	0.38	1.3	155–165	123	10.00	1.20	20 000	
CAB-381-0.5	0.50	1.90	1.3	155–135	130	10.00	1.20	30 000	
CAB-381-2	2.00	7.60	1.3	171–184	133	10.00	1.20	40 000	
CAB-381-2 BP	2.20	8.36	1.8	175–185	130	10.00	1.20	40 000	
CAB-381-20	20.00	76.00	1.8	195–205	141	10.00	1.20	70 000	
CAB-381-20 BP	16.00	60.80	0.8	185–195	128	10.00	1.20	70 000	
CAB-321-0.1	0.10	0.38	1.3	165–175	127	10.00	1.20	12 000	
CAB-171-15	15.00	57.00	1.1	230–240	161	10.50	1.26	65 000	
Cellulose acetate propionate									
CAP-504-0.2	0.20	0.76	5.0	188–210	159	10.53	1.26	15 000	
CAP-482-0.5	0.40	1.52	2.6	188–210	142	10.20	1.22	25 000	
CAP-482-20	20.00	76.00	1.8	188–210	147	10.20	1.22	75 000	
Cellulose acetate									
CA-398-3	3.00	11.40	3.5	230–150	180	10.90	1.31	30 000	Viscosity
CA-398-6	6.00	22.80	3.5	230–250	182	10.90	1.31	35 000	
CA-398-10	10.00	38.00	3.5	230–250	185	10.90	1.31	40 000	
CA-398-30	30.00	114.00	3.5	230–250	189	10.90	1.31	50 000	

[a] Properties reported here are typical of average lots. Eastman makes no representation that the material in any particular shipment will conform exactly to the listed properties. All Eastman™ cellulose esters are filtered and in the form of fine, white, dry powder except CA-394-60S, an unfiltered pellet form. Like most organic materials in powder form, these materials are capable of creating a dust explosion. Refer to NFPA. Pamphlets No 654, "Prevention of Fire and Dust Explosions in the Chemical, Dye, Pharmaceutical, and Plastics Industries."

[b] ASTM D817 (Formula A) and D1343.

[c] Number-average molecular weight values, MW_n, are polystyrene-equivalent molecular weights determined using size exclusion chromatography.

TABLE 2—Viscosities of selected CABs in various solvents

Additive	wt %	HDODA[a]	TMPTA[b]	DPGDA[c]	TPGDA[d]	Styrene
CAB-553-0.4	5	1550	1550	1190	40 000	NA
CAB-381-0.1	5	60	1670	113	180	NA
CAB-321-0.1	5	53	1420	93	128	NA
CAB-551-0.2	5	87	2080	136	204	30
CAB-551-0.01	5	29	661	40	57	7
Solus 2100	5	. . .	424	30	44	. . .
Solus 2100	20	56	1660	104	172	10

[a] HDODA—Hexanediol diacrylate.
[b] TMPTA—Trimethylolpropane triacrylate.
[c] DPGDA—Dipropyleneglycol diacrylate
[d] TPGDA—Tripropyleneglycol diacrylate.

Hydroxyl number = 33 × wt % hydroxyl

Hydroxyl equivalent wt = 1700 × wt % hydroxyl

In general, CABs are compatible with most acrylics, polyesters, phenolics, ureas, and isocyanates. They are also compatible with some epoxides and poly(vinyl acetates). CABs are often incompatible with melamines, urea formaldehydes, and most alkyds.

The molecular weight (often related to as viscosity) of cellulose esters also influences physical properties of the esters as well as coatings formulated with them. Increasing the molecular weight slightly lowers its solubility and compatibility with other polymers, but it does not affect hardness and density. Generally, toughness and flexibility are improved as molecular weight is increased.

CELLULOSE ESTERS AS FILM FORMERS, MODIFIERS, OR ADDITIVES

In some protective and decorative coatings, cellulose esters serve as the primary film-forming polymer or as a modifying copolymer to impart a specific property to the liquid or solid coating. There are four characteristics that explain the benefits cellulose esters bring to coatings when they are used as additives.

1. Due to their rapid viscosity build, cellulose esters prevent film distortion and craters, sags and runs, picture framing, poor metal flake orientation, color separation in multipigment systems, pigment flooding and floating, inconsistent gloss control with matting agents, and poor holdout.
2. Due to their Newtonian rheology, cellulose esters improve flow and leveling, rheology control, reduction of surface defects such as pinholes and craters in atomization, roll coat, and curtain coat applications.
3. Due to their high glass transition temperatures, cellulose esters provide rapid dry-to-touch times and excellent hardness development.
4. Due to their cellulose backbone, cellulose esters have good UV stability and dimensional stability.

APPLICATIONS FOR CELLULOSE ESTERS IN COATINGS

In the automotive industry, cellulose esters have been used for decades in both original equipment manufacturer and refinish basecoats, refinish primers, clear coats, and monocoats. They are often an integral component in enabling the formulator to achieve desired color effects, particularly through consistent metallic flake orientation. CAB used in the basecoat of a basecoat/clear-coat system provides improved flake alignment and resistance to redissolve from the topcoat solvents. CAB is also used in pigment dispersions for automotive applications to provide consistent tints and to achieve the maximum color development from a given pigment.

In addition to automotive metal coatings, CAB lacquers are especially useful on structural aluminum, aluminum foil, stainless steel, chromium, brass, silver, and tin, where protection of the metal surface and maintenance of the metallic luster are desired. By appropriate selection of modifying resins, butyrate lacquers may be formulated into clear or pigmented coatings that have good adhesion to metallic surfaces and that are resistant to salt-fog, oxygen, and other tarnishing and corroding elements. CABs used in metallic coil coatings reduce surface defects, improve metallic and pearlescent flake alignment, as well as providing improved flow and leveling, better gloss consistency, and purer white color value.

CAB has been used for many years in coatings for various plastic materials. Portions of the surface of molded plastic articles are frequently coated with a lacquer that primarily serves a decorative purpose; for example, metallic coatings on cell phones or casings for DVDs. CAB polymers are effective as release coatings for silicone rubber molds used in forming rigid polyurethane articles. The base release coating not only protects the mold from attack by the poly-urethane components, it also becomes an integral part of the plastic article and serves as a tie coat for other coatings on the molded article.

A major use of CAB is in wood coatings for furniture, plywood paneling, particleboard, and hardboard, both in thermoplastic and thermoset systems. It can be formulated into coatings (often a butyrate/acrylic composition) that are nonyellowing, possess good durability, stain resistance, plasticizer migration resistance, depth of finish, color, and color stability.

Crosslinking systems such as a CAB/urea-formaldehyde composition is frequently used in coating kitchen cabinets, and high quality furniture finishes exhibiting outstanding toughness and chemical resistance can be prepared by blending CAB with an isocyanate prepolymer.

TABLE 3—Selector guide for graphic arts applications		
Technology	**Cellulose Ester**	**Comments**
Digital	CAB551, CAP482	Solvent based and UV
Flexography	CAP504, CAP482, CAB553, CAB551	Solvent selection will be limited by the chemical resistance of the image roll
Gravure	CAP482, CAP504, CAB381, CAB531, CAB553, CAB551, CAB500, CA398	The inert image roll allows wide selection of resin and solvents
Screen	CAP482, CAB381, CAB531, CAB500, CA398	Viscosity is a benefit in these applications
OPV	CAB551, CAB381	Flow and leveling and improved adhesion

Flexible cloth lacquers made from CAB 381 are used in coating nonyellowing window shades and flame-resistant artificial leathers. CAB is used with urethane elastomers to coat fabrics used in the production of sportswear, rainwear, footwear, hats, coats, handbags, luggage, and upholstery for furniture and automobiles. Blending CAB with these polymers increases hardness, reduces tack, raises blocking point, improves slip, and reduces dirt pickup of the coating.

Other applications include paper and lacquer emulsions for leather topcoats. CAB is used worldwide in topcoats for leather items such as automotive upholstery, footwear, and furniture. These topcoats containing CAB are tough and have good resistance to abrasion and plasticizer migration.

Cellulose esters are used as additives in radiation curing (RC) systems as well. Here, they provide similar benefits as in solvent-borne coatings, such as flow and leveling, improved gloss control, adhesion, and reduction of surface defects. CAB 551 types are used in overprint varnishes at levels of 1–5 %. In applying RC coatings, CABs can reduce or eliminate holes in curtain coatings and reduce spattering in high-speed roll coat applications. Most commonly, the CAB is dissolved in a monomer and then added to the formulation. The viscosities of certain CABs in a variety of monomers are given in Table 2.

Cellulose esters are also used in graphic arts as thermoplastic and thermoset inks, including over print varnishes. Guidance for selecting the appropriate cellulose ester is provided in Table 3.

COMPLIANT COATINGS

Environmental legislation across the globe has resulted in the paint industry attempting to move toward greener and more “eco-friendly” lower volatile organic component (VOC) products with similar performance attributes as conventional coating formulations. Some approaches for achieving low VOC include: (a) increasing the solids loading in a solvent-based system [9]; (b) using UV curable formulations [10]; (c) replacing solvent with water [9]; and (d) using powder coatings. Applicability of conventional cellulose esters has been limited in modern reduced VOC, high solids coating systems because of their high solvent demand.

To meet the increasing demand of sustainable solutions for compliant coatings, a new class of cellulose-based additives has been introduced [11]. Solus Performance Additives are very similar to conventional cellulose esters, but these compounds have very low viscosity and allow high solids systems to be formulated.

TABLE 4—ASTM standards used in testing cellulose esters	
ASTM	**Title**
D706	Standard Classification System and Basis for Specifications for Cellulose Acetate Molding and Extrusion Compounds
D707	Standard Classification System and Basis for Specification for Cellulose Acetate Butyrate Molding and Extrusion Compounds
D817	Standard Test Methods of Testing Cellulose Acetate Propionate and Cellulose Acetate Butyrate
D871	Standard Test Methods of Testing Cellulose Acetate
D1343	Standard Test Method for Viscosity of Cellulose Derivatives by Ball-Drop Method
D1562	Standard Classification System and Basis for Specification for Cellulose Acetate Propionate Molding and Extrusion Compounds
D1695	Standard Terminology of Cellulose and Cellulose Derivatives
D2929	Standard Test Method for Sulfur Content of Cellulosic Materials by X-Ray Fluorescence
D4209	Standard Practice for Determining Volatile and Nonvolatile Content of Cellulosics, Emulsions, Resin Solutions, Shellac, and Varnishes
D5226	Standard Practice for Dissolving Polymer Materials
D5897	Standard Test Method for Determination of Percent Hydroxyl on Cellulose Esters by Potentiometric Titration—Alternative Method
E1899	Standard Test Method for Hydroxyl Groups Using Reaction with p-Toluenesulfonyl Isocyanate (TSI) and Potentiometric Titration with Tetrabutylammonium Hydroxide

TESTING OF CELLULOSE ESTERS

Cellulose acetate is tested by the manufacturer in accordance with ASTM Test Methods for Cellulose Acetates (D871), and mixed esters Cellulose Acetate Propionate and Cellulose Acetate Butyrate (D817), which cover color and haze, combined acetyl, free acidity, heat stability, hydroxyl content, intrinsic viscosity, moisture content, sulfur or sulfate content, and solution viscosity. Coatings manufacturers usually restrict their testing to viscosity of the ester, solubility and appearance, and color and haze. Viscosities

are determined using the falling-ball method, according to ASTM D1343 in the solution described as Formula A, ASTM D817. Viscosities in poises are converted to ASTM seconds equivalent to values obtained under ASTM D817. In Eastman nomenclature for cellulose esters, the viscosity of each individual ester is indicated in its product code. For example, CAB 381-2 has a viscosity of 2 s, CAB 381-20 has a viscosity of 20 seconds, and CAB 531-1 has a viscosity of 1 s. The above ASTM standard documents as well as others related to the testing and terminology used for cellulose esters are listed in Table 4. In addition to the listing in Table 4, there are numerous other ASTM test methods and documents that relate to the testing of cellulose esters for fibers, for molding compounds, and for other solid-state uses.

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4

Drying Oils

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NOTE: IT MUST BE POINTED OUT THAT FROM AN ASTM standpoint, this chapter is mainly included for historical purposes. In general, ASTM no longer deals with the standard test methods and specifications for drying oils in paints and coatings. This activity is dealt with by the American Oil Chemists' Society (AOCS) with research and technology in the area reported in the Journal of the American Oil Chemists' Society. Since the ASTM documents listed in the previous edition of this manual are found in the technical literature, this chapter provides a route to the past, some information about recent activities in the area, and information about AOCS's current role. As indicated, many of the ASTM documents listed in the previous edition of this chapter are no longer available from ASTM. Those applicable ASTM standards that can be downloaded from ASTM are so indicated. A listing of some AOCS documents that refer to drying oils can be found in Table 5.

Drying oils represent a small portion of the huge fats and oils industry.[2] Soybeans are the largest oilseed crop with a U.S. farm value of about $12.5 billion in 2000/2001. This oil accounts for about 90 % of U.S. oilseed production with the remainder comprised of oils such as cottonseed, sunflower seed, flaxseed, canola, linseed, and other oils. Argentina and Brazil are also important soybean growers and processors. Drying oils are included in the oilseed category. In regard to coatings, the industry is very mature with relatively little growth expected. The paint and coating industry's need for drying oils is in an overall decline along with other end use markets, such as binders for hardboard, sealants, plasticizers, linoleum, and core oils. Drying oils used in paints and coatings are being replaced with oil-free, synthetic, petroleum-derived oligomeric and polymeric binders carried in a variety of media or in a neat manner. The printing ink market is the only one expected to have small growth in the area of drying oils.

However, because drying oils have certain desirable attributes and represent a readily available renewable resource, interest is being renewed in certain oils through sponsorship by interested organizations and through new opportunities for modified vegetable oils. In the United States, the United Soybean Board is funding research dealing with catalysts for radiation curing of epoxidized soybean oil at Bowling Green State University's Center for Photochemical Sciences [1,2]. Other investigators are studying the use of soybean oil modifications in waterborne paints, high solids coatings, and inks [3]. In Malaysia, where palm oil is readily available, research is being conducted at the School of Industrial Technology at Universiti Sains Malaysis on epoxidized and acrylated derivatives of palm oil [4,5]. Again, the studies deal with using the products in the rapidly growing radiation curing market [6]. Oilseed Growers LLC has members who have commercially produced carambe oil in the United States since 1996 [7]. This oil is rich in mono unsaturated erucic acid, and it is used as a food emulsifier, as an ingredient in industrial slip agents, pour point depressants, lubricants, hair care, textile softening, and other end uses.

The processing techniques as well as the chemistry of drying oils have been well known for some time. However, within the past few decades, computer control and robotics, EPA and OSHA regulations in the United States and similar concerns elsewhere, rising energy costs, and similar developments have led to important improvements in the processing field whereby fish or plant components are converted into the final use-products. Lusas [8] has recently detailed a great deal of the old and new chemistry, nomenclature, and processing technology regarding drying oils in a detailed book chapter. The chapter also includes information about other animal and vegetable fats, oils, and waxes as well as edible uses for the oils and fats, industrial uses of the oils, numerous historical references, sources, and several analytical methods that have been adopted by the American Oil Chemists' Society (AOCS). This chapter and the previous edition of the chapter [9] are very useful references for those working in this field. Hutchinson [10] has reviewed new and traditional uses, technology advances, environmental factors, and development strategies for vegetable oils in surface coatings.

Most naturally occurring fatty oils have their double bonds occurring in a cis configuration, and heating such oils as in industrial processing causes a portion of the cis configured double bonds to be converted into a trans configuration. Infrared absorption spectroscopy or gas chromatography are the usual methods of determining trans content, but Milosevic and Kocak [11] used attenuated total reflection (ATR) Fourier transform infrared spectroscopy [12] to analyze oils, such as soybean oil and sunflower oil, that had been untreated and heated for various times at elevated temperatures. A FatIR heated single-reflection ATR accessory was used for the analysis. The studies demonstrated that the technique could be used for routine analysis of trans double bond content and thus permit investigation

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[2] Information about this industry is developed by the U.S. Departments of Agriculture and Commerce and can be found on websites such as www.ers.usda.gov.

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TABLE 1—Classification of drying oils by iodine value

Oil Class	Iodine Value
Drying oil	>140
Semidrying oil	125–140
Nondrying oil	<125

of reaction kinetics and the optimization of reaction parameters. Larock et al. [13] have found that small amounts of homogeneous transition metal catalysts will affect the isomerization transformation of soybean oil to conjugated oil under mild conditions. Their preliminary tests indicate that the conjugated oils have exceptional drying properties with good solvent resistance.

Although new studies are currently being conducted, modified drying oil products have been known for sometime. A variety of oils have been epoxidized [14, 15] and many of these have been further reacted to form acrylates for use in radiation curable coatings and inks [16–19]. Recent investigations of seed oils include castor oil that has been used in the preparation of a variety of oil-based binders [20], blown soybean oil that has been used in combination with acrylates such as 1,6-hexanediol diacrylate to make novel coatings [21], epoxidized soybean oil that has been used in cationic-initiated, thermally cured coatings [22], soybean oil that has been used to make phosphate ester polyols for use in novel coatings [23], the synergistic effect between metallic driers and soybean oil-based coatings [24], and a method for modifying cashew nut shell liquid by ozonolysis to form products useful in adhesives and other products [25]. A variety of drying oils have been reacted with multifunctional isocyanates to form products that have been termed "urethane oils" and are akin to alkyds [26]. Neat or raw drying oils have been mixed with polymerized drying oils to form homogenous admixtures used by artists as a painting medium [27]. Coatings that have controlled release of organic solvents, particularly formaldehyde, and improved properties have been prepared from drying oils, such as linseed oil, and waxes as the main compositional components [28]. Adhesives with substantially no or low volatile-organic-compound emissions and based on drying oils have been prepared [29]. Novel thermal processes that do not involve solvent extraction or caustic refining, which produce soybean oil that is low in phospholipids have been recently developed [30]. A method for determination of the primary hydroxyl content of soybean oil polyols by reaction with monoisocyanates, such as phenyl isocyanate, has been recently reported [31].

Usually in the fats and oils industry, products that are solid or semisolid at room temperature are referred to as fats, and products liquid at room temperature are termed oils. Often times the terms "fats" and "oils" are used interchangeably within the industry. In a general sense, fats are usually of animal origin or are vegetable oils that have been hardened by hydrogenation or some other process. Drying oils, except for fish oil, are of vegetable origin and are extracted from seeds or plant tissue.

Chemically, drying oils are water-insoluble, unsaturated glycerides of long chain fatty acids with the generalized structure:

$$\begin{array}{l} CH_2\text{–}O\text{–}OC\text{–}R_a \\ | \\ CH\text{–}O\text{–}OC\text{–}R_b \\ | \\ CH_2\text{–}O\text{–}OC\text{–}R_c \end{array}$$

Generalized Triglyceride

where R_a, R_b, and R_c are the same or different and represent the hydrocarbon chain residues of fatty acids. In simple terms, this means that most oils are mixed triglycerides. The triglycerides are produced by the condensation reaction that occurs between a glycerol molecule and three fatty acid molecules:

$$\underset{\text{Glycerol}}{HOCH_2 - CH(OH) - CH_2OH} + \underset{\text{Fatty Acid}}{3R_xCOOH} \rightarrow$$

$$R_xCOOCH_2 - CH(OOCR_x) - CH_2OOCR_x + 3H_2O$$

Triglyceride or Drying Oil

where R_x is any one of R_a, R_b, or R_c. This reaction is reversible and when the oils are heated they can transesterify with R_a, R_b, and R_c and thus are capable of changing their positions in an intermolecular and an intramolecular sense. Drying oils also contain saturated glycerides of fatty acids, but these are usually present at relatively low levels and they do not participate in drying or polymerization phenomenon. Hydrolysis of drying oils results in separation into glycerol and the fatty acid.

Drying oils can be classified in many ways, but one principal way is to divide them into drying, semidrying, and non-drying (an oxymoronic term) oils in accordance with their iodine values, which is a measure of unsaturation content. Although such classification has been rather arbitrary, Rheineck and Austin [32] defined the classes as given in Table 1.

The main fatty acids found in drying oils and their chemical compositions are given in Table 2. The unsaturated-component content of selected drying oils is given in Table 3. Stearic (18-carbon) and palmitic (16-carbon) acids are the most widely distributed saturated fatty acids found in drying oils. Except for cottonseed oil, which contains 29 % palmitic acid, the drying oils listed in Table 3 contain less than about 10 % of any particular saturated fatty acid residue. The degree of double bond unsaturation controls the drying rate. The higher the degree of unsaturation or iodine number (see below), the faster the drying or polymerization of the oil. The double bond position is also important because conjugated bonds, which is the term used to describe two carbon-carbon double bonds separated by one carbon-carbon single bond, are more susceptible to autoxidation [34].

Physical characteristics of some typical commercial drying oils are given in Table 4. The oils are particularly characterized by their iodine value, which is a measure of the amount of unsaturation present, and saponification number, which is an indication of fatty acid chain molecule weight. Selected property requirement ranges or minimum values for various drying oils. The following drying oils are the most important members of this class of coating raw materials.

Castor oil is obtained from beans of the plant *Ricinus communis*. The oil differs from the other oils in that it is

TABLE 2—Main unsaturated fatty acids found in drying oils

Fatty Acid	Number Carbon Atoms	Number Double Bonds	Structural Formula
Linolenic	18	3	$HOOC(CH_2)_7CH=CHCH_2CH=CHCH_2CH=CHCH_2CH_3$
Linoleic	18	2	$HOOC(CH_2)_7CH=CHCH_2CH=CH(CH_2)_4CH_3$
Oleic	18	1	$HOOC(CH_2)_7CH=CH(CH_2)_7CH_3$
Eleostearic	18	3	$HOOC(CH_2)_7CH=CHCH=CHCH=CH(CH_2)_3CH_3$
Licanic	18	3	$HOOC(CH_2)_2CH(O)(CH_2)_4CH=CHCH=CHCH=CH(CH_2)_3CH_3$
Ricinoleic	18	1	$HOOC(CH_2)_7CH=CHCH_2CH(OH)(CH_2)_5CH_3$

TABLE 3—Weight percentage of major unsaturated fatty acid residues in selected drying oils [32,33] (remainder of oils is essentially all saturated fatty acid residues)

	Unsaturated Fatty Acid					
Drying Oil	Linolenic	Linoleic	Oleic	Eleostearic	Licanic	Ricinoleic
Cottonseed	. . .	40	24	. . .	. . .	. . .
Castor	. . .	3	7	. . .	. . .	87
Linseed	52	16	22	. . .	. . .	. . .
Oiticica	. . .	. . .	6	. . .	78	. . .
Safflower	1	75	13	. . .	. . .	. . .
Soybean	9	51	25	. . .	. . .	. . .
Sunflower[a]	2	75–52	34–14	. . .	. . .	. . .
Tall Oil	3	41	46	. . .	. . .	. . .
Tung	3	4	8	80	. . .	. . .

[a] There is wide variation in reported values for sunflower oil.

made up of a very high percentage of the hydroxyl-containing ricinoleic acid residue. Although the fatty acid residues in this oil contain on the average only a single double bond and for this reason castor oil is essentially a nondrying oil, it can be converted into a drying oil by a dehydration process in which its hydroxyl group and an adjacent hydrogen atom are removed as water to form a double bond conjugate to the previously existing double bond. The resultant product is known as dehydrated castor oil, which has good drying characteristics.

Cottonseed oil is obtained from the plant *Gossypium malvaceae.* Although it is a drying oil, cottonseed oil is seldom used as an oil in the paint and coating industry. Its main use is as a source of fatty acids that are used in the manufacture of alkyds.

Linseed oil, which is obtained from seed of the flax plant *Linum usitatissimum,* is the most common and widely used drying oil. In the Western Hemisphere, it is the oldest known drying oil. Linseed oil has a high degree of unsaturation, which imparts a short drying time, due to its large percentages of linolenic and linoleic triglycerides. It is marketed in a number of modifications, including alkali-refined, acid-refined, boiled, blown, and polymerized linseed oil [1]. Polymerized linseed oils of various acid values and viscosities are available. The effect of water and air on the thermal oligomerization of linoleic acid has been investigated, and it was found that water inhibited the reaction and continuous air flow enhanced dimerization and trimerization [36].

Oiticica oil is obtained from the nuts of the tree *Licana rigida,* which grows wild and is only grown in Brazil. It has a very high licanic acid content, and the three conjugated double bonds of this acid result in rapid drying characteristics. When the price of linseed oil is too high, oiticica oil is used as a substitute for linseed oil and is often used as an alternative or supplement to tung oil.

Safflower oil is obtained from seed of the plant *Carthamus tinctorius.* This semidrying oil has drying characteristics between those of linseed and soybean oils. Because of its low linolenic acid content, it has low residual unsaturation after cure and very good antiyellowing characteristics.

Soybean oil is obtained from the seeds of the widely grown plant *Soja hispida.* Its main use is in the preparation of alkyds. It has a wide variety of uses other than as a drying oil. In an epoxidized form, this oil is widely used as a reactive plasticizer and as an acid scavenger. Both epoxidized soybean and linseed oil have been reacted with acrylic acid to form products with residual acrylate functionality and markedly higher viscosity. These acrylated oils have been used as components in radiation-cure coating systems that are initiated with free radicals.

Although tall oil is classified as a drying oil, it is not a triglyceride. The product is obtained as the major byproduct of sulfate or Kraft pulping of pine and certain other

TABLE 4—Physical characteristics of some typical drying oils [35]

Oil	Specific Gravity 25.5/25.5°C	Iodine Value, Wijs	Saponification Value	Acid Value	Refractive Index 25°C
Cottonseed	0.919	105	192	1.0	1.465
Dehydrated Caster	0.931	135	190	5.0	1.481
Fish	0.925	158	187	4.0	1.485
Linseed	0.926	180	190	3.0	1.478
Oiticica	0.967	150	190	4.0	1.510
Safflower	0.922	145	192	2.0	1.474
Soybean	0.920	135	190	2.5	1.473
Sunflower	0.917	135	192	2.0	1.473
Tall oil	. . .	133	196	194.0	. . .
Tung	0.915	170	192	0.2	1.517

softwoods such as spruce and hemlock that are pulped in Scandinavian countries. Crude tall oil is an approximately 50/40/10 by weight mixture of fatty acids, rosin acids, and unsaponifiable compounds, such as higher alcohols, waxes and other hydrocarbons, and sterols.

Tung oil is obtained from seeds (fruit or nuts) of the trees *Aleurites fordii* and *Aleurites Montana,* and it is mainly produced in China and South America, though in 1966 production began in the United States (Mississippi). Tung oil contains mainly eleostearic acid with smaller amounts of linoleic, oleic, and palmitic fatty acids. This relatively high viscosity and refractive index oil is rapid drying and is used in varnishes and alkyds where water resistance is of principal importance. Tung oil is also known as wood oil, Chinese wood oil, chinawood oil, and mu oil. Martyak et al. [37] have investigated the controlled oxidative curing of tung oil with cobalt driers and anti-skinning agents as the control agents. When the process is properly controlled, improved through cure and other properties are obtained.

Vernonia oil is a unique oil that contains an epoxy group and an unsaturated group in each of three vernolic acid resides that are attached to a triglyceride residue [38]. It is obtained from the weed termed *Vernonia galamensis* and is being investigated as a potential industrial crop in certain frost-free African countries. The oil has a relatively low viscosity, 100 cPat85°F, dual functionality, and a potential for derivitization into acrylates or other compounds. In addition, it has utility without alteration and may function as a reactive diluent or other additive.

Agave fiber has been treated with acid to form hydroxylates that contain furfural [39]. These plant extracts have been condensed with tannins from tamarind to form oligomers that were added to various drying oils to form varnishes with improved mechanical characteristics.

Fish oils are the only nonvegetable oils in the drying oil class. They are principally obtained from menhaden *(Alosa menhaden).* These oils are semidrying in nature and contain a significant amount of saturated fatty acid residues. In addition to 16- and 18-carbon fatty acid residues, fish oils contain 30 %–40 % of arachidonic (20-carbon with four double bonds), clupanodonic (22-carbon with five double bonds), and nisinic (24-carbon with five double bonds) acid residues. Because of the presence of acid residues with high degrees of unsaturation, fish oils have a strong tendency to yellow after cure due to residual unsaturation. Fish oils do represent a source of the very long chain fatty acids that are not present in vegetable oils. Currently, they are not widely used in the coatings industry, and their use is often dictated by relative price of linseed and soybean oils.

Although raw drying oils are used in coating formulations, the oils are often further processed before use. Such processing includes alkali-refining, dehydration, drier addition, heat polymerization that involves heating an oil to selectively advance molecular weight and viscosity, and oxidation or blowing wherein air is bubbled into heated oil and oxygen is taken up with a resultant molecular weight increase. Drying oils are also modified by reaction with maleic anhydride, by copolymerizing with vinyl monomers such as styrene, and by epoxidation.

Reaction with oxygen is the most important reaction that drying oils undergo in the drying or polymerization process [40, 41]. Oxidation can result in trans isomer formation, cleavage of the carbon-carbon chain along with formation of volatile byproducts, and polymerization. These reactions can be catalyzed with metallic salts, such as cobalt naphthenate (see next chapter), that promote free radical formation by reaction with hydroperoxides and other peroxides that are formed in the oxidation process [42]. Farmer and Sutton [43] were the first to describe the mechanism of auto-oxidation wherein they found that four different monohydroperoxides were formed when oxygen was reacted with the methyl ester of oleic acid. A different reaction path was involved when linoleic esters were auto-oxidized since two monohydroperoxides and one cyclic diperoxide were formed. Polymerization is initiated by reaction of oxygen with an unsaturated fatty acid residue and free radical formation followed by chain propagation in which free radicals react with oxygen to form peroxy radicals, which in turn react with other unsaturation sites [44]. The polymerization is terminated by combination of various free radicals that exist in the reaction mass. Availability

TABLE 5—AOCS test methods for industrial oils and derivatives. See specific methods for detailed scopes and methods

AOCS Official Method	Title	Scope—Applicable to
Tt 1a-64 (Reapproved 1997)	Acetone Tolerance	heat-bodied oils
Te 2a-64 (Reapproved 1997)	Acid Value	drying oils, epoxidized oils, fatty alcohols and esters
Tm 1a-64 (Revised 2003)	Ash	drying oils, fatty acids—not applicable to boiled oils
Td 1a-64 (Revised 2000)	Color Gardner 1963 (Glass standards)	drying oils, fatty acids and oil derivatives similar to standards
Th 1a-64 (Revised 2005)	Diene Value	all normal drying oils
Tn 1a-64	Flash and Fire Points, Cleveland Open Cup Method	drying oils and fatty acids except those with flash points below 149°C (300°F)
Tg 1-64 (Reapproved 1997)	Iodine Value, Wijs Method	normal industrial oils and derivatives
S 2-64 (Revised 2003)	Methods for the Testing of Commercial Fatty Acids	selection and use of procedures for testing drying oils used in paint and related products
Ca 2c-25 (Reapproved 1997)	Moisture and Volatile Matter Air Oven Method	animal and vegetable fats but not to drying or semidrying oils of the coconut group
Tc 1a-64 (Reapproved 1997)	Nonvolatiles (Solids) Solutions of Drying Oils, Hot Plate Method	solutions of natural and synthetic drying oils in organic solvents
Cd 7-58 (Reapproved 1997)	Polyunsaturated Acids, Ultraviolet Spectrophotometric Method	various detailed isomers
Tp 1a-64 (Revised 2003)	Refractive Index	drying oils and all fatty acids
To 1b-64 (Revised 2003)	Specific Gravity	drying oils and derivatives
Ce 5b-89 (Reapproved 1997)	Triglycerides in Vegetable Oils by HPCL	vegetable oils containing triglycerides of long-chain fatty acids
Tk1a-64 (Reapproved 1997)	Unsaponifiable Material	fatty acids, drying oils, and polymerized fatty acids

of multiple double bonds in some of the molecules results in a cross-linked polymeric network.

Solidification or polymerization of a drying oil, such as linseed oil, can be thought of in the following manner. When the drying oil is exposed to air, there is an induction period during which oxygen is absorbed and it consumes antioxidants present in the system. In this step, there is very little apparent change in physical or chemical properties. This is followed by a period in which there is a marked oxygen uptake and an appearance of peroxides that decompose to form free radicals. The free radicals then initiate an addition polymerization of the unsaturation and a cross-linked network results. During the reaction, low molecular weight cleavage products including carbon dioxide and water are formed.

ASTM D1640 Standard Test Methods for Drying, Curing, or Film Formation of Organic Coatings at Room Temperature has procedures recommended for determination of the stages and rates of film formation in the drying or curing of organic coatings that are to be used at room temperature.

Included are methods for determining tack-free, dry-to-touch, dry-hard, dry-through, print-free, and dry-to recoat times. In one instance (Section 7.5.1) a particular procedure is specified for drying oils. ASTM Standard Test Method for Gel Time of Drying Oils (D1955) deals with determination of the gel time of oiticica and tung oil. This simple test method, which involves heating the oil in a test tube and observing the time required for the oil to congeal around glass rod relative to a standard of known behavior, can be used for other oils that have conjugated double bond or other gelling characteristics. ASTM Standard Guide for Testing Drying Oils (D555) is an overall guide to selection and use of procedures for testing drying oils that are commonly used in coatings. ASTM D1640 is an active standard; however, ASTM D1955 and D555 have been withdrawn by ASTM but may still (at time of writing) be downloaded from the ASTM website. A number of other ASTM standards that were dedicated to drying oils have been withdrawn and are no longer available. However, as mentioned at the beginning of this chapter, AOCS deals with this topic. Some of their standards are listed in Table 5.

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5

Driers and Metallic Soaps

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INTRODUCTION

METALLIC SOAPS ARE COMPOUNDS OF ALKALINE metals or heavy metals and monobasic carboxylic acids containing from 7 to 22 carbon atoms. The water-insoluble metallic soaps are of particular interest to the coatings industry, although potassium and lithium soaps have limited water solubility.

Basically, the known techniques for preparation of metallic soaps are divided in two processes—a fusion process and a double decomposition process. The fusion process involves reacting a metal oxide or hydroxide with a fused fatty acid such as a triglyceride in the presence of water [1]. The process yields the desired metallic soap and glycerin. The double decomposition process involves reacting an alkali soap that is comprised of an alkaline metal salt or an ammonium salt of a fatty acid with an inorganic metal salt. Both processes are usually carried out in a batch mode; and, as a result, a product contaminated with unreacted starting materials and by-products that must be further purified is formed. To obtain a product essentially free of contamination, a continuous process [2] involving the double decomposition scheme has been devised. An aqueous solution of the alkali soap and an inorganic metal salt are separately fed onto a rotating impeller surface whereon they are instantaneously mixed. The resulting aqueous slurry is rapidly discharged and a contamination-free metallic soap results. Recently, a process for making basic zirconium carboxylates of branched-chain, five- to ten-carbon, aliphatic monocarboxylic acids has been described [3]. The compounds are useful as driers for paints and inks.

The applications of metallic soaps in coatings include their use as driers, catalysts, stabilizers, biocides, bodying agents, and flatting agents. An overview of metallic soap applications is presented in Table 1. An interesting particular end-use for metallic soaps is in the formation of a thin metallic oxide coating on a substrate [4]. A solution of the metallic soap is applied by reverse roll coating and then baked in a manner such that a thin, about 1–10 μm, film of the metallic oxide is formed. Although this chapter concentrates primarily on metallic soaps used as driers, a brief review of bodying and flatting applications for these materials is included.

METALLIC SOAPS AS BODYING AND FLATTING AGENTS

Aluminum stearates, aluminum octoates, and calcium linoleate pulp were at one time widely used as bodying and pigment-suspending agents in solvent-based coatings. Their advantages include fairly high efficiency and ease of incorporation. However, they have a number of deficiencies, including sensitivity to variations in the formulation and in the processing of paints, as well as adverse effects on film hardness and resistance properties. As a result, they have been replaced to a considerable extent by the bentonite clay and organic wax derivatives [5].

Zinc and calcium stearates are used on occasion as flatting additives in clear solvent-based coatings. However, precipitated and fumed silicas are now more commonly used for this purpose. Zinc stearate is also used to facilitate sanding of primers and sealers for wood furniture finishing [5].

THEORY OF OXIDATIVE DRYING AND FUNCTION OF DRIERS [5,6]

It is generally accepted that vehicles based on unsaturated oils, including alkyds and oleoresinous varnishes, dry by oxidation according to the following steps:

1. Induction period.
2. Oxygen absorption.
3. Peroxide formation.
4. Peroxide decomposition to free radicals.
5. Free radicals promote reactions that cause cross-linking.

The induction period occurs because most drying oils contain natural antioxidants, the effects of which must be overcome before the drying process can begin. Oxygen is then absorbed from the air at the unsaturated sites on the oil molecule, and, as the absorption continues, forms peroxides. These peroxides then decompose to form free radicals that act as catalysts to promote cross-linking of the oil or alkyd molecules at the unsaturated sites, resulting in dried films.

These same steps will occur in the absence of driers, but driers are used to accelerate the drying or curing process by means of the following mechanisms [5,6]:

1. Removal of natural antioxidants.
2. Acceleration of oxygen absorption.
3. Acceleration of peroxide decomposition.

Naturally occurring antioxidants may be considered as negative catalysts for oxidation, whereas driers are positive catalysts, counteracting the effects of the antioxidants.

The multivalent nature of the drier metal is considered to be a key factor accelerating oxygen absorption in the film. The drier metal is initially in a divalent state and is

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TABLE 1—Coatings applications of metallic soaps

Applications	Metals	Acids
Driers	Cobalt, manganese, lead, iron, rare earth, cerium, zirconium, zinc, calcium, barium, bismuth, potassium, vanadium, aluminum	Tallates, octoates, naphthenares, neodecanoates, synthetic acids, linoleates, rosinates
Catalysts	Potassium, lithium, cobalt, copper, tin, zinc, manganese	Octoates, naphthenates, laurates, neodecanoates
Stabilizers	Barium, cadmium, tin, zinc, calcium, lead	Proprietary, sulfates, carbonates, stearates
Biocides	Copper, tin, zinc, mercury	Naphthenates, octoates, phenyl acetates, phenyl oleates, laurates, butyl oxides
Bodying agents	Aluminum, calcium	Stearates, octoates, linoleates
Flatting agents	Zinc, calcium	Stearates

converted to a trivalent state by the presence of oxygen in the film. The metal then releases the oxygen to the film and is converted back to the divalent form. This action accelerates the process of oxygen absorption, peroxide formation, and peroxide decomposition, which is responsible for oxidative film drying.

DESCRIPTION OF DRIER METALS

The metals that act as catalysts to promote oxidation and which may be used in driers are indicated below:

Cobalt
Manganese } Active or Primary
Vanadium

Lead
Calcium
Zirconium
Zinc
Iron } Auxiliary or Secondary
Rare Earth
Cerium
Aluminum

Cobalt and manganese, particularly cobalt, are the most active drier metals. Cobalt promotes surface drying of films, while manganese affects both surface and through drying. Vanadium has been mentioned in the literature as an active drier but is seldom used in coating formulations. Driers based on these active metals are often termed primary driers since they have inherent catalytic action.

The auxiliary or secondary driers are seldom used alone, but rather in combination with cobalt and/or manganese or other metals. Their functions are to increase the efficiency of the active drier metals and to increase film hardness. In the past, lead was the most frequently employed auxiliary drier, but it is presently out of favor due to toxicity and other health considerations. Calcium and zirconium driers are most frequently used as lead replacements. Zinc is used primarily for improved film hardness and to prevent wrinkling of thick films. Iron driers are used mainly to improve drying of baking systems when their dark color can be tolerated. Rare earth and cerium driers are recommended occasionally for improved through drying and as oxidation catalysts for baking. Interest in aluminum compounds as auxiliary driers has recently increased with the advent of high-solids alkyds. Aluminum compounds are being recommended to improve film hardness with these compounds, but at times they may adversely affect viscosity stability and promote gelation.

DESCRIPTION OF DRIER ACIDS

To perform their function, driers should be soluble in the vehicles to which they are added. Solubility is achieved by reacting the drier metals with organic acids to form metallic soaps. The most commonly employed acids are as follows:

- Linoleates,
- Rosinates,
- Tallates,
- Naphthenates,
- Octoates (2-ethyl hexanoates),
- Synthetic acids, and
- Neodecanoates.

Chronologically, the linoleates, rosinates, and tallates were the first types developed, followed by the naphthenates and the octoates. A more recent development is the synthetic acid type, which is proprietary but closely related to the octoates. The synthetic acid and neodecanoate driers can be prepared at higher metal concentrations than the other types and are gradually replacing the older acids.

Water-dispersible driers may be prepared by adding non-ionic surfactants to naphthenate or synthetic acid driers. However, proprietary cobalt and manganese drier compounds are available that are purported to be more suitable for water-based coatings.

Trade names of the various commercial drier types available are listed in Table 2.

MISCELLANEOUS DRIERS

Restrictions on solvent emissions have stimulated the development of both higher-solids and water-reducible coatings. In the process of formulating these coatings, chemists are experiencing difficulty obtaining satisfactory drying properties with the conventional metallic soap driers. Alternative drier compounds, including both organics and proprietary metallic complexes, are currently being offered [7]. Some typical examples are shown in Table 3. They are usually recommended in combination with conventional metallic soap driers for improved drying efficiency.

Another class of metallic compounds closely related to driers is loss of dry inhibitors or "feeder" driers. These are compounds designed to prevent loss of drying efficiency of paints on aging resulting from the adsorption of driers by

TABLE 2—Commercial drier types [3]

Type of Drier	Trade Name	Supplier
Synthetic acid	Cem-All	Mooney Chemical, division of OMG
	NuXtra	Huls America
	Troymax	Troy Corp.
Octoate	Hex-Cem	Mooney Chemical, division of OMG
	Octoate	Huls America
Neodecanoate	Ten-Cem	Mooney Chemical, division of OMG
Naphthenate	Nap-All	Mooney Chemical, division of OMG
	Nuodex	Huls America
	Troykyd	Troy Corp.
Tallates	Lin-All	Mooney Chemical, division of OMG
Water dispersible	Hydro-Cem	Mooney Chemical, division of OMG
	Hydro-Cure	Mooney Chemical, division of OMG
	Nuocure	Huls America
	Troykyd WD	Troy Corp.
	Calcicat	Ultra adhesives
	Aquacat	Ultra adhesives
	Magnacat	Ultra adhesives
	Zircat	Ultra adhesives

TABLE 3—Alternate drier compounds

Trade Name	Company	Composition
Active-8	R. T. Vanderbilt Co.	1,10-phenanthroline
Dri-RX	Mooney Chemicals Inc.	2,2′-dipyridyl
Drymax	Huls America	2,2′-dipyridyl
Nutra ADR 10 %	Huls America	proprietary metal complex
Nutra LTD 18 %	Huls America	proprietary metal complex

pigments, particularly carbon black and organic red pigments. They function by dissolving gradually into the coating vehicle so that the metals are available over a period of time rather than immediately. In this manner, they replace the drier metals that have been absorbed by the pigments, thereby maintaining satisfactory drying on prolonged storage. Lead compounds, including litharge, were used formerly but have been replaced by lead-free compounds based primarily on less soluble forms of cobalt and other drier metals.

Commercially available feeder driers are listed in Table 4. All are lead-free metal complexes except for the last item [8].

TABLE 4—Commercial feeder driers

Company	Trade Name
Mooney Chemical, division of OMG	Hex-Cem LFD
Mooney Chemical, division of OMG	Hydroxy Ten-Cem Cobalt
Troy Corporation	Troykyd Perma Dry
Huls America	Nuact Cobalt 254
Huls America	Nuact NOPB
Huls America	Nuact Paste (lead-based)

DRIER LEVELS IN COATINGS

Drier requirements for coatings are usually expressed in terms of percent drier metal based on oxidizable vehicle nonvolatile content. A typical calculation is as follows [9]:

Assume:

1. In a 1,000 g paint formulation, there are 300 g of vehicle nonvolatiles.
2. Cobalt drier used is 12 % metal by weight.
3. Calcium drier used is 10 % metal by weight.
4. Required for optimum drying: 0.05 % cobalt plus 0.2 % calcium (percent metal based on vehicle nonvolatiles). per 1,000 g of paint:

cobalt metal required = 0.0005×300 g = 0.15 g

calcium metal required = 0.002×300 g = 0.6 g

The optimum levels of drier metal required will vary depending on the type of polymeric system employed and the conditions of drying. Typical metal concentrations for a number of common vehicles are indicated in Table 5. A guide to the selection of the proper ASTM test methods for determining volatile and nonvolatile content of driers and related products is ASTM D4140, Standard Guide for Determining Volatile and Nonvolatile Content of Driers, Drying Oils, Naval Stores, and Solvents.

TESTING OF DRYING EFFICIENCY

The procedures used to determine the stages of film formation during the drying of coatings are described in ASTM D1640, Test Methods for Drying, Curing, or Film Formation of Organic Coatings at Room Temperature. With coatings containing metallic driers, it is recommended that the paint samples age overnight following the drier additions before drying tests. The drying conditions, shown in Table 6, are usually specified but are subject to agreement between the purchaser and the seller.

The methods used to determine the various stages of drying may be summarized as follows:

1. *Set-To-Touch-Time*—no transfer of the coating upon lightly touching the film with the finger.
2. *Dust-Free-Time*—(a) cotton fibers dropped on the film can be removed by blowing lightly; (b) fine calcium carbonate extender dropped on the film can be completely removed by blowing gently and wiping with a cloth or brush.
3. *Tack-Free-Times*—a specified type of paper or aluminum foil will no longer adhere to the film when applied under specific conditions.

TABLE 5—Typical drier recommendations, percent metal based on vehicle nonvaluable

	Cobalt	Manganese	Zirconium	Calcium	Zinc	1,10-Phetanthroline	2,2'-Dipyridyl, 30 %
Long oil alkyd-air dry	0.04–0.06			0.1–0.3			
	0.04–0.06			0.1–0.3			
	0.04–0.06		0.1–0.2	0.1–0.2			
Medium oil alkyd-air dry	0.04–0.06		0.1–0.3				
	0.04–0.06			0.1–0.3			
	0.04–0.06		0.1–0.2	0.1–0.2			
Short oil alkyd air-dry	0.04–0.06		0.1–0.3				
	0.04–0.06			0.1–0.3			
	0.04–0.06		0.1–0.2	0.1–0.2			
Chain-stopped alkyd	0.05-0.08			0.2			
	0.05–0.08		0.1	0.1			
Medium oil alkyd-bake	0.01–0.03				0.1–0.5		
Oil-modified urethane	0.02–0.04		0.1–0.3				
	0.02–0.04			0.1–0.3			
		0.02–0.04				0.2	
Linseed oil	0.02	0.02	0.1–0.2	0.1–0.2			
		0.02–0.04	0.1–0.3		0.1–0.15		
		0.02–0.04		0.1–0.3			
Alkyd-oil house paint	0.02–0.03	0.02–0.03		0.02–0.03			
	0.02–0.03	0.02–0.03	0.02–0.03				
	0.02–0.04	0.02–0.04	0.1–0.2	0.1–0.2	0.1–0.15		
Epoxy Ester	0.03–0.05		0.1–0.2				
	0.03–0.05			0.1–0.2			
Acrylic modified alkyd	0.04–0.08		0.1	0.1			
Oleoresinous varnish	0.02–0.06			0.2			
Vinyltoluene alkyd	0.02–0.04		0.1				
	0.02–0.04			0.1			
High solids alkyd	0.04–0.06		0.5–0.9			0.2	
		0.04–0.06		0.5–0.9		0.2	
	0.04–0.06		0.2–0.4				0.2–0.4
Water-based alkyds (water dispersible driers)	0.04–0.06		0.1–0.3				
	0.04–0.06			0.1–0.3			
	0.05–0.1		0.15–0.3	0.15–0.2			0.15–0.3

TABLE 6—Standard drying conditions

Condition	Typical Value
Ambient temperature	23 ± 2°C
Relative humidity	50 ± 5 %
Film thickness (dry)	12.5 to 45 μm
Substrate	Clean glass
Lighting	No direct sunlight
Applicators	Doctor blades
Coating viscosity	Close to normal application

4. *Dry-To-Touch-Time*—the film no longer adheres to the finger when pressed firmly and does not rub up when rubbed lightly.
5. *Dry-Hard-Time*—a thumb print applied under specified conditions is completely removed from the film when polished lightly with a soft cloth.
6. *Dry-Through-Time*—the film is not distorted or detached when the thumb is applied to it in a specified manner and rotated through a 90° angle.
7. *Dry-To-Recoat*—a second coat or top coat can be applied without development of lifting or loss of adhesion of the first coat.
8. *Print-Free-Time*—army duck or cheesecloth applied at a pressure of 3.5 or 6.9 KPa no longer marks the film as

TABLE 7—Typical requirements of liquid paint driers[a]

Class	Metal	Metal Concentration %		Nonvolative Matter, % Max	Typical Specific Gravity, 25/25°C		Color Gardner[b] (Test Method D1544)	G-H Viscosity (Test Method D1545)
		Min	Max		Min	Max		
A	Calcium	3.9	4.1	50	0.884[c]	. . .	3	A
A	Calcium	4.9	5.1	60	0.894	0.912	5	C
B	Calcium	3.9	4.1	70	0.902	0.937	10	D
B	Calcium	4.9	5.1	85	0.932	0.970	11	T
C	Calcium	4.9	5.1	46	0.888	. . .	2	A
D	Calcium	3.9	4.1	66	0.890	0.918	9	B
E	Calcium	3.9	4.1	63	0.905	0.930	8	G
E	Calcium	5.9	6.1	76	0.922	0.960	5	N
F	Calcium	3.9	4.1	50	0.850	0.884	3	A
F	Calcium	4.9	4.1	60	0.900	0.936	4	B
F	Calcium	5.9	6.1	74	0.873	0.948	6	N
F	Calcium	7.9	8.1	70	0.958	. . .	5	B
F	Calcium	9.9	10.1	65	1.000	1.030	7–8	K
A	Cerium	5.9	6.1	30	0.856	. . .	8	A
B	Cerium	5.9	6.1	57	0.925	. . .	17	A1
A	Cobalt	5.9	6.1	45	0.875	0.900	Blue/purple	A
A	Cobalt	11.8	12.2	90	1.008	1.060	Blue/purple	J
B	Cobalt	5.9	6.1	67	0.918	0.970	Blue/purple	B
C	Cobalt	11.8	12.2	65	0.984	. . .	Blue	A
D	Cobalt	5.9	6.1	72	0.912	0.956	Purple	C
E	Cobalt	4.9	5.1	60	0.926	. . .	Red/purple	A
E	Cobalt	5.9	6.1	71	0.945	0.960	Blue/purple	I
F	Cobalt	5.9	6.1	70	0.870	0.958	Blue/violet	A
F	Cobalt	11.8	12.2	80	1.014	1.040	Blue/violet	J
A	Iron	5.9	6.1	50	0.900	0.930	Dark brown	A
B	Iron	5.9	6.1	67	0.960	0.990	Dark brown	M
F	Iron	5.9	6.1	50	0.905	0.930	Brown	A
F	Iron	8.9	9.1	78	0.950	0.985	Brown	M
F	Iron	11.8	12.2	75	1.068	. . .	Brown	A
A	Lead	23.8	24.2	65	1.090	1.110	3	A
B	Lead	23.8	24.2	67	1.125	1.160	11	B
C	Lead	23.8	24.2	61	1.100	. . .	2	B
D	Lead	23.8	24.2	66	1.100	1.125	10	A2
E	Lead	23.8	24.2	71	1.125	1.150	7	A
F	Lead	23.8	24.2	67	1.080	1.140	10	A
F	Lead	35.8	36.2	81	1.350	1.393	8	H
A	Manganese	5.9	6.1	50	0.888	0.920	Red/brown	A
B	Manganese	5.9	6.1	66	0.930	0.965	17	D
C	Manganese	5.9	6.1	50	0.870	. . .	10	A

(Continued)

TABLE 7—Typical requirements of liquid paint driers[a] (Continued)

D	Manganese	5.9	6.1	72	0.942	0.972	Brown	E
E	Manganese	4.9	5.1	42	0.911		Brown	E
E	Manganese	5.9	6.1	69	0.942	0.965	Brown	E
F	Manganese	5.9	6.1	55	0.870	1.020	18	A
F	Manganese	8.9	9.1	80	0.950	1.020	18	A
F	Manganese	11.8	12.2	75	1.044	. . .	16	C
A	Nickel	9.9	10.1	70	1.032	. . .	Green	A
A	Rare earth[d]	5.9	6.1	30	0.630	0.880	6	E
A	Rare earth	11.8	12.2	55	0.977	. . .	Yellow/green	C
B	Rare earth	3.9	4.1	35	0.840	0.855	10	A
C	Rare earth	5.9	6.1	35	0.876	. . .	8	A5
A	Zinc	7.9	8.1	50	0.880	0.906	6	G
A	Zinc	17.8	18.2	90	1.068	1.130	7	Z
B	Zinc	7.9	8.1	70	0.915	0.960	9	A
B	Zinc	9.9	10.1	75	0.980	1.044	8	L
D	Zinc	7.9	8.1	70	1.008	. . .	11	D
E	Zinc	7.9	8.1	42	0.946	. . .	2	A
F	Zinc	7.9	8.1	60	0.855	0.963	7	C
F	Zinc	15.8	16.2	80	1.020	1.100	3	B
A	Zirconium	5.9	6.1	30	0.860	0.864	2	A
A	Zirconium	11.8	12.2	56	0.960	0.992	4	A
A	Zirconium	17.8	18.2	55	1.070	1.074	3	A
A	Zirconium	23.8	24.2	77	1.240	. . .	2	J
C	Zirconium	5.9	6.1	23	0.864	. . .	2	A5
C	Zirconium	11.8	12.2	46	0.976	. . .	2	A
E	Zirconium	5.9	6.1	31	0.864	. . .	4	A
E	Zirconium	11.8	12.2	55	0.975	1.020	4	A
F	Zirconium	5.9	6.1	28	0.855	0.870	2	A5
F	Zirconium	11.8	12.2	55	. . .	. . .	. . .	. . .
F	Zirconium	17.8	18.2	80	1.090	1.130	4	Z
F	Zirconium	23.8	24.2	93	1.240	1.260	6	J

[a]Source: National Paint and Coatings Association, Chemical Specialties Section, Raw Material Index, April 1978 edition per Gardner Method D1544
[b]If off the scale, as observed by the unaided eye.
[c]Only one drier was listed in this category.
[d]The metal content represents total rare earth metals calculated as cerium but the drier contains cerium and lanthanum, as well as minor amounts of other rare earth metals.

determined by photographic standards shown in ASTM D2091, Test Method for Print Resistance of Lacquers.

In addition to the above subjective tests, a number of mechanical drying time recorders are available. The instrument referred to most frequently in recent literature is the Byk-Gardner improved circular drying time recorder [10]. This functions by moving a Teflon stylus over the applied film in a circular path. The pattern left in the film by the stylus after a complete revolution is observed. Recorders are available, which make complete revolutions in 1, 6, 12, or 24 h. With the use of a plastic template, set-to-touch, surface dry, and through-dry times may be noted.

Development of film hardness is also an important criterion of drier efficiency. Tests used to measure hardness include:

1. *ASTM D3363, Test Method for Film Hardness by Pencil Test*—a series of pencils varying in lead hardness from 6B (softest) through 6H (hardest) are pushed into the film, and the hardest pencil that will not penetrate the film is noted.

TABLE 8—Metal analysis by EDTA titration

Metal	ASTM Method	Solvent	Indicator	Titrating Solution
Cobalt	D2373	Glacial acetic acid	PAN[a]	Cupric sulfate
Lead	D2374	Glacial acetic acid	PAN[a]	Cupric sulfate
Manganese	D2375	Toluene-ethanol	Eriochrome black-T	Zinc chloride
Calcium or zinc	D2613	Toluene-ethanol	Eriochrome black-T	
Iron	D3869	Isopropanol	Eriochrome black-T	Zinc chloride
Zinc	D3969	HSO-HO	Xylenol orange	Bismuth nitrate
Vanadium	D3988	Isopropanol-HCL	Xylenol orange	Zinc chloride
Total rare earth	D3989	Isopropanol-HCL	Xylenol orange	Zinc chloride

[a] 1(2-Pyridylazo)-2-Naphthenol.

2. *ISO 1522 Paints and Varnishes—Pendulum Damping Test*—either a König or a Persoz pendulum hardness tester is employed with the time, in seconds, noted for the swing amplitude of the pendulum to decrease by a specified degree when set into oscillation on the dried film.
3. *ASTM D1474, Test Methods for Indentation Hardness of Organic Coatings*—either a Knoop or a Pfund indenter is applied to a film under a specified loading, and the depth of indentation is measured with the aid of a microscope. The depth is converted to either a Knoop or a Pfund hardness number using the equations in the standard.

SPECIFICATIONS FOR LIQUID PAINT DRIER

Drier specifications as described in ASTM D600, Specification for Liquid Paint Driers involve the following classes:

- *Class A*—2-Ethyl hexanoic acids in petroleum spirits.
- *Class B*—Naphthenic acids in petroleum spirits.
- *Class C*—Neodecanoic acids in petroleum spirits.
- *Class D*—Tall oil fatty acids in petroleum spirits.
- *Class E*—Any of the above, plus additives to make the driers water dispersible.
- *Class F*—Other unidentified acids and acid blends.

A comprehensive table of liquid paint driers of the above classes is given in ASTM D600. The typical properties of the driers listed and reproduced in Table 7 include percent metal concentration, percent nonvolatile content, specific gravity, Gardner color, and Gardner-Holdt viscosity.

TESTING OF LIQUID PAINT DRIERS

ASTM D564, Test Method for Liquid Paint Driers outlines the test procedures employed, including both physical and chemical tests. The physical tests include:

1. *Appearance*—visual observations may be made for clarity and cleanness.
2. *Color*—according to ASTM D1544, Standard Test Method for Color of Transparent Liquids (Gardner color scale, which employs the Gardner numerical color scale). However, a number of driers, including cobalt, manganese, nickel, and rare earth, do not fit into this scale and are reported descriptively.
3. *Nonvolatile Content*—ASTM D1644, Test Methods for Nonvolatile Content of Varnishes, according to method A or B. Method A involves heating samples at 105°C for 10 min, while method B specifies 150°C for 10 min.
4. *Miscibility with Oil*—One volume of the drier sample is mixed with 19 volumes of raw linseed oil. The mixture is observed for any signs of separation or clouding over a 24 h period.
5. *Stability*—The drier sample is stored for 7 days at 25, –20, and 50°C and examined for indications of clotting, gelation, or precipitation.
6. *Drying power*—As described in the section entitled "Testing of Drying Efficiency."
7. *Viscosity*—According to ASTM D1545, Test Method for Viscosity of Transparent Liquids by Bubble Time Method. This involves comparing the time of travel of bubbles in tubes of the sample versus Gardner-Holdt standard tubes. The standards were formerly designated by letter but are now indicated directly in stokes. A table in this test method indicates the conversion from letters to stokes.

Chemical analysis is used to determine the metal content of liquid paint driers. The EDTA method is used for most drier metals (Table 8). The liquid drier is dissolved or digested in solvents and then treated with an excess of standard EDTA solution (disodium salt of ethylenediamine tetraacetic acid dihydrate). The excess of EDTA is then titrated to an end point determined by a specified indicator. This method is applicable to single metal driers only, not to drier blends. An EDTA method is not yet available for cerium, and an oxidimetric determination is specified (ASTM D3970, Test Method for Cerium in Paint Driers by Oxidimetric Determination). Table 8 outlines the ASTM designations, indicators, and titrating solutions for analysis of drier metals by EDTAtitration.

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Alkyds and Polyesters

Dan Nelson[1]

ALKYDS ARE SYNTHETIC POLYMERIC MATERIALS that have been used in the coating industry since the 1930s. Today, they continue to be workhorse polymers for the paint, coating, and printing ink industries. Alkyds and chemically modified alkyd resins are the condensation products of poly-basic acids and polyhydric alcohols. They are used in liquid organic coatings for the architectural, industrial, automotive, and industrial maintenance markets. Alkyds are also known as oil-modified polyesters because of the presence of vegetable or marine oils or other fatty acids. These oils are coreacted into the polyester backbone. The type of oil or fatty acid present in the alkyd contributes to its oxidative cure characteristics. In a chemical sense, alkyds are polyesters that are formulated with drying or nondrying oils. In contrast, polyesters are oil free. Alkyds are often modified with other polymeric materials for particular property attainment.

Three major classifications of alkyds are those designed for conventional solids, higher solids, and waterborne coatings. Because there are a large variety of commercially available intermediates and chemical modifiers, i.e., monomers, for the preparation of alkyds, they continue to be a very versatile type of polymers for coatings and printing inks.

Most alkyds are film-forming polymers with a relatively low glass transition temperature (T_g), i.e., below 0°C. They have inherently excellent pigment wetting characteristics and readily accept additives to form coatings with a wide range of appearance, performance, and application characteristics. Alkyds and modified alkyds have a good combination of hardness and flexibility, very acceptable corrosion resistance, good gloss retention, good adhesion to ferrous and nonferrous metals, and other properties that make them acceptable for use on wood, metal, plastic, composite, and other substrates. They are used in areas such as architectural coatings, automotive under-body and under-hood coatings, coil coatings, drum and metal container coatings, electrical insulating enamels, exterior trim paints, maintenance paints, and similar end uses.

Alkyd technology has generally evolved slowly over the past few decades. The past few years have shown that technology advances have been made to (a) increase the performance of higher solids alkyds, (b) develop new methods for delivering alkyds in water, and (c) around blend and hybridization science involving other chemistries.

Polyesters used in coatings are reaction products of polyhydric alcohols and polybasic acids. Synthetic formulators have the luxury of selecting a variety of multifunctional reactants depending on end use applications, required economics, and coating performance needs.

HISTORY

Although condensation polymers of dihydric alcohols and dicarboxylic acids were known at the start of the 20th century, polyesters modified with drying oils were developed in the late 1920s by Kienle and co-workers [1–5]. The early condensation polyesters were not soluble in common solvents and did not air dry until triglyceride oils or their fatty acids were incorporated into the polymeric material. Kienle coined the term "alkyd" from the alcohols ("al") and acids ("cid") used in their preparation. Air-dry films are the result of oxicative polymerization and cross-linking that took place through free radical reaction with atomospheric oxygen at the carbon-carbon double bond of the fatty acids. The use of vegetable or marine oils and/or their fatty acids as coreactants with the early developed polyesters was the developments contributed to the general interest in the product such as new techniques for the production of phthalic anhydride, synthetic glycerin, and other new and novel multifunctional alcohols.

Typically, an alkyd could be based on glycerin as the polyol, phthalic anhydride as the polybasic acid, and soybean or linseed oil as the vegetable oil. These compounds are coreacted and then reduced with aliphatic or aromatic petroleum-based hydrocarbon solvents. Monofunctional fatty acids such as tall oil fatty acids or special blended fatty acids are commonly found in alkyds as alternatives to vegetable oils.

ALKYD SYNTHESIS, PROCESSING, AND MANUFACTURE

Three major categories of chemical intermediates are utilized in the manufacture of alkyd resins:

- Polybasic organic acid/anhydride—example, iso-phthalic acid, phthalic anhydride
- Polyhydric alcohol—example, glycerin
- Monobasic fatty acid or triglyceride oil—example, tall oil fatty acid, soya fatty acids or soybean oil

The stoichiometric proportions and the equivalent weight of these monomers led to the desired physical properties and molecular weight distribution of the resulting alkyd. The solvent selection and quantities used influence the viscosity, nonvolatile content, and the solvent evaporation rate from coating films.

Alkyd processing is mainly a condensation reaction between the hydroxyl and carboxyl groups of the chemi-

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cal intermediates. The main by-product of the reaction is water, and it must be removed during the polymerization process or it will transesterify back into the alkyd and reverse or undo the polymerization thus changing the polymer characteristics. Other chemical reactions are possible during preparation such as transesterification and dimerization of fatty acids or vegetable oils depending on their unsaturation and the alkyd processing temperature. Vegetable oils are used for manufacturing economical alkyds. Fatty acids are used in high-performance alkyds—particularly in higher solids, water reducible, and water dispersed types.

An alkyd resin can be modified with a number of intermediates. Some of the more common types are:

- Acrylates and methacrylate monomers
- Benzoic acid
- Epoxides
- Isocyanates
- Hydrocarbon resins
- Phenolics
- Polyamides
- Rosin and rosin esters
- Silicone
- Styrene
- Vinyl toluene

Alkyds can be modified with the above intermediates to significantly alter the performance attributes of coatings made with them.

MANUFACTURE

There are two major chemical processes used for developing and manufacturing alkyds. These are the fusion process and solvent reflux process.

Fusion Process

In this method, the alkyd intermediates are charged into the reaction vessel. Then an inert gas, such as dry nitrogen or carbon dioxide, is introduced to "blanket" the vapor space above at the top of the reaction vessel. The reaction mixture is heated from 350 to 500°F (175 to 260°C). The main polymerization is due to condensation reactions forming ester groups. Water, the reaction by-product, escapes at the top opening of the reactor. Vigorous mixing and inert gas must be bubbled through the reactor throughout the process to minimize reaction by-products (Fig. 1). The alkyds made by this process tend to be darker in color and higher in molecular weight than alkyds made by the solvent reflux process.

Solvent Reflux Process

In the solvent reflux process, an azeotropic solvent such as xylene or a higher boiling ketone is commonly used in the reaction mixture. The purpose of the azeotropic solvent is to aid in the removal of water formed during the condensation reaction. The reflux solvent and water volatilize together and liquefy in the condenser placed above the reaction vessel. A separator or Dean-Stark trap below the condenser collects this liquid mixture, and the azeotrope solvent is returned to the reaction vessel (Fig. 2).

In both fusion and solvent reflux processes, acid number and viscosity are measured until the final desired values are reached. During the course of the reaction, viscosity will increase and the acid number will decrease. Once the pre-established end points are reached, the alkyd is thinned with the desired type and amount of organic solvent. The amount of reflux solvent used is usually less than 3 % of the theoretical reaction yield and is retained throughout the reaction. The key advantages of the reflux process include limiting the emission of by-products into the atmosphere, faster processing time, and consistent finished product. This process is now the preferred way for manufacturing alkyds. The final alkyd physical characteristics include color, acid number, hydroxyl number, specific gravity, viscosity, and percent nonvolatiles.

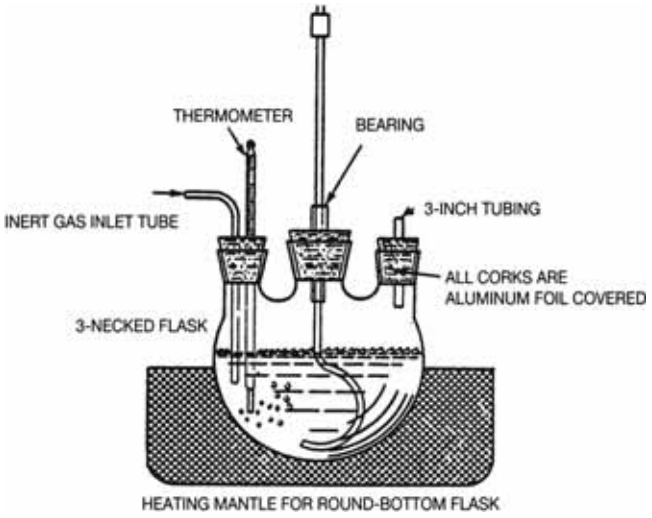

Fig. 1—Apparatus that could be used for fusion cooking of alkyds.

RAW MATERIALS USED TO MANUFACTURE ALKYD RESINS

Typical polybasic acids, polyhydric alcohols, and monobasic fatty acids or oils are given in Tables 1–3. The numerous possible raw materials available and economic considerations of these lead to versatility of alkyds and to a wide range of commercially available products.

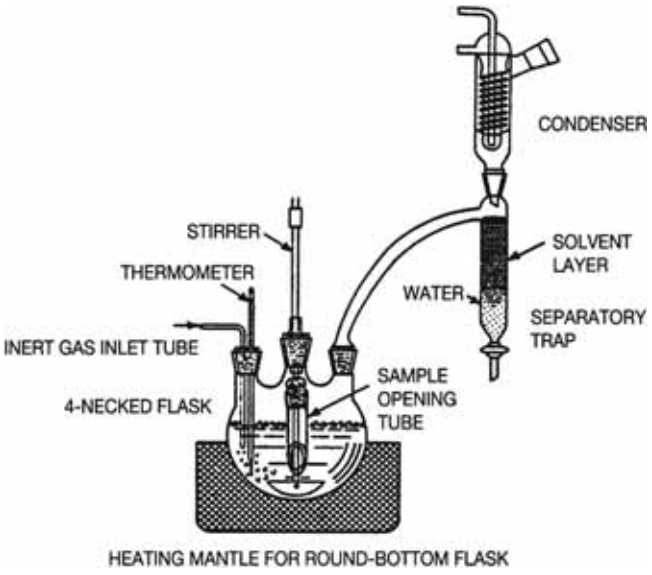

Fig. 2—Laboratory apparatus that could be used for solvent cooking of alkyds.

TABLE 1—Acids and anhydrides used in alkyd manufacture
Polyfunctional
Adipic acid
Azelaic acid
Chlorendic Anhydride
Fumaric acid
Isophthalic acid[a]
Maleic anhydride[a]
Phthalic anhydride[a]
Succinic acid
Sebacic acid
Citric acid
Trimelletic anhydride[a]
Monofunctional
Abiatic acid
Benzoic acid[a]
Caproic acid
Caprylic acid
Castor oil acids
Coconut oil acids
Cottonseed fatty acids
Lauric fatty acids
Linoleic acid
Linolenic acid
Oleic acid
Tallow acids
Tall oil fatty acids[a]
Tertiary-butyl benzoic acid
Special blended fatty acids
[a]Most commonly used in commercial alkyds.

TABLE 2—Polyhydric alcohols used in alkyd manufacture
Polyhydric Alcohols
Glycerin[a]
Ethylene glycol[a]
Propylene glycol
Trimethylol propane
Neopentyl glycol[a]
Hexylene glycol
Pentanediol
1,3-Butylene glycol

TABLE 2—Polyhydric alcohols used in alkyd manufacture (Continued)
Diethylene glycol
Triethylene glycol
Pentaerythritol[a]
Methyl glucoside
Dipentaerythritol
Sorbitol
Trimethylpentanediol[a]
Trimethylol ethane
[a]Most commonly used in commercial alkyds.

TABLE 3—Vegetable oils used in alkyd manufacture
Vegetable Oils
Castor oil
Coconut oil[a]
Corn oil
Cottonseed oil
Dehydrated castor oil
Linseed oil[a]
Safflower oil
Soybean oil[a]
Tung oil
Walnut oil
Sunflower oil
Menhadden oil[b]
Palm oil
[a]Most commonly used in commercial alkyds. [b]A nonvegetable oil derived from fish.

PHYSICAL PROPERTIES

The most common physical properties used to identify characteristics of alkyd resins are determined by the following ASTM methods.

Viscosity

Alkyds cover a wide viscosity range and must be compared to the nonvolatile content and type organic solvent used, ASTM D1545, Standard Test Method for Viscosity of Transparent Liquids by Bubble Time Method. The bubble tubes and measured times in seconds are easy to run with proper testing equipment and a constant temperature set at 25°C. Viscosity is used as a relative measure of alkyd molecular weight and of the final coating application and performance properties. It also is used as a primary means of minimizing batch-to-batch variations of a specific product. Relatively high-molecular-weight alkyds need to be reduced to application viscosity with a greater amount of solvent

or solvent mixture or with solvents that have a particular solvency for the specific alkyd.

Nonvolatile Content

The nonvolatile content of alkyd solutions is determined with ASTM D1259, Standard Test Methods for Nonvolatile Content of Resin Solutions. Alkyd specifications are designed to show a 1 or 2 % variation from an agreed upon nonvolatile by weight requirement. This method is sometimes adjusted to a higher oven temperature of 150°C and a shorter dwell time.

Alkyd resin solutions vary from 30 % nonvolatile (flat wall, medium-oil alkyds) to 100 % nonvolatile content by weight (very long oil alkyds for exterior paints, stains, latex modifiers, and similar products).

Color

The color of alkyd solutions is typically still determined by comparison with a range of color standards referred to as the Gardner-Holdt color standards, ASTM D1544, Standard Test Method for Color of Transparent Liquids (Gardner-Holdt scale). The color or degree of yellowness of the alkyd solution may or may not have an effect on the color of the final coating films.

Density

The density or specific gravity of alkyds is also referred to as the weight per gallon or density and can be determined by ASTM D1475, Standard Test Method for Density of Liquid Coatings, Inks, and Related Products.

Flash Point

The flash point of alkyds is mainly of importance as it pertains to shipping the polymers and formulated paints, i.e., bill of lading and other regulations. ASTM D3278, Standard Test Methods for Flash Point of Liquids by Small Scale Closed-Cup Apparatus, is the most common test that will provide conformance with Department of Transportation regulations. However, other ASTM methods are utilized. The method utilized depends on flash cup availability and other specified requirements.

Neat alkyds have relatively low vapor pressure. Therefore, the flash point of an alkyd solution is related to the flash point of the solvent used for dissolution. It is recommended that flash points on alkyd solutions actually be measured by laboratory methods to ensure reporting accuracy, as the flash point of an alkyd solution may be slightly different from that of the actual solvent or solvents incorporated into the solution.

Drying Properties

The drying properties of alkyds are of importance when describing the product. Metallic driers are based on cobalt, manganese, aluminum, iron, zinc, calcium, or rare earth metals reacted with synthetic organic acids, such as vegetable fatty acids, to form soaps. Mixtures of these driers are added to the alkyd-based coating and act as catalysts by accelerating the rate of air drying and cross-linking. Drier blend compositions and ratios are chosen to maximize in-can stability and provide the desired film surface dry and through dry characteristics. In recent years, synthetic acid-based metallic driers have gained popularity for two main reasons: (1) higher metal concentration in the drier and (2) greater uniformity of drier performance. Methods associated with determining drying are given in ASTM D1640, Standard Test Methods for Drying, Curing, or Film Formation of Organic Coatings at Room Temperature.

Acid Value

The free organic acid groups present in the nonvolatile portion of an alkyd resin are an important property for pigment wetting and performance properties of organic coatings. It is also part of a primary mechanism for providing water compatibility in water reducible or dispersed compositions. The acid value of alkyds is typically determined with ASTM D154, Standard Guide for Testing Varnishes. Reasonably accurate and consistent results can be obtained with this test procedure.

Hydroxyl Value

The hydroxyl value or number is a measurement of the free hydroxyl groups remaining in the alkyd that have not been reacted with carboxyl groups during the condensation stage of the alkyd resin preparation process. Hydroxyl value determinations are more difficult to perform than acid number determinations. There are several reasons for this. First, the hydroxyl group can be sterically hindered or less available within the polymer and thus difficult to reach with the reactants. Second, hydroxyl groups on primary carbon atoms are more reactive than those on secondary carbon atoms, and these are more reactive than those located on a tertiary carbon atom. Tertiary-positioned hydroxyl groups are the most difficult to esterify in this determination. Manufacturers can often specify methods that can be used for secondary hydroxyl groups.

Hydroxyl numbers are important in determining equivalent weight, which in turn is important to determining the amount of urea formaldehyde, melamine formaldehyde, or urethane prepolymer to react with baking type alkyds. In the case of oil-modified urethanes, also called uralkyds, the hydroxyl groups coreact with free isocyanate functionality. Although theoretical equivalency based on hydroxyl numbers is a good guideline to establishing performance characteristics, a ladder of coreactant ratios is important to optimizing particular performance characteristics.

Hydroxyl numbers can be determined by means of ASTM D4274, Standard Test Methods for Testing Polyurethane Raw Materials: Determination of Hydroxyl Number of Polyols, and ASTM D6342, Standard Practice for Polyurethane Raw Materials: Determining Hydroxyl Number of Polyols by Near (NIR) Spectroscopy.

ALKYD RESIN CLASSIFICATION

Unmodified alkyds are classified into four types that depend on oil content—very long-oil, long-oil, medium, and short-oil alkyds. Properties such as speed of drying, ease of brushing, film flexibility, chemical resistance, and exterior gloss retention are all dependent on the oil content. These properties are summarized in Table 4.

A summary of alkyd resins comparing types of oil/fatty acids, nonvolatile, solvent, and typical application is given in Table 5.

HIGHER SOLIDS ALKYD RESINS

Higher solids alkyds have been developed to reduce organic solvent emissions in those applications under regulatory

TABLE 4—Alkyd resin properties related to oil length

	Very Long Oil	Long Oil Medium	Short
Oil content	Highest	↔	Lowest
Speed of drying	Slowest	↔	Fastest
Ease of brushing	Best	↔	Worst
Film Flexibility	Highest	↔	Lowest
Chemical resistance	Worst	↔	Best
Exterior gloss retention	Worst	↔	Best

restrictive requirements. This is accomplished by the development of polymers with lower molecular weights than conventional alkyds. A narrower molecular weight range of the resin species is necessary to meet air-dry, non-volatility, and performance properties of the coatings. Another important factor is solvent selection. Organic solvents with greater viscosity reduction of the base or neat alkyd are needed to lower coating hydrocarbon atmospheric emissions. The release of these solvents during coating film formation is an important consideration. The higher-solids alkyd resins are available in all classes of "conventional alkyds" such as those shown in Table 6.

Higher-solids alkyds can replace their conventional solids counterparts in many coating applications, thus affording decreased atmospheric emissions. Such products are used in air-dry architectural enamels and both air-dry and baking industrial primers and topcoats.

Typical compromises of moving toward higher-solids alkyds are consequences of the polymer's lower molecular weight and include reduction in dry rates, and decreases in film performance. Recent advances in alkyd technology are now available to partially offset these deficiencies.

WATER-REDUCIBLE ALKYD RESINS

Usually, these water-reducible alkyds are medium- to short-oil compounds that have high acidity. Water reducibility is attained by amine neutralization of the carboxyl groups on the polymers and the use of coupling solvents, such as glycol ethers and four-carbon alcohols [6]. Typical coupling

TABLE 5—Description of unmodified alkyd resins

Type Alkyd	Oil or Fatty Acid	Nonvolatiles	Solvent	Typical Applications
Very long	Linseed	85–100 %	Aliphatic hydrocarbon	Exterior latex modifier
	Soya			House paint modifier
	Tall oil			Oil-based stain and ink vehicles and modifiers
Long	Linseed	60–70 %	Aliphatic hydrocarbon	Architectural coatings
	Safflower			Maintenance coatings
	Soya			One-coat enamels
	Sunflower			Exterior enamels
	Tall oil acids			Primers Topcoats
Medium	Linseed	45–50 %	Aliphatic hydrocarbon	Farm implements
	Safflower		Aromatic hydrocarbon	Railway equipment
	Soya			Maintenance
	Sunflower			
	Tall oil acids			
	Blends			
Short	Castor	50 %	Aromatic hydrocarbon or Rule 66-type solvent blend[a]	Industrial coatings
	Dehydrated castor			
	Coconut			
	Linseed			
	Soya			
	Tall oil acids			
	Blends			

[a]A typical Rule 66-type solvent is isobutanol, VM&P naphtha, and xylene at 8 % maximum volume solids. Rule 66 is a 1966 regulation from California's South Coast District that restricted the amount of aromatic hydrocarbon solvent in a coating formulation. In the 1960s, research indicated that these types of solvents contributed greatly to atmospheric ozone formation. Rule 66 legislation was adopted by many other local and state regulators.

TABLE 6—Higher-solids alkyd resin types and end uses

Type	Typical End Use
Long oil	Architectural enamels
Medium oil	Transportation enamels
Short oil	General industrial air-dry and bake enamels
Benzoic acid terminated	Implement enamels
Phenolic modified	Primers
Silicone modified	Maintenance topcoats
Copolymer	Aerosol enamels

solvents are ethylene glycol monobutyl ether (Ektasolve EB), propylene glycol monoethyl ether, propylene glycol monopropyl ether, and four-carbon alcohols such as sec-butyl alcohol. Water-borne alkyds are available in most classes of "conventional alkyds" such as those shown in Table 7. Ikhuoria et al. [7] recently described preparation of water-reducible alkyds from fumarized rubber seed oil.

Probably the next step in water-borne alkyd technology will center on alkyd dispersions, which are acrylic-alkyd co-polymers in particulate form that are dispersed in water. Typical cosolvents used in water-reducible systems may or may not be required with their use dependent on the particular binders and the application techniques involved. In such dispersion systems, the submicron particles are usually surfactant free and are felt to be shell-and-core in nature. It is thought that an alkyd core is protected from the aqueous environment by the acrylic shell.

SATURATED POLYESTERS

Saturated polyesters are also called oil-free alkyds. Due to their lack of unsaturated oil, they do not self cross-link or auto-oxidize. Polyesters are made into coatings by formulating with curing agents or cross-linkers. Depending on the type of cross-linkers used, the polyester paint film could be cured at ambient or elevated temperatures. The curing agent can be a urea-formaldehyde or melamine formaldehyde resin, both of which require baking. Polyisocyanates are formulated with polyester resins for air-dry or low-bake coatings. Due to the reactive nature of the polyisocyanates, these coatings are supplied in two separate components. The two components are mixed prior to application of the coating. A typical application time window or "pot-life" ranges from 2 to 12 h. In both types of cross-linked systems, the saturated polyester provides the hydroxyl groups for reaction with the cross-linking agent [8].

TABLE 7—Waterborne alkyd resin types and end uses

Type	Typical End Use
Long oil	Stains and enamels (limited package stability)
Medium oil	General industrial air-dry enamels
Short oil	General industrial baking enamels, automotive under-the-hood parts
Benzoic acid terminated	Implement enamels
Phenolic modified	Primers
Silicone modified	Maintenance topcoats

The physical properties of these coatings are outstanding due to the absence of the oils or fatty acids, and they afford coatings with excellent chemical resistance, color retention, flexibility, exterior durability, and hardness.

These types of materials can be adapted to provide higher-solids saturated polyesters by redesigning the polymer structure and molecular weight while using organic solvents with higher solvency (ketones or esters) rather than the customary blends of aromatic hydrocarbons with ketones, alcohols and glycolethers [9].

Water-reducible and water dispersed polyesters are available through design of polymers having acid numbers in the range of 25–60. When these products are neutralized with an amine, they become soluble in blends of water and cosolvents and yield systems with fairly low volatile organic compound content. Formulation of a coating from these products involves the use of water-soluble or water dispersible ureas, melamines, or isocyanates. The cured films offer excellent chemical resistance, hardness, gloss, and flexibility.

Recent advances in polyester technology include (a) new water delivery systems, (b) cyclo-aliphatic backbones with high UV transparency, and (c) compositions leading to highly cross-linked coatings with resistance to highly aggressive chemicals often found in aerospace applications.

SILICONE-MODIFIED POLYESTERS

Conventional Types

Silicone modification of polyesters is accomplished by use of a silicone intermediate incorporated through reaction at levels typically ranging from 30 to 50 % of the total polymer. The silicone intermediates are of hydroxy or alkoxy functionality, and when they are reacted with the polyester, water or alcohol is eliminated. This modification improves the weather-ability and/or heat resistance of the resulting organic coating. Silicone-modified polyesters are available in both self-curing and externally cross-linked types. They are used as coil coatings for prefabricated building panels, prefabricated architectural products, metal advertising sign stock, and other applications requiring excellent exterior durability and/or good heat resistance.

Higher-Solids Types of Polyesters

Higher-solids silicone-modified polyesters are made by lowering the polyester base molecular weight and/or using oxygenated solvents such as ketone and ester types as replacements for aromatic hydrocarbons. This substitution yields increased solvency, lower viscosities, lower solvent amounts, and higher nonvolatile content for the polyester solution. The end uses are similar to conventional solvent-borne silicone polyesters. However, the higher-solids, silicone-modified polyester resins do not have the self-cross-linking option available for conventional types and are always combined with an external cross-linking agent. Porreau [10] has described high-solids alkyds based on styrene-allyl alcohol oligomers.

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Amino Resins (Reaction Products of Melamine, Urea, etc., with Formaldehyde and Alcohols)

William Jacobs[1]

PREFACE

IN PREPARATION OF THIS CHAPTER, THE CONTENTS of the 14th edition of this manual were drawn upon. The author acknowledges the author of the chapter in the 14th edition, J. Owen Santer. The current edition will review and update the topics as addressed by the previous author, introduce new technology, and include up-to-date references.

INTRODUCTION

Definition and Description

Amino or aminoplast resins for coatings are mainly the products of the reaction of either urea (Fig. 1) or melamine (Fig. 2) with formaldehyde and an alcohol. Besides urea and melamine, other compounds with similar functionality—such as benzoguanamine, glycoluril, etc.—are also used in specific applications where certain property advantages are required. However, the sales of amino resins are dominated by those based on urea and melamine, with U.S. consumption increasing from about 100 million lb in 1990 to over 400 million lb by 2004 [1].

As prepared, amino resins are usually water-white viscous materials that may contain added solvent to reduce viscosity for ease of handling. Where a solvent is used, it is most often an alcohol such as *n*-butanol, iso-butanol, or isopro-panol, all of which are excellent solvents for amino resins. Mixed solvents, such as *n*- or iso-butanol with xylene, are also used, especially for the higher-molecular-weight resins made with butanol as a co-reactant. Some amino resins are water soluble or water reducible with co-solvent.

Amino resins for coatings are grouped somewhat arbitrarily into two classes: (1) high-solids resins, i.e., resin solutions at 80 % or higher solids (weight/weight), including resins that contain no solvent, and (2) conventional resins, i.e., resin solutions at <80 % solids (weight/weight).

History

Historically, the first amino resins used in coatings were the reaction products of urea or melamine with formaldehyde and butanol (either *n*-or iso-). They were substantially polymeric and were formulated at about 50 %–60 % solids in butanol/xylene mixtures. They have been commercially available at least since the 1940s. Parenthetically, it should be noted that resins made by reacting urea or melamine with formaldehyde without subsequent reaction with an alcohol had been available even earlier. These resins are used as molding powders and adhesives and are generally unsuitable for coatings applications.

High-solids coating resins, usually made with higher ratios of reacted formaldehyde than the older, conventional resins, have been widely available since the 1970s. They are almost always made with methanol or combinations of methanol and butanol, although a small number of high-solids resins are available, which are made exclusively with butanol.

Applications

Amino resins are used in coatings to cross-link the primary film-former, usually an acrylic, polyester, or alkyd resin typically carrying primary or secondary hydroxyl groups, although other nucleophilic functionality, such as carboxyl, amide, or carbamate, are sometimes employed. The cross-linking reaction ("cure") is principally one of trans-etherification between hydroxyl groups on the primary film-former and alkoxymethyl or alkoxybutyl groups on the amino resin. In addition to the trans-etherification reaction, the amino resin almost always undergoes self-condensation reactions to some extent, more or less dependent upon the amino resin type.

The major by-products of the cure reaction include methanol and/or butanol, formaldehyde, and water. Cure temperatures are typically in the range of 180–465°F (82–232°C) for times that vary from 15 to 30 min at the lower end of the temperature range to perhaps only a few seconds at the upper end. An acid catalyst may be used to accelerate cure, depending on the cure temperature and the particular amino resin used. There are highly catalyzed amino resin formulations that cure at room temperature, such as those found in the wood and plastics coatings industry, but the majority of commercially available formulations for metal substrates are typically cured at elevated temperatures.

Urea resins are less expensive than melamine resins, which is understandable given that melamine is made from urea. Urea resins are also faster curing than melamine resins, but are moisture sensitive and therefore not suitable for use outdoors. They are used widely for wood finishing, e.g., furniture, kitchen cabinets, and in paper, film, and foil

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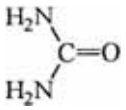

Fig. 1—Urea.

applications. Wood and paper applications capitalize on the relatively rapid cure of the urea resin since lower temperatures must be used to avoid damage to the substrate. As mentioned previously, in some wood applications, the cure temperature is often at ambient or only slightly higher.

Melamine resins, on the other hand, find much broader application since they are not nearly as water sensitive as the ureas. Perhaps the largest single use for melamine resins is in automotive OEM (original equipment manufacture), where the finished paint must stand up to extremes of temperature, humidity, the degradative effects of sunlight, etc. Melamine resins are used also in coil coatings, metal containers, etc. (see End Uses of Amino Resins).

SYNTHESIS OF AMINO RESINS

Reactions of Synthesis

The synthesis of amino resins for coatings is a two-step process. In the first step, the parent compound is reacted with formaldehyde (methylolation reaction). In the second, the methylolated intermediate is reacted with an alcohol (etherification reaction). Equations (1)–(4) exemplify the process, with urea as the parent compound. Reactions with melamine are analogous.

$$H_2NCONH_2 + CH_2O \rightarrow \underset{\text{monomethylolurea}}{H_2NCONHCH_2OH} \quad (1)$$

$$H_2NCONHCH_2OH + CH_2O \rightarrow \underset{\text{dimethylolurea}}{HOCH_2NHCONHCH_2OH} \quad (2)$$

$$HOCH_2NHCONHCH_2OH + ROH \rightarrow HOCH_2NHCONHCH_2OR + H_2O \quad (3)$$

$$HOCH_2NHCONHCH_2OR + ROH \rightarrow \underset{\text{bis(alkoxymethyl)urea}}{ROCH_2NHCONHCH_2OR} + H_2O \quad (4)$$

Reactions shown in Eqs (1) and (2) proceed quite rapidly when catalyzed by either acid or base. Reactions shown in Eqs (3) and (4) take place only under acid conditions, with the rate of reaction strongly *p*H dependent; the lower the *p*H, the faster the reaction. All four reactions are equilibrium reactions. Hence, the extent of the reaction is dependent on the charge ratios of the various reactants and on whether or not the reactions are driven by removal of by-products in order to shift the equilibrium.

The reactions of melamine are similar to those of urea with one exception. With urea, two of the four available hydrogens are readily reacted with formaldehyde [Eqs (1) and (2)], while the remaining two hydrogens react more slowly and require an excess of formaldehyde to force the reaction toward completion. With melamine, on the other hand, all six hydrogen atoms may be reacted with relative ease to give hexa(methylol)melamine.

The kinetics of the methylolation reactions of urea and melamine has been studied extensively [2–8], but there is little in the literature on the kinetics of the etherification reaction. Although both of these reactions are superficially straightforward, a number of other reactions may take place that complicate the kinetics. These reactions are all self-condensation reactions in which two or more molecules of the parent species are joined together through either a $>NCH_2N<$ (methylene) or $>NCH_2OCH_2N<$ (methylene ether) bridge. The reactions leading to self-condensation may be written as follows:

$$>NCH_2OR + HN< \rightarrow >\underset{R=H,alkyl}{NCH_2N<} + ROH \quad (5)$$

$$>NCH_2OH + HOCH_2N< \rightarrow >NCH_2OCH_2N< + H_2O \quad (6)$$

The bridging groups in amino resins manufactured for coatings applications can be either methylene or methylene ether bridges, but methylene bridges tend to dominate. It should be noted that methylene ether bridges could still readily participate in curing reactions whereas methylene bridges are virtually inert. When formulated and cured, additional bridges of both types may be formed. How many of each will depend on factors such as the composition of the amino resin, cure temperature, and catalyst level.

It can be seen, then, that a variety of amino resins may be prepared, with properties that depend on such factors as the choice of starting material, i.e., urea, melamine, etc., the combining ratios of the various reactants, the choice of alcohol (or alcohols, if more than one is used), and the degree of polymerization of the resin. The principal manufacturers of amino resins for coatings typically offer a product line of 25 or more resins. A generalized composition of a typical melamine resin is shown in Fig. 3.

Structure/Property Variations

The difference between conventional solids and high-solids amino resins represents not so much a difference in solids content as it does a distinction between resin structures. The conventional solids (<80 %) resins are made from melamine or urea reacted with relatively low levels of formaldehyde, typically 1.5–2.0 mol for urea resins and 2.5–3.5 mol for melamine resins and those etherified with either *n*-or iso-butanol. Because of these low reaction ratios, considerable self-condensation takes place during the synthesis, leading in the case of melamine resins to products with degrees of polymerization (DP) of 3 and perhaps somewhat higher for the ureas. Because of the rela-

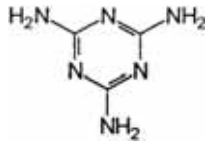

Fig. 2—Melamine.

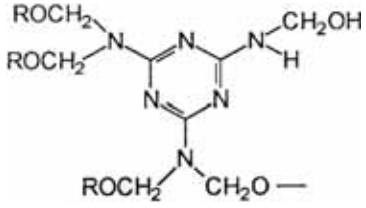

Fig. 3—Representative structure of a melamine resin.

tively high polymer content, these resins are viscous and must be reduced with solvent to less than 80 % to obtain a manageable viscosity.

Another, possibly the major, contributor to high viscosity is the residual imino (>NH) and methylol (>NCH_2OH) groups on the amino resin, which can form strong hydrogen bonds with unshared electrons on nitrogen and oxygen.

The high-solids amino resins have much higher levels of combined formaldehyde than the conventional solids resins. Typical values for combined formaldehyde are in the range 2.0–2.7 for urea resins and 3.5–6.0 for melamine resins. The etherifying alcohol is most often methanol, although resins made with both methanol and butanol or even butanol alone are also widely used. These resins are less polymeric, with DP <3, and usually more fully etherified and so less polar than the conventional resins. In some cases, these resins are sufficiently low in viscosity that no solvent is needed. Where solvent is required, it is usually either isopropanol or butanol (<*n*-or iso-). Resins are also made which can be reduced with water.

Analysis/Analytical Methods

Structural analysis of amino resins has been reviewed by Christensen [9]. Methods discussed include ^{1}H NMR and ^{13}C NMR for determining levels of combined formaldehyde and alcohol, analysis of alkoxy groups by Zeisel cleavage, and by trans-etherification followed by gas chromatography. A more detailed analysis for melamine resins by ^{13}C NMR is due to Tomita and Ono [10]. An overview of the IR spectra of various triazines has been published by Larkin, Makowski, and Colthup [11]. The study involves the observed IR and Raman vibrations for several ring modes where decreased vibrational coupling with the substituents explains why certain bands make good group frequencies in related melamine resins. Christensen [9] and Kambanis and Rybicki [12] also describe non-destructive methods for removing solvent from amino resin solutions in order to determine nonvolatile content.

Classically, amino resins for coatings have been characterized by three test procedures. These procedures, which tell the coating formulator most of what he needs to know with regard to formulation and cure conditions, are measurement of (1) solids content, (2) viscosity, and (3) solvent tolerance. These are discussed below.

Solids Content

The most common methods used to determine solids content are gravimetric. Solvent is allowed to evaporate from a weighed sample under carefully controlled conditions of time and temperature. The sample is then reweighed. The loss in weight gives a measure of solvent content, and the solids content is obtained by difference. One difficulty with this test is the tendency of amino resins to deformylate and/or self-condense when heated, with evolution of formaldehyde, alcohol, and water. To the extent that this occurs, the measured solids content will be lower than the "true" value. Frequently, however, the paint formulator is interested in the "contributed solids," i.e., what fraction of the amino resin solution remains in the cured film. In that case, a solids test method that approximates the time and temperature of cure might be more appropriate.

For these reasons, solids test methods fall into two groups: (1) Methods that reflect the solids content in the absence of self-condensation, etc., and (2) other methods, which reflect varying degrees of self-condensation in addition to loss of formaldehyde and solvent(s).

The more common of the first methods is the so-called "foil solids test," which is used almost universally for high-solids amino resins. Essentially, a 1 g sample of resin solution is weighed onto a piece of pre-weighed aluminum foil. The foil is folded over on itself and the sample compressed between the two foil surfaces to provide a thin film about 3–4 in. (7–10 cm) in diameter. The foil is then opened up to give a thin film on each foil surface. The foil is placed in a 45°C oven for 45 min, at the end of which time it is removed, reweighed, and the solids content calculated. These conditions are known to be sufficiently mild that no resin condensation occurs, nor does the resin lose formaldehyde via demethylolation. Surprisingly, the foil solids test may on occasion overestimate the solids content, particularly when (1) the resin is relatively polar, i.e., carries appreciable >NH and >NCH_2OH groups, and (2) the solvent is not low boiling. Apparently, the increase in viscosity as solvent evaporates slows the diffusion rate and effectively prevents complete removal of solvent within the time frame of the test. There may also be a hydrogen-bonding effect between solvent and resin that contributes to the retention of solvent.

Other test methods involve much higher temperatures, where resin condensation/degradation does occur. One standard method is the ASTM Test Methods for Volatile Content of Coatings (ASTM D2369), where a small resin sample (0.3–0.5 g) is diluted with xylene and placed in a 110°C oven for 1 h. There are a number of other, similar tests.

Viscosity Measurement

Amino resin viscosities are most commonly measured by the Gardner bubble viscometer method. This method is similar to the Test Method for Viscosity of Transparent Liquids by Bubble Time Method (ASTM D1545). A tube containing the resin under test is placed in a rack containing reference tubes of known viscosity. The tubes are equilibrated to 25°C in a constant temperature bath. The rack is quickly inverted, and the rate of rise of an air bubble in the sample tube is compared against similar bubbles in the reference tubes. The reference tubes are letter graded A–Z and Z1–Z6.

Solvent Tolerance

There are a number of different solvent tolerance tests. All involve titrating a weighed sample of the amino resin with a standard reagent (solvent). The object of the test is to measure how much of the reagent the amino resin can accept before the solution turns cloudy/milky. Results are typically reported in milliliters of reagent per gram of sample. Typical reagents used include xylene, iso-octane, and the iso-octane/decahydronaphthalene/toluene mixture described in ASTM Test Method for Solvent Tolerance of Amine Resins (D1198), which was withdrawn (with no replacement) in March 2007 in accordance with section 10.5.3.1 of the Regulations Governing ASTM Technical Committees.

While the immediate objective of the solvent tolerance test is to determine the amount of reagent that the amino

resin can accept before solution clouding occurs, the real purpose of the test is to gain insight into the structure and composition of the resin and hence have a better understanding of how it will perform in a given coating application. In general, amino resins of high molecular weight, or having high levels of polar functional groups, i.e., >NH and >NCH_2OH, will have limited compatibility with the typical hydrocarbons used and hence will give low tolerance test results. Experience shows that a low tolerance value means a faster curing resin and vice versa, especially in the absence of acid catalyst. However, although the tolerance test represents a quick and easy way to measure potential cure response, it does not uniquely define the resin structure. Thus, a low tolerance reading can be caused by either high polarity or high molecular weight or both.

Size Exclusion, High-Performance Liquid Chromatography, and Mass Spectrometry

To obtain more detailed knowledge of resin structure, amino chemists now rely very heavily on gel permeation or size exclusion chromatography (SEC) and on high-performance liquid chromatography (HPLC) sometimes coupled with mass spectrometry (Mass Spec). The size exclusion chromatograph provides an excellent measure of number and weight-average molecular weight and molecular weight distribution (polydispersity), while HPLC, which fractionates the resin components primarily by functional groups, provides information on resin composition, especially if coupled with Mass Spec. Typically the more polar species are eluted first, followed by the less polar fractions. Thus, taken together, SEC and HPLC provide detailed information on molecular weight and functionality, which cannot be directly obtained or inferred from any of the various solvent tolerance tests. Size exclusion and liquid chromatograms for a representative commercial high-solids methylated melamine resin are shown in Figs. 4 and 5.

More recently the combined technique of liquid chromatography and mass spectrometry has been used to obtain very detailed knowledge of amino resin structure. Advances in ionization techniques have resulted in mass spectra capable of discerning individual components in even the higher molecular weight oligomeric portions in amino resin compositions. This unique ability to discern numerous individual components and their concentration

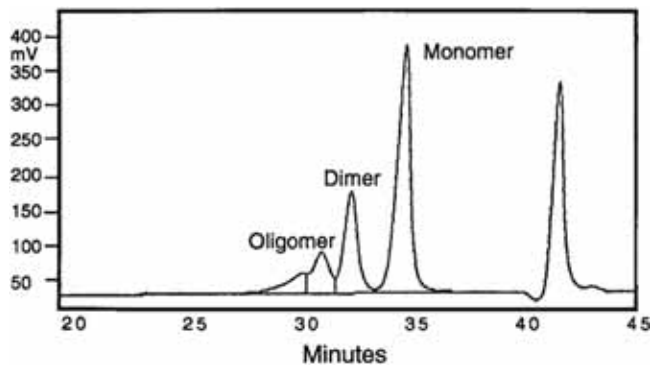

Fig. 4—Size exclusion chromatogram of a typical high-solids methylated melamine resin.

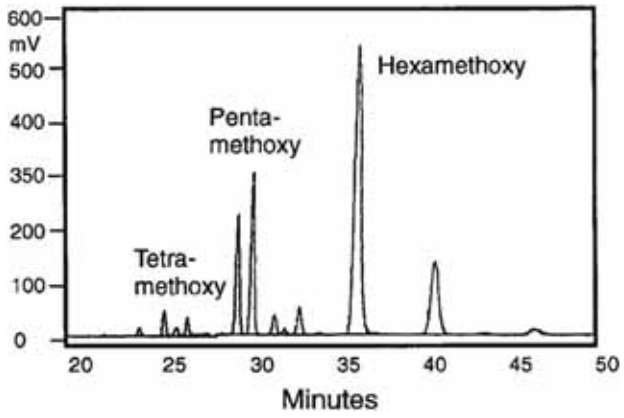

Fig. 5—High-performance liquid chromatogram of a typical high-solids methylated melamine resin.

by LC-Mass Spec techniques is described in various publications by Chang [13].

Combining Ratios

Amino resins may also be characterized by measurement of the amounts of formaldehyde and alcohol that have reacted. For example, see hexa(methoxymethyl) melamine (HMMM) (Fig. 6), which has exactly 6 mol each of combined formaldehyde and methanol per mole of melamine. Unlike HMMM, most resins are, of course, mixtures of products, which are best described by an average composition. One of the most widely sold commercial high-solids methylated melamine resins has an average combining ratio melamine/formaldehyde/methanol of about 1/5.6/5.1. Because methanol reacts with an already-reacted formaldehyde molecule, a resin can never have combined methanol greater than the combined formaldehyde. The excess formaldehyde, 0.5 mol in the commercial example, represents formaldehyde that has not reacted with methanol and which must therefore be present as methylol (>NCH_2OH), bridging groups (>NCH_2N<) or (>NCH_2OCH_2N<), and acetals (>$NCH_2OCH_2OCH_3$>). Acetals are formed when an excess of formaldehyde is used in the synthesis. They are therefore present in many high-solids amino resins.

Determination of combining ratios may be done most easily by either ^1H or ^{13}C NMR techniques [9,10]. Older methods involve complete hydrolysis of the resin to the starting materials, followed by wet-chemical analysis for nitrogen and formaldehyde and gas chromatographic determination of alcohol(methanol or butanol).

Free Formaldehyde

Amino resins always contain some unreacted formaldehyde, usually referred to in product specifications as "free" formaldehyde. Free formaldehyde may be analyzed quantita-

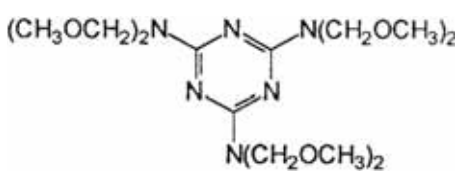

Fig. 6—Hexa(methoxymethyl)melamine.

tively by a number of methods. One of the most commonly used is the sodium sulfite method [14]. Formaldehyde reacts rapidly and completely with aqueous sodium sulfite to form a bisulfite addition complex. Sodium hydroxide is liberated quantitatively on a mole-for-mole basis.

$$CH_2O + Na_2SO_3 + H_2O \rightarrow NaOH + HOCH_2SO_2Na \quad (7)$$

The NaOH is either titrated directly with a standard HCl solution, or neutralized with a known excess of standard HCl, which is then back-titrated with NaOH. Care must be taken to ensure that reacted formaldehyde, particularly methylol groups, is not analyzed as free formaldehyde. This can occur because of the following reaction, which can be minimized by performing the titration as rapidly as possible at cool temperatures, e.g., room temperature or lower.

$$> NCH_2OH \rightarrow\!\!> NH + CH_2O \quad (8)$$

PHYSICAL PROPERTIES

General

Amino resins are typically viscous liquids with an amine-like odor. Depending on composition, they may also smell of formaldehyde and/or solvent. They are readily soluble in alcohols, ketones, hydroxyl-functional glycol ethers, esters, etc., but have limited solubility in hydrocarbons. Some resins, especially methylol-rich resins with low levels of both combined formaldehyde and combined methanol, are water soluble. Many more are water reducible in the presence of other solvents, e.g., alcohols and glycol ethers.

Because of their resinous nature, aminos have neither a well-defined freezing point nor boiling point. Uncured resins typically have glass transition temperatures around –40°C. When heated at temperatures above about 140°C, some aminos, especially urea resins, may undergo decomposition with release of formaldehyde and alcohol. This tendency to decompose causes difficulties in determining the solids content of resin solutions, as described in Analysis/Analytical Methods. The problem is particularly acute with resins having high methylol functionality.

Viscosity

The viscosity of an amino resin is a function of (1) polymer content (degree of polymerization) and (2) the nature of its functional groups. The latter may be a more important contributor to viscosity than the former. Amino resins are not generally very polymeric, especially in comparison with other coating resins, e.g., polyesters, alkyds, and acrylics. Typically, average degrees of polymerization are in the range of 1–5. High-molecular-weight "tails" increase viscosity significantly.

Because of strong hydrogen bonding, resins carrying significant amounts of >NH and $>NCH_2OH$ functionality are quite viscous, even though they may not be highly polymerized. There is a marked drop in viscosity when amino resins are diluted with solvent, largely due to breaking of hydrogen bonds. Good solvents (e.g., alcohols) are more effective at reducing viscosity than poor ones [15]. Methanol is probably the best, although it is not widely used because of its low boiling point. Isopropanol is almost as effective, and because it is somewhat higher boiling, represents a good compromise.

Surface Tension

The surface tension of amino resins is quite strongly related to the nature of the etherifying alcohol and is much less affected by the level of combined formaldehyde and alcohol. Surface tension measurements on high-solids, solvent-free resins using a DeNouy tensiometer have given values ranging from about 45 dynes/cm for methylated resins to about 28 dynes/cm for butylated resins [16]. Mixed methyl/butyl resins give intermediate values, depending on the methyl and butyl content. The reduction in surface tension when butanol is the etherifying alcohol may be one reason that high-solids butyl and methyl/butyl resins provide improved flow and leveling in high-solids formulations compared to their fully methylated counterparts.

REACTIONS OF AMINOS IN COATINGS

Cure Reactions

Amino resins in coating formulations cure by reactions that are chemically and mechanistically similar to those that take place during synthesis of the resin. The principal reaction of cure is one of trans-etherification, wherein a hydroxyl group on the primary film-former (acrylic, polyester, or alkyd) reacts with an alkoxymethyl group on the amino resin

$$> NCH_2OR + HO - A \rightarrow\!\!> NCH_2O - A + ROH \quad (9)$$

where:

R = alkyl and
A = primary film-former.

Additionally, direct etherification may take place, the end result being the same

$$> NCH_2OH + HO - A \rightarrow\!\!> NCH_2O - A + H_2O \quad (10)$$

where:

A = primary film-former

These two reactions both result in chemical bond formation between the amino and the primary film-former (co-condensation). Two other reactions may also take place, both of which involve reaction of the amino resin with itself (self-condensation). These are

$$> NCH_2OR + HN <\!\!\rightarrow\!\!> NCH_2N < + ROH \quad (11)$$

where:

R = H, alkyl

$$> NCH_2OH + HOCH_2N <\!\!\rightarrow\!\!> NCH_2OCH_2N < + H_2O \quad (12)$$

Besides the co-condensation and self-condensation reactions, hydrolysis and deformylation reactions may also occur:

$$> NCH_2OR + H_2O \rightarrow\!\!> NCH_2OH + ROH \quad (13)$$

$$> NCH_2OCH_2OR + H_2O \rightarrow\!\!> NCH_2OH + CH_2O + ROH \quad (14)$$

$$> NCH_2OH + H_2O \rightarrow\!\!> NH + CH_2O \quad (15)$$

The relative contributions to cure of the co-condensation and self-condensation reactions will depend on a variety of factors. These include:

1. The functionality of the amino resin, i.e., the relative proportions of $>NCH_2OR$, $>NCH_2OH$, and >NH groups present initially, as well as those generated during formulation and/or cure.

2. The functionality (hydroxyl, carboxyl, amido, carbamyl, etc.) and the equivalent weight (i.e. hydroxyl number, carboxyl number, etc.) of the primary film-former (co-reactant).
3. The amino/co-reactant ratio.
4. The level and type of catalyst (weak acid/strong acid).
5. Cure time and temperature.

A co-reactant resin with a low hydroxyl number is best if formulated with a "polar" amino (i.e., one rich in >NH and/or NCH_2OH) since these groups help build molecular weight during cure via self-condensation, particularly if little or no catalyst is present. Conversely, a high hydroxyl resin is best if matched with an alkoxymethyl-rich amino and cured with a strong acid catalyst. Where high cure temperatures are employed (e.g., can or coil coating operations), the choice of amino resin is less obvious, and, in practice, both polar and nonpolar aminos are used.

Acid catalysts are usually used as an aid in curing amino-based formulations. These catalysts include very strong acids, such as *p*-toluenesulfonic acid (PTSA), dodecyl-benzenesulfonic acid (DDBSA), dinonylnaphthalenedisulfonic acid (DNNDSA), etc., and weaker acids, such as phenyl acid phosphate (PAP), butyl acid phosphate (BAP), etc. Amine blocking agents are sometimes used to help minimize resin advancement prior to cure. Some coatings, particularly those designed for high-bake temperatures, need no catalyst, relying instead on the combination of high temperature and perhaps carboxylic acid functionality on the primary film-former to bring about cure [17]. While all of the various reactions that take place during cure are accelerated by either acid or heat, it is fair to say that reactions of trans-etherification are most influenced by catalyst level and type, while reactions of self-condensation are most influenced by heat. The trans-etherification reaction takes place very rapidly under strong acid catalysis, even at low temperatures. This is especially true for aminos with a high level of alkoxymethyl substitution, i.e., a very low NH content, which tends to inhibit catalysis. Thus, most formulations involving resins with high alkoxymethyl ether content and designed for low-temperature cure (250°F or lower) will call for a sulfonic acid catalyst, either blocked or free.

Although the individual reactions of cure are reasonably well understood and have been described in numerous papers [18–23], there is still much to be learned about the overall behavior of amino resins during cure, in particular the relative contributions of each of the various reactions. One of the difficulties is, of course, that the coating becomes intractable as cure progresses. Hence, a majority of studies involve analysis of the by-products of cure [18,22,24]. Other methods, such as dynamic mechanical analysis [25], nuclear magnetic resonance [26,27], FTIR [22], ESCA, etc., investigate the structure of the cured film.

These techniques are useful not only for analyzing the freshly cured coating, but also as a means of following the coating through its lifetime, either natural or accelerated.

Degradation and Weathering

Amino-based crosslinked coatings exposed to the atmosphere are subject to both hydrolysis and UV-degradation at different rates dependant upon their structures. The mechanisms by which melamine resins hydrolyze have been described in detail by Berge and co-workers [28–30], who was the first to distinguish between mono- and di-substituted nitrogen with respect to their behavior towards acid or base hydrolysis. Thus, in an alkaline medium, hydrolysis of an alkoxymethyl group on a singly substituted nitrogen is initiated by removal by the base of the proton attached to nitrogen:

$$-NHCH_2OR + B \rightarrow -^{-}NCH_2OR + BH^{+} \quad (16)$$

$$-^{-}NCH_2OR \rightarrow -N=CH_2 + ^{-}OR \quad (17)$$

$$-N=CH_2 + H_2O \rightarrow -NHCH_2OH \quad (18)$$

$$^{-}OR + BH^{+} \rightarrow ROH + B \quad (19)$$

This mechanism is clearly not applicable to di-substituted nitrogen ($N(CH_2OR)_2$), and these groups are in fact extremely resistant to alkaline hydrolysis.

On the other hand, acid hydrolysis takes place readily for both mono- and di-substituted nitrogen. Berge proposed two mechanisms: (a) specific acid catalysis

$$>NCH_2 - OR + H^{+} \rightarrow\!\!> NCH_2OHR^{+} \quad (20)$$

$$>NCH_2OHR^{+} \rightarrow\!\!> NCH_2^{+} + HOR \quad (21)$$

$$>NCH_2^{+} + H_2O \rightarrow\!\!> NCH_2OH + H^{+} \quad (22)$$

and (b) general acid catalysis

$$-NHCH_2OR + HA \rightarrow -NHCH_2OHR^{+} + A^{-} \quad (23)$$

$$-NHCH_2OHR^{+} + A^{-} \rightarrow -N=CH_2 + ROH + HA \quad (24)$$

$$-N=CH_2 + H_2O \rightarrow -NHCH_2OH \quad (25)$$

The work of Berge and co-workers with melamine resins is undoubtedly relevant to acid hydrolysis of paint films based upon hydroxyl functional primary film formers, which has been studied by a number of workers.

English and co-workers [31,32] found that coatings prepared from highly alkylated melamines underwent extensive hydrolysis of residual methoxy groups during two years' exposure in Florida, but there was no evidence of hydrolysis of bonds between melamine and the primary film-former. Bauer and Briggs [33,34] used IR to analyze acrylic-melamine coatings exposed to both UV and moisture and found evidence of hydrolysis of both residual methoxy groups and acrylic-melamine bonds, with the rate of hydrolysis being faster in the presence of UV light. The rate of hydrolysis was slowed considerably when a hindered amine light stabilizer was used.

During the early 1990s, degradation of melamine-containing automotive coatings had become particularly severe because of etching and spotting due to acid rain. The problem was compounded because the high-solids automotive coatings used very high levels of melamine resins (35 %–45 % of total binder weight) to help meet the lower amount of volatile organic (VOCs) requirements, giving rise to correspondingly high levels of acrylic-melamine bonds and residual alkoxymethyl groups in the cured film, all of which are susceptible to hydrolysis under acid conditions. The suppliers of high-solids coatings for automobiles were faced with a dilemma—either switch to more expensive alternative crosslinkers, such as isocyanates and aliphatic epoxies, which are more stable under

acid rain conditions, or modify the hydroxyl functional backbone to achieve increased resistance to spotting due to acid rain. An interesting aspect of the acid etch problem was that the damage was always more severe on relatively new coatings. If a newly painted automobile was protected from the acid environment for the first 6 to 12 weeks, damage thereafter was much less severe. One theory at the time was that the paint is undergoing some type of additional cure. Another possibility is that some type of protective surface oxidation occurs as it ages. In fact, Lamers et al. [35] eventually presented evidence that the melamine methylene ether carbon, involved in crosslinking, can be oxidized to a more acid etch-resistant urethane linkage in the presence of UV light and oxygen, lending support to the latter, protective surface oxidation theory. This protection mechanism (by oxidation to urethane) has since been all but proved by Wu et al. [36] with the introduction of acid etch-resistant automotive top coats based on tris-(alkoxycarbonylamino) triazine (TACT). The chemical structure of crosslinked hydroxyl functional acrylics and TACT is the same as those first prepared by Jacobs and DiLeone [37] using melamine tri-isocyanate as the crosslinker for hydroxyl functional automotive acrylic top coats. TACT forms crosslinks with hydroxyl functional acrylics by a trans-carbamylation reaction, affording acid etch-resistant melamine-urethane bonds.

Since these early observations, suppliers of high-solids coatings have essentially solved the acid etch problem for automobiles in a very clever way by modifying their acrylic backbones (primary film-former) from hydroxyl functionality to primary and/or secondary carbamate functionality. This is usually done by a trans-carbamylation reaction on the poly-hydroxyl functional acrylic similar to TACT chemistry, but with mono-functional alkyl carbamates, such as methyl carbamate, to avoid premature cross-linking [38,39]. High levels of melamine resins can once again be used with the new carbamate functional acrylics, but this time resulting in melamine-primary carbamate cross-links, or melamine-secondary carbamate cross-links, both of which are very resistant to acid etch damage [40–42].

Automotive paint manufacturers are also actively pursuing water-borne systems, which use higher molecular weight, less hydroxyl functional co-reactant resins, and lower levels of melamine cross-linker. Mostly, these water-borne systems are used in the base coat, where in any case, the protective clear top coat minimizes acid attack. It is the clear top coat, with its high melamine content, that provides the excellent gloss and "distinctness of image" (DOI), characteristic of basecoat/clear coat technology. The melamine resin also minimizes the amount of solvent required because of its low viscosity at high-formulated solids, behaving in some ways as a reactive diluent and plasticizer.

End Uses of Amino Resins

Amino-based surface coatings protect and decorate the substrate to which they are applied. Their technology and use has developed over many years. As already mentioned, resins based on urea and melamine dominate the field. Urea resins are traditionally used in clear coatings for wood, e.g., furniture, kitchen cabinets, in paper, film, and foil applications, and in some appliance and general industrial coatings. They are also used to some extent in automotive primers. Urea resins cannot be used in automotive topcoats because of their sensitivity to hydrolysis.

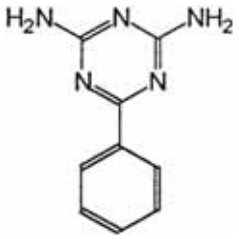

Fig. 7—Benzoguanamine.

Melamine resins are much more widely used than urea resins. They give better chemical resistance, as well as resistance to weathering in exterior applications, despite some of the earlier difficulties described in connection with acid etch of automobiles before the use of carbamate functional acrylics. Besides automobiles, they are used in appliance formulations (both coil appliance and conventional post-sprayed), general metal applications, container coatings (beer and beverage cans), etc.

In choosing an amino resin for a particular application, consideration must be given not only to interior versus exterior use, but also to possible restrictions on cure conditions and compatibility of the amino resin with its co-reactant resin, both when formulated and as the paint film is formed during solvent flash-off and cure, etc. Compatibility of the amino is especially important in water-borne coatings, which are becoming more widely used. Another factor is the stability of the amino toward advancement (molecular weight buildup) during storage of the formulated paint.

Benzoguanamine-based (Fig. 7) amino resins are used where film flexibility and hardness are required, as in some appliance applications (e.g., refrigerator doors made from coil stock, etc.). They also have good corrosion, humidity, and detergent resistance. Their use is limited by cost and poor exterior durability due to the pendant phenyl group on the benzoguanamine molecule.

Glycoluril (Fig. 8) resins have been available since the late 1970s.

In some pigmented formulations, they may require a higher cure temperature or a higher catalyst level than melamine-based resins, but show excellent corrosion and humidity resistance and release lower amounts of formaldehyde during cure [43]. Because of their increased resistance to hydrolysis, the glycolurils often find uses in container coatings where retort resistance is important and in some very interesting specialty applications, such as rheological thickeners for waterborne paints [44] and as curatives for optical electronics and photoresist fine line applications [45,46]. The tetra functional, fully methylated methylol glycolurils are high melting solid resins that find use in durable powder coatings [47], especially the wrinkle or "textured" finish applications [48].

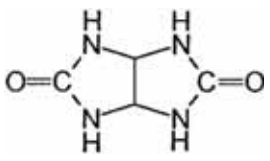

Fig. 8—Glycoluril.

ENVIRONMENTAL/TOXICITY

At least since the end of the 1970s, and perhaps starting even earlier, there has been an increased emphasis on the quality of the environment both in the workplace and beyond. In the coatings industry, this has meant strict controls on exposure of workers to hazardous ingredients in the coating formulation when applied, as well as on the nature and amounts of VOCs released to the environment when the formulation is cured.

Amino resin suppliers have responded to these environmental challenges in a number of ways. Chief among these has been a progressive shift towards higher-solids, lower-molecular-weight aminos, which are now the resins of choice of coatings formulators. Many amino resins are supplied at 100 % non-volatiles, especially for the automotive industry. Where solvents are needed, those presenting the least hazard to worker and environment are selected. For their part, paint producers have increased the functionality of the co-reactant resin while lowering its molecular weight to minimize solvent use with the object of building molecular weight to the maximum possible extent during cure. This has meant using higher levels of amino resin, as much as 40 %–50 % of total binder weight in some cases.

Perhaps the most intractable environmental problem with amino resins is the use of formaldehyde in their manufacture. Formaldehyde is recognized by the International Agency for Research on Cancer as a carcinogen. The American Conference of Governmental Industrial Hygienists lists formaldehyde as an "A2" substance, i.e., one suspected of carcinogenic potential for man, and the Occupational Safety and Health Administration (OSHA) has set workplace exposure limits of 0.75 ppm (8 h time weighted average) and 2 ppm (15 min short-term exposure limit).

The formaldehyde content of amino resins is predominantly "combined," i.e., chemically reacted, and represents about 30 %–50 % by weight of the resin. A small amount, ranging from about 0.1 % to about 3 % is present free, or un-reacted (see the section entitled Analysis/Analytical Methods). Amino resin suppliers have made considerable progress over the past several years in lowering the level of free formaldehyde in their products, which is important because of OSHA labeling requirements.

In an ideal situation, all of the combined formaldehyde would remain in the coating after cure as part of the polymer network. In practice, however, some of the combined formaldehyde and all of the free formaldehyde is released during cure and may reach the environment, depending on the mechanics of the coating and curing operation. Since typically the free formaldehyde from reputable amino resin suppliers is very low, it is the partial release of combined formaldehyde during cure that is of concern. Efforts should be taken to optimize formulations for minimal release, not just for performance properties. Of course, scrubbing or incineration of any off gases, where possible, is one of the surest solutions.

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9

Ceramic Coatings

Richard A. Eppler[1]

CERAMIC COATINGS ARE AN ALTERNATIVE TO organic or polymer based coatings for selected surface coating applications. When protecting a surface, it is usually less expensive to use organic coatings rather than other materials such as ceramic coatings. However, organic paints have limitations and will not meet all service requirements. Though more expensive, for some applications ceramic coatings may be a more suitable form of protection.

Vitreous (glassy) ceramic coatings are chosen for application over a substrate for one or more of several reasons [1]. These reasons for selecting a ceramic coating in preference to an organic paint include rendering the surface more chemically inert, impervious to liquids and gases, more readily cleanable, and more resistant to service temperature, abrasion, and scratching.

The chemical durability of ceramic coatings in service substantially exceeds that of organic paints [2]. Vitreous coatings are formulated to be resistant to a variety of reagents, from acids to hot water to alkalies, as well as to essentially all organic media. The only important exception is hydrofluoric acid, which readily attacks all silicate glasses. This outstanding durability, combined with a very smooth surface, renders many ceramic coatings suitable for applications requiring the highest standards of cleanability, such as ware that comes in contact with food and drink. These coatings are also suitable for applications requiring true hermeticity, usually to protect sensitive electronic equipment. No organic resins are truly hermetic.

Even the most thermally stable organic resins depolymerize at temperatures on the order of 300°C. Hence, organic paints are not suitable for applications requiring thermal stability above 300°C. For example, stove side panels are painted, but stove tops are porcelain enameled. A similar argument can be made for abrasion resistance. Organic resins are soft (Moh 2–3). By contrast, vitreous coatings are harder (Moh 5–6), and some plasma coatings are much harder. For example, alumina coatings, plasma sprayed, have Moh = 9.

Vitreous coatings are thin layers of glass fused onto the surface of the substrate. When the substrate is a ceramic, the coating is called a glaze. When the substrate is a metal, the coating is called a porcelain enamel. When the substrate is a glass, the coating is called a glass enamel.

GLAZES

A ceramic glaze is a vitreous coating applied to a ceramic substrate, usually a whiteware. Glazes are applied to their substrates by one of several powder-processing techniques: dipping, spraying, and waterfall or bell application. The raw materials are both crystalline oxides and frits. In these wet processes the raw materials are dispersed in an aqueous slip for application. After application, the coatings must be dried and fired at high temperatures (up to 1300°C, typically 1000–1100°C) to fuse them onto the substrate.

Applications for Glazes

Ceramic glazes find their way into a wide range of applications ranging from coffee mugs to automotive spark plugs. The major markets for ceramic coatings have different requirements, but one common theme is chemical durability and cleanability.

The major products that normally use glazes are distributed as follows:

44.5 %	sanitary-ware,
31.1 %	wall and floor tile,
12.4 %	tableware,
11.9 %	artware,
10 %	electrical porcelain and electronics.

The total market for these products in the United States is estimated to be $12.4 billion for 2005 [3], of which the glaze component typically consumed 10 %–15 % of the total manufacturing cost. Hence, the value of the protective, functional, and decorative properties provided by the coating usually far outweighs the cost.

Leadless Glazes

Glazes are essentially mixtures of silica with other oxides added to permit the glaze to form at a readily achievable temperature. In a leadless glaze, the alkali and alkaline earth oxides, together with magnesia (MgO), zinc oxide (ZnO), and boron oxide (B_2O_3), are used to provide the fluxing action. Table 1 gives the formulas of a few typical ceramic glazes. Glaze 1 is a feldspathic glaze suitable for use on soft paste porcelains or hard stoneware [4]. This glaze is typical of that used on medieval Chinese porcelains.

Glaze 2 is a sanitary-ware glaze [5]. It is derived from the soft paste porcelain glaze by the addition of ZnO. In the tile industry, the trend to ever faster firing rates (as low as 35 min cold-to-cold) has led to the formulation of glazes such as glazes 3 or 4 [6]. Here the melting rate is increased by both increasing the percent of fluxes, and increasing the alkaline earths and zinc oxide at the expense of the alkalis. Glaze 3 is opacified, while glaze 4 is a clear base for dark colors. To produce a glaze for tableware, the coefficient of

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TABLE 1—Typical ceramic glazes in weight percent

Glaze	Li_2O	Na_2O	K_2O	CaO	MgO	ZnO	SrO	BaO	PbO	B_2O_3	Al_2O_3	SiO_2	ZrO_2
1	0.00	2.24	3.24	9.71	4.44	0.00	0.00	0.00	0.00	0.00	14.44	69.90	0.00
2	0.00	2.05	3.12	11.15	0.00	5.39	0.00	0.00	0.00	0.00	18.58	59.71	0.00
3	0.00	3.24	1.56	8.81	0.07	3.50	2.29	0.00	0.00	3.29	9.54	56.51	11.20
4	0.00	2.78	2.82	11.68	0.08	3.16	0.11	0.00	0.00	4.55	11.89	62.37	0.57
5	0.00	1.81	2.71	9.16	0.62	10.94	30.7	2.50	0.00	5.47	7.37	55.79	0.57
6	0.20	4.24	0.43	2.18	0.00	1.86	4.73	12.23	0.00	17.78	8.13	48.22	0.00
7	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	88.14	0.00	0.00	11.86	0.00
8	0.00	2.15	2.24	16.52	0.00	1.07	2.10	0.00	0.00	3.26	7.95	55.37	9.35

thermal expansion must be reduced to match that of the ware. Glaze 5 is an example of a glaze for vitreous hotel china [7]. When the durability requirements of a food contact surface are not needed, processing can be improved by the use of a more fluid glaze, such as the spark plug glaze 6 [6].

Lead-Containing Glazes

Although historically important, the use of lead oxide in glazes is no longer acceptable, except in special applications [6]. The cost of meeting the regulalatory requirements for handling lead oxide are prohibitively expensive for most applications [6]. An exception is the coatings used on integrated circuit packages to seal them [8].

Satin and Matte Glazes

Satin and matte effects are due to dispersed oxide crystals of appropriate refractive index in the glaze [5]. Calcium aluminosilicate and zinc silicate crystals are commonly used. The crystals must be very small and evenly dispersed if the glaze is to have a smooth, velvet appearance. Glaze 8 in Table 1 is an example of a matte glaze.

Testing of Glazes

ASTM Committee C21 on Ceramic Whitewares and Related Products has developed several test methods to evaluate the physical properties of ceramic glazes. These are listed in Table 2 [9]. These tests form the basis for most quality control testing programs.

There are several methods concerned with the fit of the glaze to the substrate. These include: C554—Test Method for Crazing Resistance of Fired Glazed Ceramic Whitewares by a Thermal Shock Method; C424—Test Method for Crazing Resistance of Fired Glazed Whitewares by Autoclave Treatment; C1300—Test Method for Linear Thermal Expansion of Glaze Frits and Ceramic Whiteware Materials by the Interferometric Method; and C372—Test Method for Linear Thermal Expansion of Porcelain Enamel and Glaze Frits and Fired Ceramic Whiteware products by the Dilatometer Method.

Several other ASTM methods are concerned with chemical durability. These include: C650—Test Method for Resistance of Ceramic Tile to Chemical Substances; C1378—Test Method for Determination of Resistance to Staining; and C556—Test Method for Resistance of Overglaze Decorations to Attack by Detergents. Of particular concern are ASTM methods used to control release of lead and cadmium from glazed surfaces. These include: C738—Test Method for Lead and Cadmium Extracted from Glazed Ceramic Surfaces; and C895—Test Method for Lead and Cadmium Extracted from Glazed Ceramic Tile.

PORCELAIN ENAMELS

Porcelain enamel coatings are ceramic coatings designed for application to metals. Conventional porcelain enamel coatings are prepared in an aqueous system and applied to the substrate by spray, dip, or flow coating. The coating is dried before firing. Newer technology involves dry application of powdered porcelain enamel by electrostatic spray.

The total market for porcelain-enameled products was reported to be $6.0 billion in 1999 [10]. About 86 % of the products are appliances, such as ranges, water heaters, home laundry, and dishwashers. About 6 % are cast-iron sanitary ware, and 8 % are architectural, cookware, and miscellaneous items.

A porcelain enamel must be formulated such that it will bond to the metal substrate. For proper adherence of the enamel to the metal, it is necessary to develop a continuous electronic structure across the interface [11]. This structure is developed by saturating the enamel coating and the substrate metal with an oxide of the metal [12], which for iron and steel substrates is ferrous oxide.

Certain transition metal oxides, such as cobalt oxide, nickel oxide, and cupric oxide, can be added to an enamel formulation to improve the adherence between the metal and the substrate. Ground coat enamels contain adherence oxides, while cover coat enamels do not.

Ground Coat Enamels

A general-purpose ground coat enamel such as Enamel 1 in Table 3 is an alkali borosilicate containing small amounts of adherance oxides to promote the bonding process. Enamel 2 is a home laundry enamel that has been formulated for outstanding alkali resistance through the addition of large quantities of zirconia [13]. Hot water tank coatings such as Enamel 3 have very stringent thermal- and corrosion-resistance requirements.

Enamel 4 is a continuous clean coating. This is a porous coating that provides a means of volatilizing and removing food soils from the internal surfaces of ovens during normal operation [14].

TABLE 2—Test methods for ceramic glazes [9]	
Number	**Title**
C1378	Test Method for Determination of Resistance to Staining
C1027	Test Method for Determining Visible Abrasion Resistance of Glazed Ceramic Tile
C650	Test Method for Resistance of Ceramic Tile to Chemical Substances
C609	Test Method for Measurement of Light Reflectance Value and Small Color Differences Between Pieces of Ceramic Tile
C554	Test Method for Crazing Resistance of Fired Glazed Ceramic Whitewares by a Thermal Shock Method
C424	Test Method for Crazing Resistance of Fired Glazed Whitewares by Autoclave Treatment
C556	Test Method for Resistance of Overglaze Decorations to Attack by Detergents (withdrawn)
C1300	Test Method for Linear Thermal Expansion of Glaze Frits and Ceramic Whiteware Materials by the Interferometric Method
C372	Test Method for Linear Thermal Expansion of Porcelain Enamel and Glaze Frits and Fired Ceramic Whiteware Products by the Dilatometer Method
C1028	Test Method for Determining the Static Coefficient of Friction of Ceramic Tile and Other Like Surfaces by the Horizontal Dynamometer Pull Meter Method
C584	Test Method for Specular Gloss of Glazed Ceramic Whitewares and Related Products
C738	Test Method for Lead and Cadmium Extracted from Glazed Ceramic Surfaces
C895	Test Method for Lead and Cadmium Extracted from Glazed Ceramic Tile
C1192	Standard Practice for Safe Spraying of Ceramic Glazes (withdrawn)

TABLE 3—Typical porcelain enamels in weight percent							
Oxide	**Enamel 1**	**Enamel 2**	**Enamel 3**	**Enamel 4**	**Enamel 5**	**Enamel 6**	**Enamel 7**
Li_2O	0.88	0.81	1.33	0.52	0.89	1.10	1.76
Na_2O	13.15	12.60	13.92	7.30	9.41	8.58	12.23
K_2O	2.30	1.56	0.00	1.47	6.13	9.15	3.83
CaO	6.18	2.80	2.04	0.65	0.00	0.00	0.00
MgO	0.00	0.18	0.00	0.00	0.00	0.00	0.00
ZnO	0.00	0.26	1.27	0.00	0.00	1.04	0.00
BaO	7.27	0.73	0.56	0.00	0.00	0.00	0.00
CoO	0.47	0.36	0.47	0.03	0.00	0.00	0.00
NiO	0.29	0.31	0.00	0.03	0.00	0.00	0.00
CuO	0.20	0.00	0.00	13.99	0.00	0.00	0.00
B_2O_3	15.37	15.99	7.60	1.18	16.13	16.53	7.11
Al_2O_3	6.354	11.50	2.02	41.38	2.25	1.34	2.72
Cr_2O_3	0.00	0.00	0.00	1.24	0.00	0.00	0.00
Sb_2O_3	0.00	0.00	0.00	0.30	0.00	0.00	0.00
SiO_2	44.01	41.55	56.05	24.20	40.97	46.74	59.07
ZrO_2	0.00	6.36	11.66	7.24	0.00	0.00	7.86
TiO_2	0.00	2.55	0.00	0.03	20.97	13.25	3.58
MnO_2	0.20	0.66	1.81	0.03	0.00	0.00	0.00
P_2O_5	0.70	0.45	0.00	0.00	1.30	0.00	0.00
Nb_2O_5	0.00	0.00	0.00	0.00	0.06	0.00	0.00
WO_3	0.00	0.00	0.00	0.00	0.05	0.00	0.00
MoO_3	0.00	0.00	0.00	0.00	0.00	0.00	0.47
F	2.71	2.31	2.19	0.72	3.17	3.93	2.35

TABLE 4—Test methods for porcelain enamels [16]	
Number	**Title**
C148	Test Methods for Polariscopic Examination of Glass Containers
C282	Test Method for Acid Resistance of Porcelain Enamels (Citric Acid Spot Test)
C614	Test Method for Alkali Resistance of Porcelain Enamels
C756	Test Method for Cleanability of Surface Finishes
C538	Test Method for Color Retention of Red, Orange, and Yellow Porcelain Enamels
C839	Test Method for Compressive Stress of Porcelain Enamels by Loaded-Beam Method
C536	Test Method for Continuity of Coatings in Glassed Steel Equipment by Electrical Testing
C743	Test Method for Continuity of Porcelain Enamel Coatings
C374	Test Methods for Fusion Flow of Porcelain Enamel Frits (Flow-Button Methods)
C346	Test Method for 45-degree Specular Gloss of Ceramic Materials
C872	Test Method for Lead and Cadmium Release from Porcelain Enamel Surfaces
C539	Test Method for Linear Thermal Expansion of Porcelain Enamel and Glaze Frits and Ceramic Whiteware Materials by the Interferometric Method
C537	Test Method for Reliability of Glass Coatings on Glassed Steel Reaction Equipment by High Voltage
C283	Test Method for Resistance of Porcelain Enameled Utensils to Boiling Acid
C285	Test Method for Sieve Analysis of Wet-Milled and Dry-Milled Porcelain Enamel
C703	Test Methods for Spalling Resistance of Porcelain Enameled Aluminum
C385	Test Method for Thermal Shock Resistance of Porcelain Enameled Utensils

Cover Coat Enamels

Cover coat porcelain enamels are formulated to provide specific color and appearance characteristics, abrasion resistance, surface hardness, and resistance to corrosion, heat, and thermal shock. They can be clear, semi-opaque, or opaque. Opaque enamels such as Enamel 5 are used for white and pastel coatings [15]. They contain high concentrations of titania to provide the opacification. Semi-opaque enamels such as Enamel 6 are used for most medium-strength colors. Clear enamels such as Enamel 7 are used to produce strong bright colors. They are similar to ground coat formulations without the adherance oxides.

Testing of Porcelain Enamels

Test methods for porcelain enamel coatings are under the jurisdiction of ASTM Committee B-8 on Metallic and Inorganic Coatings. The methods are listed in Table 4. Again, they form the basis for most quality control test programs.

Several of these test methods are concerned with the chemical durability of porcelain enamels. They include: C282—Test Method for Acid Resistance of Porcelain Enamels (Citric Acid Spot Test); C614—Test Method for Alkali Resistance of Porcelain Enamels; C756—Test Method for Cleanability of Surface Finishes; C538—Test Method for Color Retention of Red, Orange, and Yellow Porcelain Enamels; C872—Test Method for Lead and Cadmium Release from Porcelain Enamel Surfaces; and C283—Test Method for Resistance of Porcelain Enameled Utensils to Boiling Acid. A related issue is the possibility of defects providing a pathway from the surface to the substrate, usually called continuity of coating. Methods in this area include: C536—Test Method for Continuity of Coatings in Glassed Steel Equipment by Electrical Testing; C743—Test Method for Continuity of Porcelain Enamel Coatings; and C537—Test Method for Reliability of Glass Coatings on Glassed Steel Reaction Equipment by High Voltage.

GLASS ENAMELS

Glass enamels are vitreous coatings applied on glass. They provide a means of decoration, not an improvement in chemical durability or in cleanability. These coatings must be matured at temperatures below the deformation point of glass (1000–1200°F, or 538–649°C). Hence, they require large quantities of fluxing elements so that chemical durability is difficult to achieve.

Glass enamels are produced in ready-to-use form (paste, thermoplastics, spray mediums, ultraviolet curable mediums) by a few select manufacturers. They represent a specialty product that is more akin to organic paints than to other ceramic coatings. The markets for this specialty product are categorized as tableware, glass containers, architectural, lighting, and automotive. As supplied to the user, glass enamels are mechanical mixtures of pigments, fluxes, and organic suspending media. The requirement for low maturing temperatures necessitates the use of very high lead oxide containing borosilicates for the flux. Leadless fluxes are now available, but have not yet achieved properties equal to the lead-containing fluxes. The organic suspending media are similar to materials used to make organic paints.

TABLE 5—Test methods for glass enamels [9]	
ASTM Method	**Subject**
C724	Test Method for Acid Resistance of Ceramic Decorations on Architectural-Type Glass
C735	Test Method for Acid Resistance of Ceramic Decorations on Returnable Beer and Beverage Glass Containers
C675	Test Methods for Alkali Resistance of Ceramic Decorations on Returnable Beverage Glass Containers
C676	Test Method for Detergent Resistance of Ceramic Decorations on Glass Tableware
C824	Standard Practice for Specimen Preparation for Determination of Linear Thermal Expansion of Vitreous Glass Enamels and Glass Enamel Frits by the Dilatometer Method
C927	Test Method for Lead and Cadmium Extracted from the Lip and Rim Area of Glass Tumblers Externally Decorated with Ceramic Glass Enamels
C978	Test Method for Photoelastic Determination of Residual Stress in a Transparent Glass Matrix Using a Polarizing Microscope and Optical Retardation Compensation Procedures
C777	Test Method for Sulfide Resistance of Ceramic Decorations on Glass

Testing of Glass Enamels

Test methods for glass enamels are under the jurisdiction of Subcommittee 14.10 on Glass Decoration of ASTM Committee C-14 on Glass and Glass Products. These methods [9] are listed in Table 5.

Most of these methods are concerned with the chemical durability of glass decorations. They include: C724—Test Methods for Acid Resistance of Ceramic Decorations on Architectural-Type Glass; C735—Test Method for Acid Resistance of Ceramic Decorations on Returnable Beer and Beverage Glass Containers; C675—Test Methods for Alkali Resistance of Ceramic Decorations on Returnable Beverage Glass Containers; C676—Test Method for Detergent Resistance of Ceramic Decorations on Glass Tableware; and C927—Test Method for Lead and Cadmium Extracted from the Lip and Rim Area of Glass Tumblers Externally Decorated with Ceramic Glass Enamels.

REFRACTORY COATINGS

Flame spray techniques can be used to apply ceramic coatings in the molten state to heat-sensitive or massive substrates that cannot themselves be heated to high temperatures. Most ceramic coating materials used currently can be applied by flame spraying [17]. Silicates, silicides, carbides, oxides, and nitrides have all been deposited by this process.

In these processes, the coating material is melted and projected as heated particles onto the substrate, where it instantaneously solidifies as a coating. Three methods of heating and propelling the particles in a plastic condition to the substrate surface include: (1) combustion flame spraying, (2) plasma arc flame spraying, and (3) detonation gun spraying. Combustion flame spraying is used for coating materials that melt readily. Plasma arc flame spraying is used for very refractory materials such as metal carbides. Detonation gun spraying is used for hard, wear-resistant materials such as tungsten carbide.

Flame spray coatings generally lack smoothness and are usually porous. They are, therefore, limited to applications such as thermal barrier coatings, where porosity is a virtue, and wear-resistant coatings, where the materials cannot be applied readily by any other technique.

Testing of Refractory Coatings

There is only one test method for flame spray coatings in the ASTM standards: C633—Test Method for Adhesion or Cohesive Strength of Thermal Spray Coatings [16].

COATING APPLICATION

Ceramic coatings are applied to their substrates by one of several powder-processing techniques. In wet processes, the raw materials are dispersed in a slip. Slip preparation involves mixing the ingredients, particle-size reduction, dispersion in water, and the addition of minor amounts of additives to modify the rheological properties of the slip [18,19]. These processes are carried out together in a ball mill comprising a rotating cylinder partly filled with freely moving impact-resistant shapes.

The application process for a ceramic coating must be straightforward and foolproof, reproducible, economical, and flexible [6]. Selection of the application technique is one of the most important decisions the coatings engineer makes. Criteria for this selection are type of ware, shape and size of ware, throughput required, energy and labor costs, and space available. All of these factors affect the quality and the cost of a coating process so that the best solution must be determined on an individual basis.

Dipping is a simple, efficient, rapid technique requiring no capital equipment. The ware is immersed in the coating slip, moved around in a controlled way, removed from the slip, shaken to remove excess slip, and set down to drain and dry. Any bare spots are touched up with a finger wet with coating material. Its limitations are extreme sensitivity to operator skill and difficulty in automating volume production.

Spraying is a process whereby a coating slip is broken down into a cloud of fine particles that are transferred to the substrate by either pneumatic, mechanical, or electrical forces. The method requires a gun, a container or feed mechanism, an impelling agency, and a properly designed hood or booth maintained under negative pressure [20], Spraying lends itself to high-volume automated systems [21]. The articles are continuously fed under a battery of angled spray guns. Coating reclaim is an essential part of automated systems.

Slip can also be applied mechanically with a rotating atomizer. Slip is passed onto a set of closely spaced rotating

disks, which throw the coating into a fan of droplets. Costs are similar to spraying. The primary use of this technique is in producing textured coatings on tile.

If the substrate is conductive (that is, a metal), the surface quality and uniformity of a ceramic coating can be improved by using the electrostatic spray coating technique [22,23]. In this system, the slip is broken into droplets either by air atomization or by centrifugal force from a sharp-edged rotating surface. The drops acquire a high negative charge and are dispersed as a fine mist. They are driven forward to the grounded substrate following the lines of force. Hence, coating material can reach the underside of the ware, and full-edge coverage is achieved.

There are other techniques for specific applications. Tile require only one face to be glazed, but with a very smooth coating. This suggests the Bell or waterfall technique [6], where a continuous feed of tiles is carried under a curtain of fluid slip made by pouring a stream of slip over a bell shaped device. Painting and brushing are seldom used except for special effects and for applying glaze to inaccessible areas.

For substrates that require precisely positioned areas of coating, the silk screen process can be used [20]. Finely powdered dry coating material is dispersed as a smooth paste. Using a squeegee, this paste is pressed through the open areas of a fine mesh screen stretched on a frame. For coating a total piece, costs are excessive.

There are a few techniques of application that do not require the preparation of a slip. They include flame spraying, dry powder cast iron enameling, and electrostatic dry powder enameling.

Flame spraying can be used to apply ceramic coatings in the molten state to heat-sensitive or massive substrates. Flame spray coatings generally lack smoothness and are usually porous. Equipment and material costs are generally high.

In dry powder cast-iron enameling, a casting is heated in a furnace to red heat. It is then withdrawn from the furnace and, while still hot, dusted with dry powdered frit by means of a vibrating sieve placed over the surfaces to be coated. The powdered frit melts and adheres as it falls on the hot surface. This process is also extremely operator sensitive. Recently, it has been adapted for robot application, which serves to reduce variations over time.

The most important dry application method, and the one most recently introduced, is dry powder electrostatic application of all-fritted coatings to conductive substrates. This technique involves charging individual coating particles at a high voltage and then spraying them towards the substrate surface. Charging of particles is accomplished by encapsulating the coating material with an organic silane. It is then suspended in clean compressed air in a fluidized bed container [24]. The fluidized powder is siphoned and propelled through powder feed tubes to special electrostatic powder guns for low-pressure application. The powder carries a potential of up to 100 kV, which causes it to seek out and attach itself to the grounded workpiece. Capital costs of this process are substantial, but operating costs are reduced through elimination of slurry preparation and drying of the ware.

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10

Epoxy Resins in Coatings

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PREFACE

THE AUTHOR COLLABORATED WITH RONALD Bauer and Edward Marx in preparing this chapter for the previous or 14th edition of this manual. This revised edition includes expanded descriptions of epoxy materials and curing agents currently used in coating formulations. Epoxy resins are versatile materials that are used in a wide variety of coatings. In the interests of brevity, this chapter focuses on the epoxy resins, curing agents, and coating types that are commercially most important and account for the largest usage of epoxy resins. As an example, epoxy coating technologies, which reduce volatile organic compound (VOC) emissions, have grown rapidly. Waterborne, high solids, and powder epoxy coatings account for about 80 % of all epoxy resin used in coatings. On the other hand, low solids epoxy coatings have declined significantly in importance and account for less than 15 % of epoxy resin usage. So this chapter naturally focuses on the low VOC technologies. Similarly, epoxy ester coatings were described in the previous edition, but have declined in importance, so they are not discussed here. Also, epoxy coatings are formulated with other materials described in this manual, and attempts have been made to reference those chapters where appropriate.

INTRODUCTION

Generically, epoxy resins can be characterized as a group of oligomeric materials that contain one or more epoxy (oxirane) groups per molecule. Almost all commercially significant epoxy functional materials are derived by reacting epichlorohydrin with various materials containing groups with active hydrogen (such as phenolic hydroxyl, aliphatic hydroxyl, carboxylic acid, or amine). The initial reaction yields a chlorohydrin, which is subsequently dehydrochlorinated to yield the glycidyl (epoxy) group. One exception to this generalization is the class of cycloaliphatic epoxy resins discussed in Chapter 16, Miscellaneous Materials and Coatings, in this manual. Another exception is represented by epoxy functional acrylic resins that are made by copolymerizing various acrylic monomers with glycidyl methacrylate or similar epoxy functional acrylic monomers.

Epoxy resins based on bisphenol A (BPA) and epichlorohydrin are commercially the most important epoxy resins by a very wide margin. These resins have become technologically important materials that find extensive application in high-performance coatings, adhesives, and reinforced composites. Almost since their commercial introduction in about 1947 [1], epoxy resin systems have been used in protective coatings. Historically, protective coatings were the largest single end use for epoxy resins. Although in recent years the non-coating applications of epoxy resin have been growing, coatings still represent about half of the annual epoxy resin usage.

The principal components of any epoxy coating system are the epoxy resin and the curing agent or hardener. Epoxy resins are reactive intermediates that can be liquid or solid, and they are converted into the final coating by reaction with curing agents (hardeners). Curing agents function by reacting with specific groups in the epoxy resin molecule to give a three-dimensional, infusible polymer network. Although the resin and curing agent are common to all epoxy coatings, other materials are incorporated to achieve the desired rheological characteristics, cure speed, appearance, and film performance.

BPA EPOXY RESINS

BPA-based epoxy resins were developed independently by Pierre Castan in Switzerland and by Sylvan Greenlee in the United States during the 1930s and 1940s [1–3]. The generalized structure for these resins is given in Fig. 1. In commercial products, the n value ranges from 0 to about 60. Table 1 displays a range of typical epoxy resins that are commercially available, along with their properties and applications. As n increases, the epoxy equivalent weight increases, as does the number of hydroxyl groups. Thus epoxy resins with low n values are normally cured by reaction of the epoxy group, whereas those resins with higher n values are cured by reaction of the hydroxyl functionality. The highest molecular weight BPA epoxy resins, or phenoxy resins, are described in Chapter 16, Miscellaneous Materials and Coatings, in this manual.

Resins having n values less than 1 are viscous liquids; they are used mainly in two-pack, ambient-temperature cure coatings, as well as in electrical castings, flooring, electrical laminates, and fiber-reinforced composites. Resins having n values in the range of about 1–2 are low melting solids that are used in solution in two-pack, ambient-temperature cure coatings. Resins having n values in the range of about 2–6 are solids, which do not sinter at room temperature. They are predominately used in powder coatings. All of these applications are cured through the epoxy groups. The higher n value resins, particularly those with $n > 10$, are normally used in solution and find their greatest application in heat-cured coatings. In these resins, the concentration of epoxy groups is low, and so they are cured with materials that react with the hydroxyl groups along the backbone.

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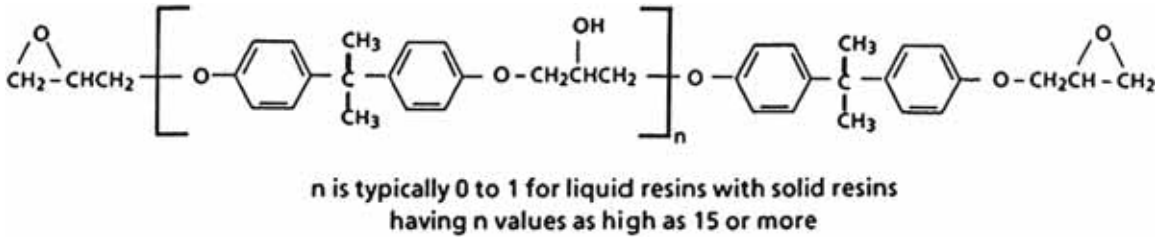

Fig. 1—Idealized structure of a bisphenol epoxy resin.

Coatings based on BPA epoxy resin offer a unique combination of performance characteristics and are used in a wide variety of technologically important end uses. These characteristics include exceptional adhesion and corrosion resistance, excellent chemical resistance, low shrinkage, high strength, good heat resistance, toughness, and excellent electrical properties. Because of the adhesion and corrosion resistance, epoxy resins have been used in corrosion-resistant primers and coatings since epoxy resins were first commercialized. In addition, the excellent chemical resistance has resulted in the formulation of epoxy coatings that provide outstanding protection against severe corrosive environments. They are used extensively in coatings for refineries, chemical plants, and marine equipment, such as ships and offshore platforms. Other important applications where epoxy resin coatings are used almost exclusively because of the corrosion protection they afford include automotive, aircraft, and appliance primers as well as coatings for both the inside and outside of pipelines.

The chemical and corrosion resistance resulted in the development of BPA epoxy coatings used for the interior linings of beer and beverage cans, the interior linings of food cans, and for chemical-resistant linings of pails and drums. Guidelines for the safe use of coatings based on BPA epoxy resins for direct food contact have been established by the U.S. Food and Drug Administration [4]. These coatings are used not only to protect the metal of the container from corrosion, but also to protect the flavor of the contents, which can be affected by direct contact with metal.

The one significant weakness of coatings based on BPA epoxy resins is that they are not resistant to ultraviolet (UV) exposure. When exposed to direct sunlight, they tend to yellow and chalk. The aromatic structure of the BPA backbone absorbs the UV energy and the backbone degrades. Thus, BPA epoxy resins are typically used as primers, which are subsequently top coated with coatings that are resistant to UV degradation. This strategy takes advantage of the excellent corrosion resistance of the epoxy primer, while protecting it from its one weakness.

OTHER EPOXY MATERIALS USED IN COATINGS

Although BPA-based epoxy resins are far and away the largest volume commercial epoxy resins, other epoxy functional materials are also important. The diglycidyl ether of bisphenol F is a low viscosity liquid epoxy resin that it useful in high solids or 100 % solids coatings or floorings. For comparison, the viscosity of the standard commercial grade of BPA liquid resin is about 120–140 Poises at 25°C, while that for a typical BPF liquid resin is about 25–45 Poises. This advantage over BPA resins diminishes at higher molecular weights so BPF solids resins are not generally used.

Epoxy phenol novolacs, epoxy alkylphenol novolacs (i.e., epoxy cresol novolacs), or epoxy BPA novolacs are multifunctional epoxy resins that are used to increase cross-link density and subsequently increase the chemical resistance, hardness, heat deflection temperature, etc. for epoxy coatings and other applications. These

TABLE 1—Typical properties of BPA-based epoxy resins

Average Molecular Weight	Average EEW[a]	Approximate Average Value of *n*	Viscosity (P @ 25°C)	Softening Point (°C)[b]	Applications
350	182	0	80	. . .	Solventless and solvent-borne ambient cure coatings, electrical encapsulation, flooring, and filament winding
380	188	0.2	140	. . .	Solvent-borne, ambient cure coatings
600	310	1	Semi-solid	40	Solvent-borne, ambient cure coatings
900	475	2	Solid	70	Solvent-borne, ambient cure coatings
1400	900	4	Solid	100	Powder coatings
2900	1850	10	Solid	130	Heat cured, solvent-borne coatings for cans, drums, primers, etc.
3750	3050	13	Solid	150	Heat cured, solvent-borne coatings for cans, drums, primers, etc.

[a] EEW—epoxide equivalent weight, grams of resin providing 1 mole of epoxide. Also referred to as WPE (weight per epoxide) and EMM (epoxy molar mass). All three terms are interchangeable.
[b] Softening point by Duran's mercury method (ASTM D1763).

resins have epoxy functionality in the range of 2–8. (By comparison, BPA resins and BPF resins have typical functionality of about 2.) As an example, epoxy novolac resins are used in combination with BPA resins in powder coating formulations to enhance chemical and corrosion resistance.

Another multifunctional resin that may be used is the glycidated tetraphenol of ethane. This has a nominal epoxy functionality of 4. As with the epoxy novolacs, it can be used along with BPA epoxy resins to improve chemical and corrosion resistance.

Brominated epoxy resins can be prepared from epichlorohydrin and tetrabromobisphenol A, or from liquid BPA epoxy resin and tetrabromobisphenol A. These have a broad use in electrical laminating (i.e., circuit board) applications. The bromine content makes them suitable for flame retardant coatings.

Epoxy resins such as the polyglycidyl ether of castor oil are multifunctional resins that are used with BPA epoxy resins to improve the flexibility and water resistance.

A whole series of epoxy functional materials are used as reactive diluents and modifiers in epoxy coatings. Monofunctional epoxies are typically used as reactive diluents in high solids or 100 % solids, two-pack ambient cure coatings. One group of monofunctional epoxies are made by reacting epichlorohydrin with alcohols. One widely used example is the glycidyl ether of mixed alkyl C_{12}–C_{14} alcohols. Another commercially important example is the glycidyl ether of mixed alkyl C_8–C_{10} alcohols. The glycidyl ether of *n*-butanol gives the best viscosity reduction of any reactive diluent in BPA epoxy systems and is also important commercially. Another group of monofunctional epoxies are made by reacting epichlorohydrin with phenol or alkylphenols. The most widely used example is *o*-cresyl glycidyl ether. Other examples include phenyl glycidyl ether, *p*-tert-butylphenyl glycidyl ether, and nonylphenyl glycidyl ether. A third type of monofunctional epoxy is the glycidyl ester of neodecanoic acid.

Monofunctional epoxies of this type are useful as reactive diluents to reduce viscosity and VOC. However, because they are monofunctional, they also decrease crosslink density of the cured coating, generally resulting in some loss of chemical resistance, corrosion resistance, hardness, etc. So the coatings formulator must carefully balance the need for low viscosity with other coating performance requirements.

A group of multifunctional epoxies are available to serve as reactive diluents, but still maintain functionality and cured film properties. These are generally prepared by reacting epichlorohydrin with polyols. Examples include neopentyl glycol diglycidyl ether, butanediol diglycidly ether, cyclohexanedimethanol diglycidyl ether, trimethylolpropane triglycidyl ether, and trimethylolethane triglycidyl ether.

Resorcinol diglycidyl ether is an effective difunctional reactive diluent. Unfortunately, it is a strong skin irritant and sensitizer and can cause severe allergic reactions. Therefore, relative to other reactive diluents, it is difficult to handle safely.

Another specialty epoxy resin is made by reacting epichlorohydrin with hydrogenated BPA. Since this material is saturated, rather than aromatic, it has UV resistance superior to that for BPA epoxy resins.

CURING AGENTS

Epoxy resins are reactive intermediates composed of mixtures of oligomeric materials containing one or more epoxy groups per molecule. To convert epoxy resins into useful products, they must be cross-linked or "cured" into a three-dimensional polymer network. Cross-linking agents, or curing agents as they are generally called, function by reaction with or cause the reaction of epoxide or hydroxyl groups in the epoxy resin. The number of curing agents that have been developed over the years for epoxy resins is overwhelming. Selection of the curing agent is as important as that of the base resin; it is dependent on the performance requirements of the film and the constraints dictated by the specific method of application.

The most widely used types of curing agents employed in epoxy resin coatings are the amine-functional materials for ambient-cure coatings, dicyandiamide or acid-functional polyesters for powder coatings, and amino resins (see Chapter 8, Amino Resins, in this manual) or phenolic resole resins (see Chapter 11, Phenolics, in this manual) for heat-cured liquid coatings.

The principal amine-functional curing agents used in two-pack, ambient-cure epoxy coatings are polyamides (see Chapter 12, Polyamides, in this manual). Amidoamines, aliphatic amines, and epoxy-amine adducts are also used. Specialty amine curing agents include phenalkamines, cycloaliphatic amines, and ketimines. These materials cure epoxy resins by reaction of the amine with the epoxy groups. Typical aliphatic amines used include diethylenetriamine (DETA), triethylenetetramine (TETA), and tetraethylenepentamine. Aliphatic amines such as DETA and TETA can be pre-reacted with low molecular weight epoxy resins to make epoxy-amine adducts that are very useful as epoxy curing agents. Amidoamines are made by reacting fatty acids with aliphatic amines (i.e., DETAor TETA).

Polyamides are made by reacting dimerized fatty acids with aliphatic amines (i.e., DETA or TETA). More pounds of polyamide curing agents are consumed annually in the United States than any other type of epoxy resin curing agent. Polyamide cured epoxy coatings develop superior adhesion to moist and poorly prepared surfaces, and they provide a high degree of corrosion resistance. Like epoxy resins, polyamides are also mixtures of oligomers. Thus, a range of polyamides that vary in viscosity, amine equivalent weight, and reactivity is available. Polyamide cured coatings exhibit somewhat better retention of flexibility and impact resistance on aging than polyamine adducts. Although resistance to solvents and acids is not quite as good as with other types of amine curing agents, polyamides are adequate and cost-effective for most applications where amine cure epoxy coatings are used.

Typical cycloaliphatic amines include isophorone diamine, bis(*p*-aminocyclohexyl)methane, and 1,2-diaminocyclohexane.

Ketones add reversibly to primary amines with the loss of water to give ketimines. The ketimines obtained from the typical polyamine curing agents have rather low volatility compared to the precursor polyamine. Ketimine curing agents can be considered blocked polyamines, which in the presence of water hydrolyze to produce a ketone and a polyamine. These ketimines react at a practical rate of cure under ambient conditions. Atmospheric moisture, which is absorbed during and following application of the coating,

serves as the source of water required to activate the curing agent. Ketimine curing agents are similar in behavior to the aliphatic amine polyamines and amine adducts in rate of cure and performance of cured films, but they provide much longer pot lives.

Epoxy resins are formulated with acid-functional polyesters to make hybrid powder coatings. Catalysts are often used to facilitate this reaction. The ratio of epoxy to polyester is typically in the range from 50:50 to 30:70. When the powder coating is baked, the acid groups on the polyester react with the epoxy groups to make a cured polymer matrix. The principal curing agent for epoxy powder coatings is dicyandiamide. At elevated temperature, this reacts with the epoxy groups to cure the coating. Catalysts such as imidazoles or epoxy-imidazole adducts are commonly used to speed up this reaction. Strong bases such as imidazole-type catalysts can also be used alone as curatives. They cause homopoly-merization of epoxy groups as a means of cure. Specialty curing agents for powder coatings include phenolic-functional polyethers, phenolic resoles (see Chapter 11, Phenolics), and anhydrides.

Baked liquid coatings employ high molecular weight epoxy resins. These resins contain relatively low epoxide functionality and relatively high hydroxyl functionality. These are cured through the hydroxyl groups with melamine-formaldehyde resins and urea-formaldehyde resins (see Chapter 8, Amino Resins), as well as phenol-formaldehyde resins (see Chapter 11, Phenolics). Strong acids, such as phosphoric acid or p-toluene sulfonic acid, are used as catalysts. Strong organic acids blocked with volatile amines can also be used to achieve enhanced package stability. The acid-amine salt is non-catalytic. However, at elevated temperature, the amine volatilizes, leaving the acid to catalyze the curing reaction.

EPOXY COATINGS

The four coating types that account for the highest usage of epoxy resins are powder coatings, high solids solvent-borne coatings, electrodeposition coatings, and waterborne coatings. These coating types account for over three quarters of epoxy resin usage in coatings. Low solids, solvent-borne epoxy coatings are clearly declining in volume. This is not surprising, as a major driver for change in the coatings industry is the reduction of VOCs in coatings. These four coating types are used to reduce VOC emissions.

EPOXY POWDER COATINGS

Powder coatings are produced by melt blending homogenous dispersions of solid resins, curing agents, pigments, fillers, and various additives. The dispersion is solidified by cooling, ground into a finely divided powder form, and classified by particle size for subsequent use. The resultant powder is normally electrostatically deposited onto grounded substrates and, through the application of heat, converted into very high performance thermoset films. The process of applying coating powders allows nearly 100 % powder utilization and evolves almost no VOCs.

The 1970s volatiles regulations and energy concerns raised interest in powder coating technology. The real sustaining driving forces for growth, however, have been improvements in powder coating raw materials, formulations, manufacturing technology, and application equipment. The advantages for the use of powder coatings can best be summed up in the "Four E's," used by the Powder Coating Institute: (1) Excellence of finish, (2) Economy in use, (3) Energy efficiency, and (4) Environmental acceptability. The Clean Air Act, as amended in 1990, has contributed to even greater interest in the use of powder coatings to meet more stringent volatile organic requirements. Powder coatings comprise one of the fastest growing areas of coatings technology. Current growth rate for epoxy powder coatings is approximately 6 % versus about 2 %–4 % for other coating types.

The unique characteristics of solid epoxy resins account for their choice by formulators for use in powder coatings applications. BPA-based epoxides with equivalent weights greater than about 650 are non-sintering and friable. They have relatively low melt viscosity and high reactivity via the terminal oxirane functionality. The addition reaction with amines, phenolics, or carboxylic acid functional curatives allows a wide range of formulations. The primary limitations for BPA-based epoxy resins in powder coatings are yellowing and loss of gloss that occur when these coatings are exposed to exterior weathering conditions.

Powder coatings are broadly divided into either "functional" or "decorative" uses. Functional coatings are normally applied at film thicknesses greater than about 3 mils and are expected to withstand some rather severe service. Examples of functional uses are coatings for exterior and interior pipe, rebar, and various electrical devices. Although decorative powder coatings are functional, these are normally used at a film thickness of 3 mils or less and are not expected to perform significantly better than baked films derived from "wet" coatings. Some examples of decorative uses are coatings for appliances, furniture, and under hood automotive parts.

HIGH SOLIDS, SOLVENT-BORNE COATINGS

Industrial maintenance and marine paints account for nearly all of these coatings. These are two-package, ambient cure coatings. A two-package coating is comprised of the epoxy component and the curing agent, which are packaged separately and often in volume ratios of 2 to 1 or 4 to 1 of epoxy component to curing agent. Two-package epoxy coatings are mixed just prior to application and are characterized by a limited working life or pot life after the resin and curing agent components are mixed. Commercial systems will have pot lives of a few hours to a couple of days, with typical working times of about 4–8 h.

Historically, maintenance and marine coatings were formulated with solid epoxy resins (average n approximately 2) in solution, cured with high molecular weight polyamides. These gave excellent corrosion protection, but were high in VOC (about 4 lb/gal, or more). In order to achieve lower VOC and higher solids, formulations have shifted to using lower molecular weight BPA epoxy resins (n = 0.2) or BPF liquid epoxy resin with lower viscosity curing agents, such as amidoamines, aliphatic amines, phenalkamines, cycloaliphatic amines, and ketimines. By using lower viscosity resins and curing agents, higher solids systems can be achieved. Another strategy to reduce VOC has been to formulate coatings with some exempt solvents, such as acetone, methyl acetate, *t*-butyl acetate, and *p*-chlorobenzotrifluoride.

ELECTRODEPOSITION COATINGS

Epoxy resin electrodeposition coatings are waterborne coatings formulated from either anionic or cationic epoxy

resin polymers. The part to be coated is dipped into the electrodeposition bath, and an appropriate electrical charge is applied, causing the coating to deposit onto the part. The part is then removed from the bath, rinsed, and baked to cure the coating. In the United States, epoxy-based electrodeposition coatings account for over 90 % of all electrodeposition coatings. Epoxy-based cathodic electrodeposition (CED) automotive primers dominate this application, accounting for over 70 % of all electrodeposition coatings. Over 40 million pounds of epoxy resin are used in the United States in CED automotive primers, making this one of the largest single end uses for epoxy resins in coatings. Virtually every automobile made in the United States, Europe, and Japan is primed with an epoxy CED primer. CED primers are used because they afford exceptional corrosion protection and because they are deposited uniformly to all areas of the automobile, even in areas that would be inaccessible to other coating application methods such as spray. Because of their major importance, the remainder of this discussion will deal with CED automotive primers.

The preparation of CED [5] coatings generally begins by reacting a BPA-based liquid epoxy with BPA to give an epoxy resin with an epoxy equivalent weight in the range of 500–1000. This epoxy resin may then be reacted with a flexibilizing diol. This diol can be an aliphatic diol or a polyether diol. The principal requirement is that the diol contain primary hydroxyl functionality. These primary hydroxyls are reacted with the epoxy groups in the presence of a suitable catalyst (e.g., a tertiary amine) to form ether linkages between the epoxy and the flexibilizing diol. At this point, the resin may have an epoxy equivalent weight in the range of 1000–1500. The remaining epoxy functionality is then reacted with amines. Generally, secondary amines are chosen to minimize further chain extension. One favored method to accomplish this is to use a diketimine of diethylenetriamine. During coating preparation, the ketimine groups decompose to give primary amines. These primary amines are fairly basic, resulting in stable dispersions at a relatively high bath *p*H (*p*H > 6). At this point, the CED resin preparation is complete. In practice, specialized CED resins are used to make the pigment grind pastes. These are developed to efficiently make stable pigment dispersions, which retain good stability in the CED coating bath.

Curing agents used are generally blocked isocyanates. These are chosen to be stable and unreactive in the coatings bath, but to unblock and cure the coating at baking temperature. An example of such a curing agent would be the reaction product of 3 mol of toluene diisocyanate with 1 mol of trimethylolpropane. This is then reacted with 3 mol of a suitable blocking agent. Historically, 2-ethyl-1-hexanol has been used. However, much research has been done in recent years to find blocking agents that unblock at lower temperatures, permitting lower bake temperatures and energy savings. One example of many is provided in Ref. [6], where oximes are used as blocking agents. Catalysts such as tin or lead salts are generally used to facilitate unblocking and coating cure. Recent formulation efforts have eliminated lead catalysts. One example of many is provided in Ref. [7]. The coating is prepared by blending the resin with pigment paste, curing agent, catalysts, additives, and solvents. A low-molecular-weight organic acid, such as lactic or acetic acid, is then added to the mixture to make ammonium salts with the amine groups in the resin. This mixture is then dispersed in water to make the CED coating. Solvents may be required in the preparation of the CED resin or other components. In order to reduce the VOC content of the finished coating, it is usually subjected to a vacuum stripping step, which can reduce VOC to less than 0.7 lb/gal. When the automobile is dipped into the CED bath, a negative charge is applied to it (making it the cathode) relative to counter electrodes in the bath. Electrolysis of water occurs, forming hydroxide ions in the immediate vicinity of the automobile surface. These hydroxide ions react with the ammonium ion groups in the resin near the surface, regenerating the neutral amine groups and causing the coating to be deposited onto the surface. In this way, a uniform film is applied to the entire conductive surface of the automobile. The automobile is then removed from the bath, rinsed, and baked.

WATERBORNE COATINGS

It was determined early on that epoxy coatings are safe and highly effective linings for food and beverage cans. Historically, these coatings were solvent borne. Recently, there has been concern about low molecular weight materials that may be extractable from can linings, such as BPA, BPA diglycidyl ether (BADGE), or derivatives of BADGE. Although research is ongoing, the current consensus is that epoxy-based can linings are safe and effective [8–10].

The need to reduce VOC has driven the development of waterborne food and beverage can linings [11]. Waterborne linings for beer and beverage cans are used exclusively and are an important use for epoxy resins. This is not surprising when one considers that over 100 billion beer and beverage cans are manufactured in the United States every year. These coatings are based on high-molecular-weight epoxy resins (average n of about 10–13), onto which are grafted acrylic terpolymers (i.e., styrene/methacrylic acid/ethyl acrylate). These epoxy/acrylic graft polymers are neutralized with base, such as dimethylethanolamine, to give a resin easily dispersible in water. The dispersed resin may be cured with an amino resin (see Chapter 8, Amino Resins) to give coatings with properties that make them suitable for beer and beverage containers.

Food can linings are typically solvent-borne high-molecular-weight epoxy resins (average n of about 10–13), which are cured with amino resins (see Chapter 8, Amino Resins) or phenolic resins (see Chapter 11, Phenolics). Generally, food can linings require more chemical resistance than beer and beverage cans. Waterborne epoxy food can linings have been developed, which are based on similar technology to the beer and beverage can linings. These coatings are being used, and are growing in share of the food can lining market.

Waterborne two-pack ambient-cure coatings comprise a small but growing end use for epoxy resin. BPA-based epoxy resins are rather hydrophobic and are not easily dispersed in water. Initial waterborne epoxy resins were modified with large amounts of surfactants to form stable dispersions. But the surfactant made subsequent coatings relatively hydrophilic, resulting in loss of corrosion resistance when applied to metallic substrates. These early waterborne epoxy coatings performed well when applied to non-metallic (e.g., cementitious) substrates. One solution to this problem was to make aqueous epoxy dispersions by using nitroparaffin cosolvents in place of surfactants [12–14]. The nitroparaffin

evaporates from the coating after application and does not affect the hydrophobicity or performance of the coating. This approach has been used to formulate waterborne aerospace coatings. Advances in surfactant technology and in dispersion technology have resulted in waterborne epoxy resins and curing agents, which give excellent performance on metallic substrates [15–17]. The need to lower VOC is encouraging the use of these systems in industrial maintenance, aerospace, and railroad coatings.

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Phenolics*

John D. Fisher[1]

HISTORY

PHENOLIC RESINS, INITIALLY COMMERCIALIZED in 1909, were the first completely synthetic materials of the burgeoning plastics business. The expansion of several new technologies of the time, namely the electrical, communications, and automotive industries, all required and depended on new materials that had better electrical insulating properties, higher heat resistance, and improved resistance to chemicals, acids, oils, and moisture. The heat-reactive or "resole" resins, developed by Dr. Leo H. Baekeland [1], were formulated into blends that were convenient for mass production of compression molded parts that satisfied these requirements. Improved and new items, such as coil supports, commutators, distributor heads, telephone sets, vacuum tube bases, radio parts, and electrical switches, all blossomed onto the market within a few years.

FIRST PHENOLIC RESIN-BASED COATINGS

Concurrent with the above developments, the non-heat-reactive phenolic resins or "novolak" resins were prepared as a hoped-for substitute for shellac. These resins were not as resilient as shellac and, when used alone, were not successful in coatings. However, combined with a formaldehyde donor such as hexamethylene tetramine, the novolaks could be compounded into another family of thermosetting molding materials, which found early use in phonograph records.

While novolaks had to wait for success in coatings, the resole resins in alcohol solutions by 1911 were found to form excellent films when cross-linked by baking [2]. These coatings, still in wide use today, are hard and glass-like and have excellent resistance to chemicals, acids, water, and solvents. Early applications included protective coatings for brass beds as well as other hardware items. These solution resins also initiated the manufacture of laminates, which were used to make early radio circuit boards and, later, printed circuit boards.

PHENOLIC RESINS IN COATINGS

Coatings Based on Phenolic Resins

The early coatings based on phenolic resoles developed over time into a family of products used as protective coatings. Coatings based on similar technology are still found in a variety of applications. Chemically resistant protective coatings for stationary and mobile tanks, drums, and pipes are produced based on phenolic resole solutions that are applied and then cured in place with the application of heat. Regulations limiting the release of volatile organic compounds led to the development of higher solids versions and waterborne versions in the 1970s and 1980s, but other than these changes the products are essentially the same as the products developed many years ago. Coatings of this nature possess excellent chemical resistance, good high temperature performance, high hardness, and hence good abrasion resistance and good specific adhesion to metal substrates. They suffer from low flexibility and deterioration upon prolonged exposure to UV light. Their use is limited to applications with rigid substrates and applications where UV light exposure will not be a concern.

One innovation by scientists at the General Electric Company in the early 1950s led to the development of phenolic resins modified by reaction with allyl chloride [3–8]. Coatings produced from phenolic resins that use this technology have even greater chemical resistance than typical phenolic resins due to the replacement of the mildly acidic proton of the aromatic hydroxyl group with the allyl group. This yields a coating that is less susceptible to reaction with strong bases than a typical phenolic resin-based coating and hence has higher chemical resistance. However, this modification does not significantly help the flexibility of the coating (Fig. 1).

Coatings Based on Polymer Alloys with Phenolic Resins

As noted, coatings based wholly or primarily on phenolic resins possess some properties that make them desirable coatings, but they suffer from being extremely brittle. While they are suitable for applications where little or no flexibility is required, the lack of flexibility precludes them from use in many applications where this property is required or desired. Use of phenolic resin technology in a wider variety of applications had to wait for further developments. This came in two ways. The first was modification of the phenolic resins to achieve compatibility with traditional resins used in coating applications. The second was the development of other synthetic resin technology for use in the coatings market.

One of the traditional coating technologies is the use of drying oils of various types as the principal vehicle to

*DEFINITION: a polymeric, resinous reaction product of a phenol with an aldehyde. Said products may be used alone or in formulations with other polymers to produce useful coatings.

[1] *Schenectady International, Inc., PO Box 202, Pattersonville, NY 12137.*

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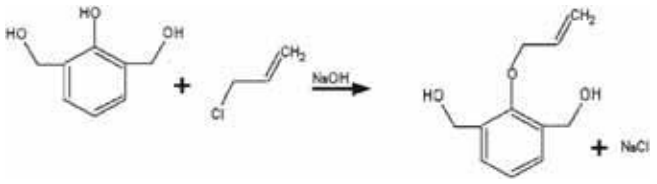

Fig. 1—Modification of resoles with allyl chloride.

carry and bind pigment to a variety of substrates. Over time it was found that "cooking" the oils with various other ingredients improved the performance of the coating made from the oil. This technology developed into what are now known as alkyd resins, which are essentially oil modified polyester resins. Modification of alkyd resins with phenolic resins held the promise of improving performance of the alkyd resin-based coatings, but the compatibility of early phenolic resins with the oil-based alkyd resins was not good and found limited application. Once technology advanced to the production of phenolic resins from alkylated phenolic monomers, the higher aliphatic content provided by the alkylated phenolic monomers greatly improved the compatibility with the oil-based alkyd resins. A variety of improvements in performance was observed for the phenolic resin modified alkyds, including greater abrasion resistance, better high temperature performance, improved chemical resistance, and improved adhesion to metallic substrates. Early phenolic resin modified alkyds were made from resole resins based on alkylated phenolic monomers that had to be cooked into the alkyd resins during manufacture of the alkyd resins. Later, higher molecular weight phenolic resins that could be "cold cut" into the alkyd resins were developed. Both technologies are still in use today [2]. The use of alkylated phenolic monomers to produce phenolic resins with improved compatibility with other coating ingredients led to a wide range of new products that took advantage of the improved heat resistance and hardness of the phenolic resins and the good film-forming properties of the drying oils and the alkyd resins derived from them. One of the areas that depended strongly on this developing technology was electrical insulation coatings where phenolic resins were alloyed with other coating resins to upgrade the performance of both primary and secondary electrical insulation coatings where products with much better performance allowed manufacturers to build electrical motors with improved performance and durability [9].

The development of other new synthetic polymers with potential applications in the coatings industry also created new opportunities for the use of phenolic resins in a wider range of coating applications. Particularly significant was the development of epoxy resins. When cured, epoxy resins exhibit a level of flexibility far higher than the phenolic resins. Also, the similarity in structure between phenolic resins and the predominant commercial epoxy resins makes them compatible across a wide range of blending ratios giving the coatings formulator the opportunity to balance the flexibility of the epoxy resin with the chemical resistance of the phenolic resin for each given application. Further, the aromatic hydroxyl group present throughout the phenolic resin structure is reactive with the oxirane group characteristic of the epoxy resins. When fully reacted the blend of the two polymers becomes one homogeneous film.

Use of phenolic/epoxy alloys in coatings has been employed in a variety of coating applications. One area where they have found wide acceptance is the formulation of coatings for metals, particularly in the packaging coatings industry. In this industry, the ability of phenolic resole/epoxy alloys to provide very good chemical resistance allows packaging of food stuffs and beverages in metal cans coated with very thin film weight coating. These coatings take advantage both of the reaction between the epoxy and the phenolic resin as well as the homopolymerization of the phenolic resole, both of which occur when the coating is baked onto the substrate. Phenolic resole/epoxy alloys are also used in wash or pretreatment coatings. In these applications, a very dilute coating is applied during the wash process and in preparation for painting for the purpose of preventing flash rust formation and/or to improve adhesion of the permanent coating to the substrate.

Phenolic novolak/epoxy alloys have also found use in coating applications. Powder coating formulations take advantage of the relatively low melt viscosity, the good friability, and film forming of the phenolic resin. In addition, the thermally induced reaction of the phenolic hydroxyl with the oxirane encourages the use of the novolak resins as cross-linkers for the epoxy resins to make chemically resistant powder coatings. This addition reaction has the added benefit that no volatiles need to be released, which is especially important in powder coatings where no solvent is present to facilitate the release of volatile components from the film without pinhole formation (Fig. 2).

In addition to being used in alloys to produce epoxy and alkyd based coatings, phenolic resins have proved useful as modifiers at low levels for a variety of other synthetic resins for coating applications. Some examples are the use of phenolic resins as adhesion promoters for a variety of synthetic polymer-based coatings, These include SBR, NBR, and poly-(vinyl chloride) resins, to name a few. In addition the resole phenolic resins are often added as a cross-linking agent to formulations based on polyvinyl butylral or polyvinyl alcohol resins.

PHENOLIC RESINS AS PHOTO-IMAGABLE COATING

Phenolic novolak resins have also found application in the area of photo-imagable coatings. For this application, a coating of phenolic novolak mixed with a photo-sensitive base is applied to a substrate. The coated article is partially exposed to an image and the photo-sensitive base forms a salt with the phenolic novolak where the light activates the base. The phenolic resin salt has a distinct solubility difference from the phenolic novolak that has not reacted with base and so may be selectively removed, exposing the substrate below. The article is then able to be further processed and the exposed portion of the substrate may be selectively reacted while the unexposed substrate is protected by the remaining phenolic resin coating. This technology is used commercially on silicone wafers to make semiconductor chips and on aluminum plates to make planographic printing plates.

PHENOLIC RESIN CHEMISTRY

The reaction between phenols and aldehydes to produce resinous products was difficult to understand in the early years because many of the products were insoluble or

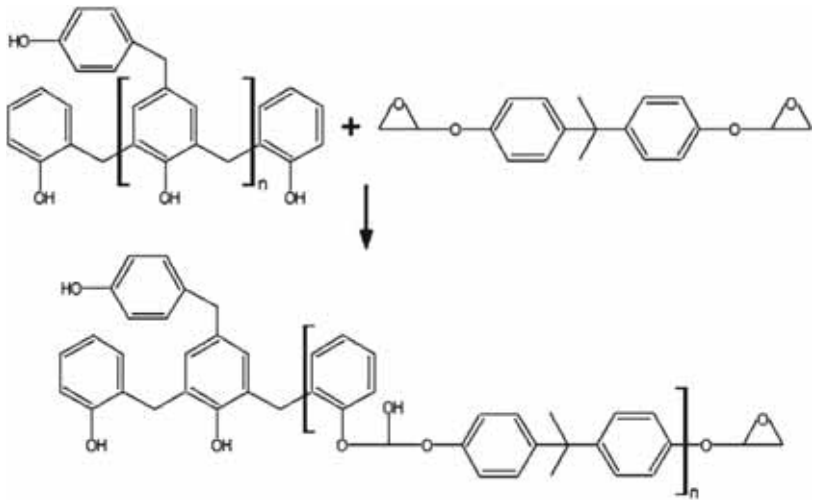

Fig. 2—Reaction between epoxy resin and phenolic resin.

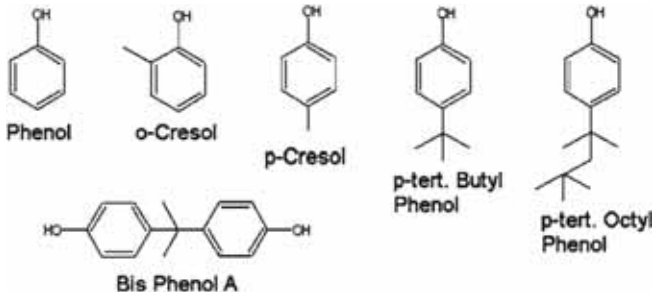

Fig. 3—Typical phenolic starting materials.

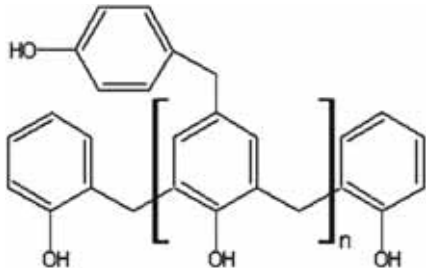

Fig. 4—Typical phenolic novolak structure.

infusible. With the advent of modern analytical tools, the chemistry of the reactions has been more fully defined by various workers. [10–12].

Raw Materials

The commercially important phenols used in coatings resins are shown in Fig. 3. While phenol is the most common, the substituted phenols are also used to vary the solubility, reactivity, and physical properties of resins. The cresols, alkylated phenols and bisphenol-A, are widely employed in various coating applications. Phenolic resins based on other phenolic monomers are used but have limited or specialty uses.

Phenol has three ring positions that are active for reaction with aldehydes; the two and six carbon atoms (ortho) and the four position (para). Phenols with substitution in the above positions have lower functionalities and are frequently used to modify resin properties.

The aldehyde co-reactant of choice for reaction with the phenols is formaldehyde, the most reactive of those commercially available. Formaldehyde is a gas but is conveniently handled as an aqueous solution (formalin), as an alcohol solution (formcel), or in a solid polymeric form known as paraform. Formaldehyde in aqueous solution exists as hydrated glycols or low-molecular-weight glycol ethers, which are easily broken down into formaldehyde under normal reaction conditions. Alternative aldehydes and other bridging agents are employed in the production of phenolic resin, but these alternatives comprise a minute minority of the commercially available phenolic resins.

Acid Catalysis

Acid-catalyzed phenol-formaldehyde reaction proceeds through an unstable addition intermediate to form condensed, methylene-linked phenolic rings (Fig. 4). Acid catalyzed phenol-formaldehyde oligomers and polymers are generally referred to as "novolaks." Novolaks are thermoplastic and require the addition of other materials to further polymerize. When phenol is used, highly branched novolaks are obtained. However, when substituted phenols are used, the functionality of the phenolic monomer is reduced to two and linear resins or cyclic calixarenes are formed [13]. Most novolak resins are produced as solids but are readily soluble in a variety of solvents.

Base Catalysis

The use of base to catalyze the reaction between phenol and formaldehyde produces initial reaction products such as the methylolated phenols, as shown in Fig. 5. Further reaction causes the methylol groups to condense with other ring positions to form a methylene link or to etherify with other alcohol groups to form dibenzyl ether links (Fig. 6). Base catalyzed phenol-formaldehyde oligomers and polymers are

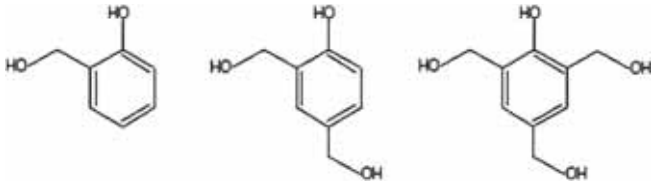

Fig. 5—Methylolated phenols.

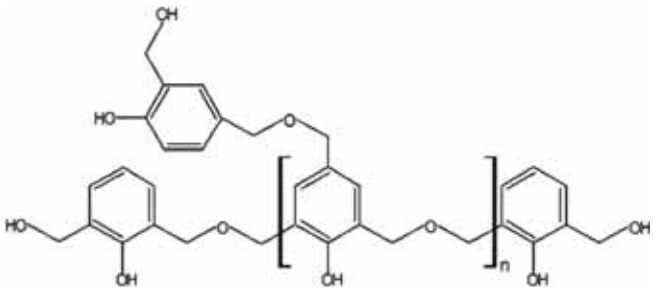

Fig. 6—Typical phenolic resole structure.

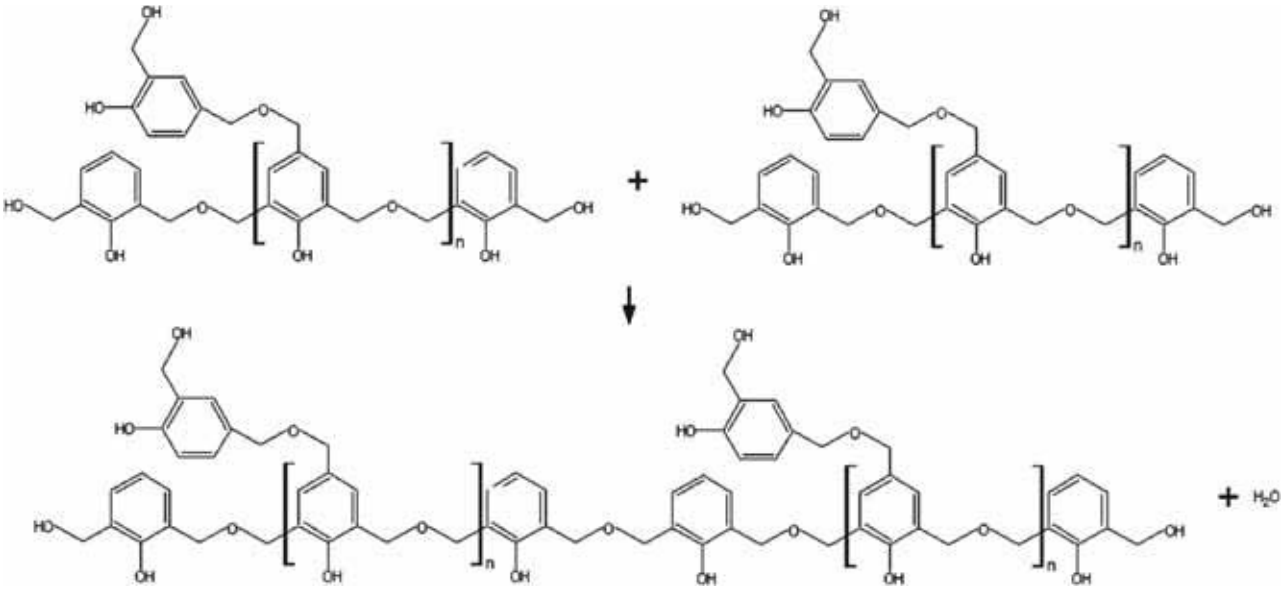

Fig. 7—Homopolymerization of phenolic resole resins.

generally referred to as "resoles." Unlike novolaks, resoles are thermosetting and will further polymerize upon heating (Fig. 7). Additional reaction raises the molecular weight of resoles. As with novolaks, phenol is poly-functional towards formaldehyde and will form highly branched polymers. These highly branched polymers will ultimately reach a highly cross-linked "gelled" state with continued exposure to heat. Phenolic resins produced with substituted phenols will have lower functionality if the reactive ortho or para-sites are blocked. Resins produced using substituted phenols will chain extend or form cyclic calixarenes upon continued exposure to heat. Resole resins are typically produced as solutions in solvents, but some are available as solids.

TESTING OF PHENOLIC RESIN PRODUCTS

Typical quality control tests for phenolic resin products may include the following:

1. Gel time [ASTM Test Method for Determining Stroke Cure Time of Thermosetting Phenol-Formaldehyde Resins (D4640-86)] (heat-reactive resins).
2. Viscosity (solution).
3. Color (Gardner).
4. Specific gravity.

Other tests to characterize resins may be used:

1. Molecular weight distribution by gel permeation chromatography.
2. Structure analysis—NMR and IR.
3. Thermal analysis—TGA, DSC, and TMA (curing curves).
4. Free residual formaldehyde by various methods.
5. Free residual phenols by gas chromatography.

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Polyamides

Robert W. Kight[1]

POLYAMIDES

POLYAMIDE RESINS ARE POLYCONDENSATION products of dimerized fatty acids and polyamines. Reactive liquid polyamide resins are oligomers designed primarily for use in the manufacture of two-component epoxy/polyamide coatings and adhesives. The two-component coatings are generally labeled Part A and Part B, with the liquid polyamide resin usually (though not always) contained in Part B. The polyamide resin may function as the curing agent, core-actant, or hardener for epoxy resin. Polyamide resins should not be considered as catalysts although they may initiate the reaction; the polyamide resin reacts with the epoxy resin and becomes part of the polymer. The majority of polyamide resins used in coatings are viscous liquids that are usually supplied by the coatings manufacturer as a solution in organic solvents. The solution may be a clear amber liquid or may contain pigments in colored systems.

Current trends in the coatings industry are toward higher solids, lower volatile organic compound (VOC)-containing products. These products require lower viscosity reactants, such as liquid epoxy resins cured with amidoamines rather than polyamides. Amidoamines are condensation products of monobasic fatty acids and polyamines and are therefore lower in viscosity. These products are less compatible with epoxy resins so commercial examples are adducts of amidoamines. Adduction improves compatibility, though generally increases viscosity, so high boiling, compatible solvents, such as benzyl alcohol, are commonly used to reduce viscosity. Benzyl alcohol becomes trapped in the cured film due to its structural similarity to epoxy resins based on bisphenol A and does not migrate through the film to the surface. Many commercial high-solids curing agents are amidoamine adducts containing benzyl alcohol.

ACIDS

The dibasic fatty acids of commercial importance used to manufacture polyamide curing agents are prepared by dimerizing unsaturated C_{18} fatty acids from linseed, soya, or tall oils. Linseed and soya fatty acids are extracted from flax and soybeans, respectively. Crude tall oil is a by-product from the Kraft process for papermaking and is a mixture of fatty acids and rosin acids, from which the fatty acids are separated by distillation. The tall oil fatty acids are a mixture of C_{18} isomers with a variable number of double bonds. Some of the isomers combine via Diels–Alder addition and other mechanisms to form C_{36} dibasic acids or dimer acids. The dimer acids produced may be acyclic, monocyclic, or polycyclic in structure, depending on the location and number of double bonds in the feedstock. Many isomers are present in commercial dimer acids, most of which are difunctional carboxylic acids [1]. Examples of three possible isomer types follow: acyclic (Fig. 1), monocyclic (Fig. 2), and polycyclic (Fig. 3).

AMINES

The dimer acids are reacted with various polyamines to form polyamide resins and a variety of other useful products. The liquid polyamide resins commonly used in industry are polyethylene polyamines of various chain lengths that are linear, branched, or cyclic. The linear polyethylene polyamines are characterized as secondary amine groups separated by ethylene chains, terminated on either end by primary amine groups. Diethylenetriamine is an example of a simple linear polyethylene polyamine (Fig. 4).

The cyclic and branched polyamine isomers contain tertiary amine groups in addition to the primary and secondary amine groups. Longer chain length polyethylene polyamines available commercially, such as triethylenetetramine and tetraethylenepentamine, are mixtures of linear, branched and cyclic polyamine isomers. Aminoethylpiperazine is an example of a cycloaliphatic polyamine (Fig. 5).

The reaction between dimerized fatty acids and polyamines yield amide oligomers with amine group termination. These amide oligomers are used as coreactants with epoxy resins in high-performance coatings, as well as components of a variety of other useful commercial compositions including two-component adhesives.

EARLY HISTORY

Polyamide resins were commercialized in the late 1950s for use with epoxy resins in the manufacture of two-component adhesives and high-performance coatings. The early commercial epoxy/amine coatings contained aliphatic amines, primarily diethylenetriamine, which had several negative features, such as requiring critical mix ratios and toxicity. The introduction of liquid polyamide resins allowed the coatings manufacturer to produce high-performance coatings characterized by convenient mix ratios, such as 1:1 or 2:1, with very low toxicity.

Epoxy/polyamide coatings find utility in a wide variety of applications, such as industrial maintenance coatings, machinery and equipment enamels, and marine applications. The presence of the long fatty chains gives coatings with much better flexibility as well as better wetting and adhesion than was obtained with the earlier aliphatic amine cured systems.

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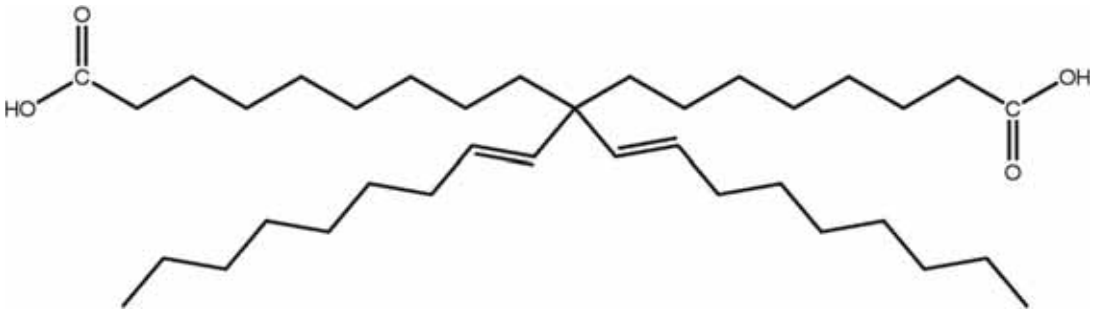

Fig. 1—Acyclic dimer acid.

SYNTHESIS OF POLYAMIDES

Polyamide resins are polycondensation products of difunctional fatty acids and polyfunctional amines. In a typical commercial example, 1 mol of dimer acid is reacted with 2 mol of diethylenetriamine. During this condensation reaction, 2 mol of water are evolved. As the reaction proceeds, an interesting side reaction occurs: An additional mole or so of water evolves from a secondary reaction. One of the primary amine groups reacts with the dimer acid to form an amide linkage, which is a nitrogen bonded carbonyl. In addition, the ethylene chain next to the amide function and the secondary amine nitrogen are incorporated into a five-membered ring, known as an imidazoline ring. This condensation reaction, which also evolves water, eliminates an active hydrogen to yield a tertiary amine group. The degree of cyclization obtained is controlled to yield a product with specific useful properties, such as improved solubility and compatibility and longer pot life. Similar reactions occur at the other carboxylic acid group of the dimer [2]. If 50 % of the diethylenetriamine present in the polyamide is cyclized to imidazoline, a total of 3 mol of water of reaction is evolved. These products are shown in the following structures: the polyamide (Fig. 6) and the imidazoline (Fig. 7).

Commercial products range from about 35 % to more than 80 % imidazoline to allow the coating formulators latitude in customizing the properties of their products.

Other properties of the polyamide resin that are important to the coatings formulator are the amine value, which is related to active hydrogen equivalent weight, and the viscosity level of the polyamide resin in organic solvents. Amine values range from about 100 to about 400, with active hydrogen equivalent weights of about 550-125, respectively. The active hydrogen equivalent weight is used to calculate the amount of polyamide resin required to react with a given amount of an epoxy resin of known epoxide equivalent weight. The ratio of these values, known as the stoichiometric mix ratio, is most often only a starting point for the formulator. By varying the mix ratio of the polyamide resin to the epoxy resin, certain properties of the cured coating are enhanced (and others are sacrificed) to obtain specific application properties.

CHEMICAL PROPERTIES

The total amine value of liquid polyamide resins is determined by potentiometric or colorimetric titration using dilute hydrochloric or perchloric acid to neutralize the amine base. Generally, 0.1*N* hydrochloric acid dissolved in an alco-

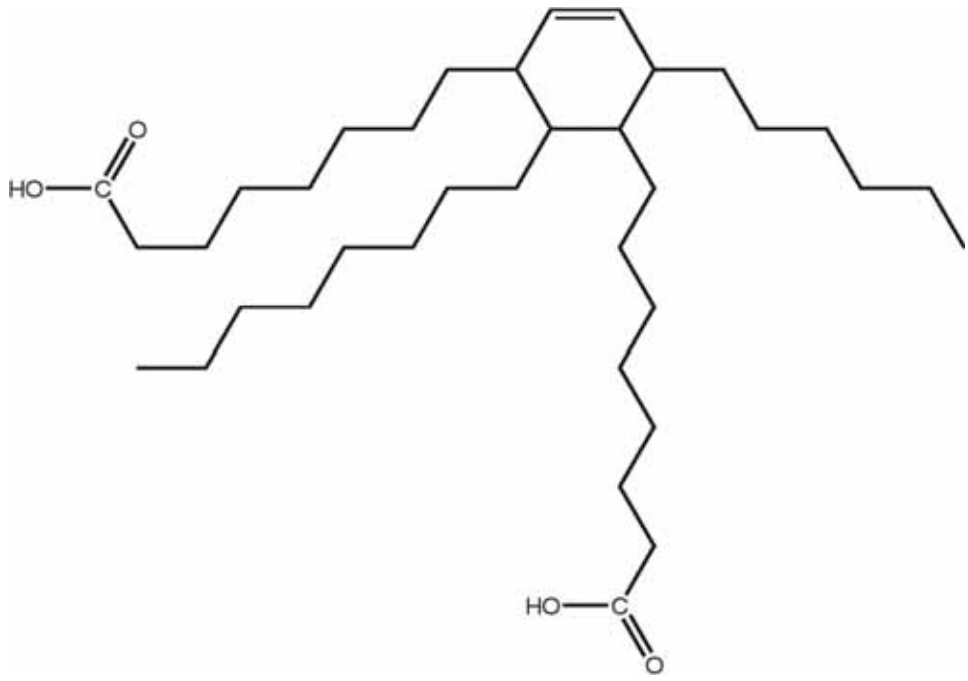

Fig. 2—Monocyclic dimer acid.

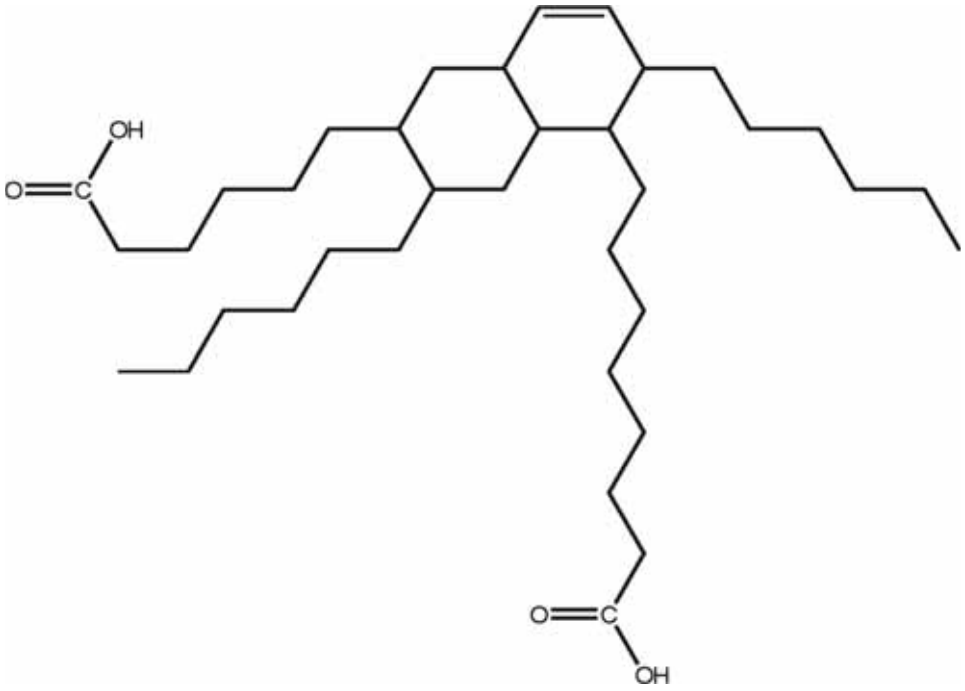

Fig. 3—Polycyclic dimer acid.

hol is used to titrate liquid polyamide resins having < 100 amine value and 0.1*N* perchloric acid dissolved in glacial acetic acid is used to titrate liquid polyamide resins having > 100 amine value. The amine value is commonly listed in the specification properties of commercial liquid polyamide resins and is defined as the number of milligrams of potassium hydroxide equivalent to the basicity in 1 g of sample.

The acid value, generally less than 5, which is also specified in commercial liquid polyamide resins, is defined as the number of milligrams of potassium hydroxide required to neutralize 1 g of sample. The acid value may be determined using ASTM Test Method for Acid Number of Naval Stores Products Including Tall Oil and Other Related Products (D465-05).

The imidazoline content is not specified in commercial liquid polyamide resins except in special cases where the level is deemed critical. The level of imidazoline is usually controlled by the polyamide resin manufacturer to provide products with specific compatibility and/or solubility. Imidazoline level can best be measured by scanning the polyamide resin with an infrared spectrophotometer and comparing the absorption at 6.25 μm to the absorption at 6.05 μm. The imidazoline ring absorbs at 6.25 μm, and the nitrogen-bonded carbonyl, or amide, absorbs at 6.05 μm. The result is reported as either a ratio of imidazoline:amide (I/A) or as a percentage. In the example reaction described previously, the imidazoline ratio would be 1.0 and the percentage would be 50 %.

PHYSICAL PROPERTIES

Polyamide resins are supplied commercially in solution or as 100 % reactive liquids depending on the handling and storage requirements of the coatings manufacturer. For ease of handling, they may be supplied in various solvents. Most liquid polyamide resins suitable for coatings applications are quite viscous, and these polyamide resins are soluble in a variety of organic solvents including alcohols, glycol ethers, ketones, and aromatic hydrocarbons. Thus the coatings manufacturer has considerable latitude in selecting specific solvents for optimum applications properties.

The percent nonvolatile content of polyamide resin solutions may be determined in accordance with ASTM Test Method for Nonvolatile Content of Resin Solutions (D1259-06). Commercial liquid polyamide resins are generally supplied in a single organic solvent at between 60 % and 80 % solids, which provides a handleable viscosity. The coatings formulator further dilutes the polyamide resin solution with more of the same solvent, or with a solvent blend, to form one component of the two-component system.

The polyamide component may be clear or may contain pigments in colored coatings formulations. The color of the liquid polyamide resin or polyamide resin solution is determined in accordance with ASTM Test Method for Color of Transparent Liquids (Gardner Color Scale) (D1544-04).

The viscosity of the liquid polyamide resin may be measured at elevated temperature in accordance with ASTM Test Method for Rheological Properties of Non-Newtonian Materials by Rotational (Brookfield type) Viscometer (D2196-05). The viscosity of commercial liquid polyamide resins is typically specified at 40 or 75°C. The

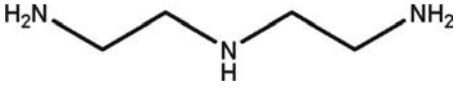

Fig. 4—Diethylenetriamine.

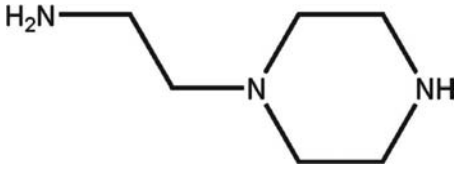

Fig. 5—Aminoethylpiperazine.

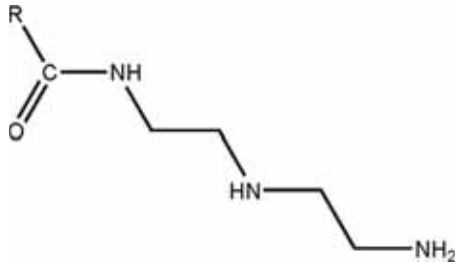

Fig. 6—Polyamide structure.

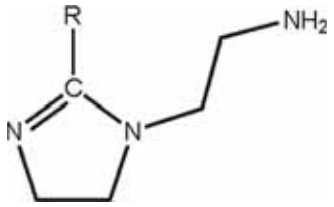

Fig. 7—Imidazoline structure.

viscosity of polyamide resin solutions that may also be measured by this method is generally specified at 25 or 40°C. The viscosity of polyamide resin solutions may also be measured in accordance with ASTM Test Method for Viscosity of Transparent Liquids by Bubble Time Method (D1545-07). A modification of ASTM D1545 is usually used in which the polyamide resin solution is placed in a sample tube, the viscosity is compared to Gardner-Holdt letter standard tubes, and the observation is reported as the alphabetic letter of the tube most closely matching the sample. A plus (+) or a minus (–) is then used to indicate that the viscosity is greater or less than the designated letter.

REACTION OF POLYAMIDE RESINS IN COATINGS

Polyamide resins react with epoxy resins in several stages to form a complex insoluble cross-linked matrix. The initial reaction is between the terminal primary amine groups of the polyamide resin and the oxirane ring of the epoxy resin. The active hydrogen opens the ring and the oligomers join end to end. This initial reaction can be represented by the following simplified structure (Fig. 8).

The reaction of the oxirane ring and active hydrogen, which also occurs at the secondary amine sites in the polyamide resin, is one mechanism for the cross-linking that occurs. A secondary reaction occurs between pendant hydroxyl groups in the epoxy resin molecule and other oxirane rings present, which is another mechanism for the cross-linking reaction [3]. Because of this later reaction, it is desirable to mix the polyamide resin and epoxy resin in less than a stoichiometric ratio to provide coatings with maximum cross-link density. Such coatings will be characterized by excellent impact and chemical resistance but will tend to be less flexible. To provide more flexible coatings with greater elongation, the use of close to or greater than the stoichiometric ratio is recommended.

Epoxy/polyamide coatings contain organic solvents, which when applied appear to dry because of solvent evaporation. This early dry time is not, however, an indication of cure. Cure results from a chemical reaction between the liquid polyamide resin and epoxy resins that generally requires about 8–10 h before the film will resist mechanical deformation. The rate can be accelerated by adding a catalyst, such as 2,4,6-tri(dimethylaminomethyl)phenol, to achieve a 4–6 h cure. Chemical resistance of the coating is not achieved before 3–4 days, and ultimate cure is achieved after about three weeks with ambient curing. Cure rates are faster at elevated temperature and become slower as application temperatures decrease. Below 50°F, liquid polyamide resins cure very slowly, or often will not react with epoxy resins.

Epoxy/polyamide coatings may be applied by any conventional commercial applicator, including spray, brush, or roller. The coatings formulator may design the solvent system for a particular type of applicator. Epoxy/polyamide coatings may be applied to wood, concrete, or steel. For optimum adhesion to the substrate, the surface to be coated should be thoroughly cleaned and degreased. Epoxy/polyamide coatings are not normally applied to wood: When so

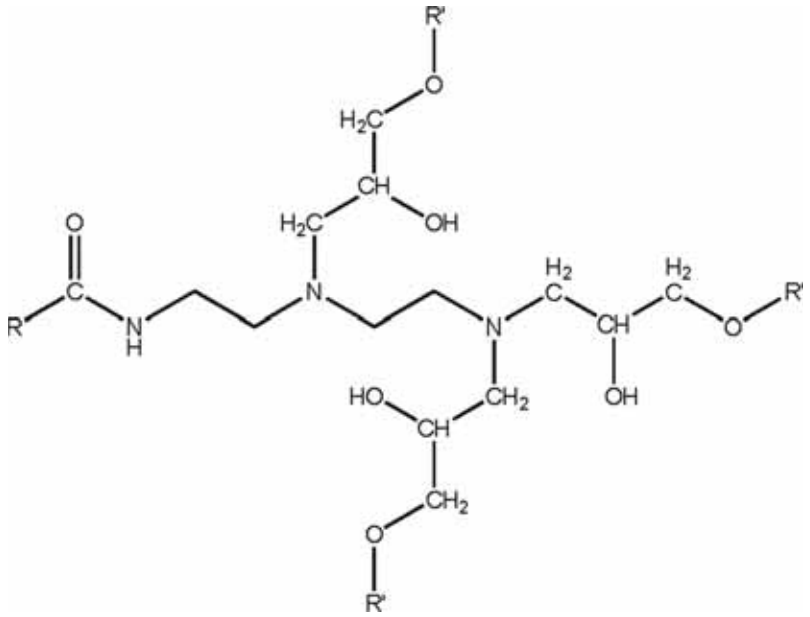

Fig. 8—Polyamide resin reaction with epoxy resin.

used, the wood surfaces should be first cleaned thoroughly and any old loosely adhering paint removed. Concrete surfaces may be chemically acid etched or mechanically brushed. Steel surfaces should be sandblasted, if possible, or at a minimum should be wire brushed and chemically cleaned [4,5].

ENVIRONMENTAL/TOXICITY CONSIDERATIONS

In response to environmental concerns over the emission of organic compounds into the atmosphere, many coatings manufacturers have begun to produce high solids coatings that contain much lower levels of VOCs. The VOC content is measured in accordance with ASTM Standard Practice for Determining VOC Content of Paints and Related Coatings (D3960-05). These products contain low molecular weight polyamide resins or polyamide adducts often dispersed in benzyl alcohol; or amidoamines, products formulated from monomer fatty acid rather than dimer acid [6]. A significant volume of higher VOC epoxy/polyamide coatings continues to be used.

Though liquid polyamide resins are less toxic than aliphatic amines and amine adducts, direct contact exposure with the skin, eyes, and the respiratory system must be avoided. Polyamide resin solutions must also be handled with care to avoid exposure to ignition sources as they contain flammable or combustible solvents and the vapor level from polyamide resin solutions must be monitored in the workplace to avoid overexposure to the organic solvents present.

Polyamide resin manufacturers supply material safety data sheets (MSDSs), which should be consulted for hazard information and guidance on the safe use of the products. The MSDS also contains information regarding procedures to follow if a spill occurs, as well as guidelines for hazardous waste disposal. Those polyamide resin solutions that are classified as hazardous waste due to the presence of organic solvents must be incinerated. Liquid (100 %) polyamide resins are not generally classified as hazardous waste though their disposal may be regulated as an oil because of their liquid nature: These products must be either incinerated or absorbed by a suitable solid absorbent medium, such as a ground clay absorbent product, and placed in a sanitary landfill.

Though liquid polyamide resins are reactive in the presence of epoxy resin, they are quite stable compounds when kept in a cool, dry environment, and they may remain unchanged for a year or more. Liquid polyamide resins may be stored in phosphatized steel drums or tanks constructed of stainless steel or aluminum. Carbon steel tanks should be avoided because of darkening of the product from iron contamination.

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Polyurethane Coatings

Han X. Xiao[1] and Joseph V. Koleske[2]

INTRODUCTION

THE CHEMISTRY OF POLYISOCYANATES WAS FIRST described by Professor Otto Bayer in the laboratories of the I. G. Farbenindustry, today's Farbenfabriken Bayer, in Leverkusen, Germany. Polyurethanes are mainly characterized by the linkage –NH–C(CO)–O–, though they may also contain other functional groups such as ester, ether, urea, and amide. The most important commercial route for the synthesis of such polymers is the addition polymerization that occurs when di- or higher functionality isocyanates and di- or higher functionality hydroxyl compounds, such as hydroxyl-terminated acrylics, polyesters, or polyethers, are combined and undergo rearrangement reactions. When di-functional reactants are used, linear or thermoplastic polyurethanes are produced. Cross-linked or thermoset polyurethanes are formed if the functionality of at least one of the reactants is greater than 2. The historical and commercial developments as well as the chemistry and applications of polyurethanes have been reviewed by a number of authors [1–23]. Polyurethanes have found extensive applications in the coating industry due to the fact that they exhibit excellent abrasion resistance, toughness, chemical and corrosion resistance, as well as a wide range of useful mechanical properties.

Polyurethanes are widely used in coatings, adhesives, sealants, foams, elastomers, and RIM (reaction injection molding, composites, fibers, etc.). Excluding coatings, the 1988 United States consumption of polyurethanes was about 2,750 million pounds (1.25 million metric tons). In 1991, the national market for polyurethane coatings was about 209 million pounds (95,000 metric tons) [24, 25].[3] Although the market for polyurethane coatings is large and growing, it is readily apparent that it represents only about 5 %–10 % of the total domestic polyurethane market. The growth in this industry is exemplified by the fact that in 2002 the amount used in the United States was about 5,500 million pounds (2.51 million metric tons), and about 6,390 million pounds (2.90 metric tons) in North America. Reasons for the use of polyurethane coatings include high performance characteristics such as flexibility, toughness, strength, abrasion, chemical, and stain resistance, good light stability when aliphatic isocyanates are used, and good low temperature properties. The latter factor is an important reason for use of polyurethane coatings on plastic substrates.

DEFINITIONS

ASTM [8] in its 2003 document defines *urethane coatings* as "coatings based upon vehicles containing a minimum of 10 % by weight (nonvolatile vehicle basis) of a polyisocyanate monomer reacted in such a manner as to yield polymers containing any ratio, proportion or combination of urethane linkages, active isocyanate groups, or polyisocyanate monomer. The reaction products may contain excess isocyanate groups available for further reaction at time of application or may contain essentially no free isocyanate as supplied." ASTM has further classified such polyurethanes into six general types [8]:

> "*Type I, one-package prereacted*—urethane coatings characterized by the absence of any significant quantity of free isocyanate groups. They are usually the reaction product of a polyisocyanate and a polyhydric alcohol ester of vegetable oil acids and are hardened with the aid of metallic soap driers." The curing cross-linking reaction functions by means of an oxidation of double bonds present in the system, that is, the same reaction that takes place with drying oils. For example, linseed oil and glycerol may be first reacted and then modified with a diisocyanate that reacts with a part or all of the available hydroxyl groups. If any residual isocyanate is present, it is removed by addition of a monofunctional alcohol. Catalysts such as dibutyltin oxide and dibutyltin dilaurate are used to promote urethane-linkage formation. Type I urethane coatings are often used as wood and floor finishes because they provide improved scuff, water, and stain resistance over those of conventional alkyds.
>
> "*Type II, one-package moisture cured*—urethane coatings characterized by the presence of free isocyanate groups and capable of conversion to useful films by the reaction of these isocyanate groups with ambient moisture." The curing mechanism results in mainly urea linkages forming by water molecules reacting with free isocyanato groups. The final coating is a polyurethane/polyurea coating. The rate of cure depends on ambient humidity and the presence of certain tertiary aminecatalysts that accelerate the isocyanato-water reaction. For the most part, type II

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[3] The purpose of this chapter is not to give current market information, and the data used are used for illustration purposes. The numbers change and are usually quite far behind any current date. Interested readers might consider browsing various websites, particularly national government sites, for detailed information regarding production figures.

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urethane coatings are clear, but pigmented systems are becoming somewhat popular. They are often used as sealers for concrete and wood as well as floor and deck finishes.

"*Type III, one-package heat cured*—urethane coatings that dry on cure by thermal release of blocking agents and regeneration of active isocyanate groups that subsequently react with substances containing active hydrogen groups." Because of the mechanism of cure—release of blocking agents—these urethane coatings are stable at room temperature. The deblocking reaction takes place at elevated temperatures that usually are greater than 150–160°C, releasing active isocyanato groups that react with active hydrogen groups contained in the formulation. Type III coatings will also cure at lower temperatures and at short times if a catalyst is included in the formulation. The coatings are often used in coil coatings and electrical wire coatings.

"*Type IV, two-package catalyst*—urethane coatings that comprise systems wherein one package contains a prepolymer or adduct having free isocyanate groups capable of forming useful films by combining with a relatively small quantity of catalyst, accelerator, or cross-linking agent such as a monomeric polyol or polyamine contained in a second package. This type has limited pot-life after the two components are mixed." Two groups of catalysts are usually utilized with these coating systems. One group is reactive in nature and is comprised of molecules that contain hydroxyl groups such as alkanolamines. The other group are nonreactive catalysts, such as tertiary amines and metal salts of carboxylic acids. These coatings are not widely used.

"*Type V, two-package polyol*—urethane coatings that comprise systems wherein one package contains a pre-polymer or adduct or other polyisocyanate capable of forming useful films by combining with a substantial quantity of a second package containing a resin having active hydrogen groups with or without the benefit of catalyst. This type has limited pot-life after the two components are mixed." The compounds containing an active hydrogen group are usually low to medium molecular weight polyols with, for example, a polyester, polylactone, polyether, or polyacrylic backbone. These coatings, which are usually high-solids in nature, are used in high performance areas, such as automobile re-finish coatings, original automotive equipment clear coats over pigmented decorative coatings, aircraft, bus, and bus coatings, and industrial-structure maintenance coatings.

"*Type VI, one-package, nonreactive lacquer*—urethane coatings characterized by the absence of any significant quantity of free isocyanate or other functional groups. Such coatings convert to solid films primarily by solvent evaporation." Basically, these urethane coatings are solutions of high molecular weight polyurethanes (weight-average molecular weight of about 40,000–100,000) with thermoplastic properties. They are characterized by the absence of nil or essentially nil free isocyanato groups, and properties are developed by controlled solvent evaporation. In addition, they are low solids, about 10 %–15 %, in nature because of the high molecular weights involved and concomitant high viscosity of such molecules in solution. The films resulting from type VI urethane coating solutions have very high gloss and are used in the textile and furniture industries to achieve the "wet look" that was popular in the late 1970s. They are currently used in the cast transfer-process fabric coatings as well as other fabric coatings.

There are other polyurethane coatings besides these six types included in the ASTM classifications. They may be described as follows.

Two-package polyurea and poly(*urethane-urea*) *coatings*, which are composed of one package that contains amines along with fillers, pigments, and additives and a second package that contains monomeric multifunctional isocyanates and/or prepolymeric adducts of diisocyanates [26–33]. If the second package contains no pre-polymers, it will produce polyurea coatings after the two packages are blended and reaction takes place. If there are prepolymers in package 2, the resultant coatings will be poly(urethane-urea) in nature. In these systems, the isocyanates react very rapidly with amines to form urea groups, which have very good adhesion and mechanical properties. The success achieved when preparing this type of coating depends on the following alternatives:

1. The use of hindered aromatic amines to slow down the reaction that forms the urea groups.
2. The use of aliphatic isocyanate-based prepolymers or adducts followed by reacting with aromatic amines or long-chain aliphatic amines to slow down urea formation that takes place when or if aromatic isocyanates are used in prepolymer preparation.
3. The use of especially designed spray systems in which a small, powerful mixing chamber with high efficiency and very short residence time is employed.

A solvent-free, 100 % solids polyurea can be formulated by proper selection of a low viscosity, multifunctional isocyanate such as polyarylpolyisocyanate, often termed PAPI, or the adduct/trimer of hexamethylenedisocyanate (HDI). In addition, to achieve such a goal, an amine with low viscosity such as polypropylene diamines is needed.

Waterborne polyurethane coatings, which are mainly anionic and cationic in nature, though nonionic types are available [33–59]. Most commercial waterborne polyurethane coatings or waterborne polyurethane dispersions (WPUDs) are anionic in nature and a few are cationic in nature. The anionic WPUDs are made in the following manner:

1. Preparation of isocyanate-terminated and carboxyl-containing prepolymers from polyols, diisocyanates and dimethylolpropionic acid (DMPA).
2. Neutralization of the above prepolymers with an organic base such as triethylamine to form the pendant, internal hydrophilic salt groups.
3. Dispersion of the above neutralized isocyanate-terminated prepolymers with water.
4. Chain extension of the above prepolymer dispersion to introduce urea groups.

A large number of anionic WPUDs with extensive mechanical properties can be produced by changing the type of polyols, diisocyanates, neutralizing agents, and chain extenders as well as the acid group concentration from DMPA. If desired, the anionic WPUDs can be cross-linked with melamine compounds, azeridine, polyisocyanates, and blocked polyisocyanates. These could be made as one- or two-package systems.

Cationic WPUDs are prepared in a similar manner as the above with the following changes:

1. A tertiary amine-containing diol such as N-methyldiethanolamine is used to replace DMPA. This introduces a tertiary amine group into the polymer backbone.
2. Inorganic or organic acidic compounds are used to neutralize the tertiary amines and form the internal hydrophilic salt group.
3. In the chain extension step, care should be taken to avoid destroying the hydrophilic internal salt groups.

Various cationic WPUDs can be produced by changing the nature of the raw materials and the concentration of tertiary amine groups.

Nonionic WPUDs are also used. They have a preparation procedure that is similar to that of the anionic/cationic WPUDs except that an internal hydrophilic nonionic group is introduced to replace the internal ionic groups. In comparison to the anionic/cationic WPUDs, nonionic WPUDs have excellent stability in any reasonable range of *p*H values and are commercially available.

WPUDs are suitable for a variety of applications including automotive, furniture, textile, wood, leather, paper, nonwoven fabrics, and construction coatings.

Polyurethane powder coatings [33,60,61], are finely divided, powdered polyurethanes prepared from polyols, difunctional isocyanates, urethane-modified polyesters, and hydroxyl-containing polyacrylics. They are usually cured with melamines or blocked isocyanates. When polyurethanes are prepared for this industry, factors such as ability to convert the polymer to a finely divided state, the final flexibility or impact strength, glass transition temperature, and sintering characteristics are factors that need to be considered. High glass transition temperatures, which might enhance powdering characteristics, may have a deleterious effect on impact strength. In contrast, a low glass transition temperature might result in good impact strength but have a negative effect on powdering factors and cause sintering difficulties. The key to successful powder coatings, polyurethane or other, is related to the ability to balance molecular weight and its concomitant effect on melt viscosity, glass transition temperature, and a cross-linking mechanism that is stable under storage conditions and that is not affected to any significant degree until flow and leveling takes place at the curing temperature. The major end uses for polyurethane powder coatings are the major appliance markets and automotive.

Interpenetrating polymer network (*IPN*) *coatings* [62–77] are a relatively novel type of polymer alloys that consist of two or more cross-linked polymers, which in the general case of IPNs need not be polyurethanes. They are more or less intimate mixtures of two or more distinct cross-linked polymer networks held together by permanent entanglements and with only accidental covalent bonds between two networks—for example, they are polymeric "catenanes." IPNs are produced either by swelling a cross-linked polymer with monomer and cross-linking agent of a different polymer and curing these compounds in situ or by blending the linear polymers, prepolymers, or monomers in some "liquid" form—solution or bulk—together with cross-linking agents and simultaneously curing the component polymers. Combination of various chemical polymer types into IPNs results in different compositions that have controlled morphologies and synergistic behavior. Xiao and Frisch et al. [67–77] have prepared many different types of IPN coatings. Sperling et al. [64,65] have developed two-layer coating systems termed "silent paint," which is capable of attenuating noise and vibration over a broad temperature range.

CHEMISTRY AND REACTIONS

Basic Urethane Chemistry

The high reactivity of the isocyanate, especially with nucleo-philic compounds, has always been of intriguing interest for the organic chemist. However, multifunctional isocyanates only gained technical importance through polyaddition chemistry. The reactivity of the —N=C=O group is mainly determined by the pronounced positive charge of the carbon atom in the double bond sequence that consists of nitrogen, carbon, and oxygen. The positive charge on this carbon atom becomes obvious if one considers the resonance structure as shown below [33]:

$$R-N=C=O \rightleftharpoons R=N=\overset{+}{C}-\overset{-}{C} \rightleftharpoons R-\overset{-}{N}-\overset{+}{C}=O \rightleftharpoons \overset{-}{R}=N-\overset{+}{C}=O$$

With R an aromatic radical, the negative charge can be localized into it as described. This also explains that aromatic isocyanates have higher reactivity than aliphatic isocyanates. In the aromatic isocyanates, the electron-donating substituents lower reactivity of the isocyanato (NCO) group. Therefore, the major chemical reactions of the isocyanato group are as follows.

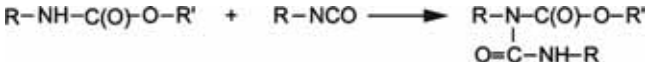
URETHANE

Hydroxyl-containing compounds can be reacted with NCO groups to form the major and important urethane structure, which is the main structure in polyurethane products.

$$R'-OH + R-NCO \rightarrow R-NH-C(O)-O-R'$$

ALLOPHANATE

The urethane that has formed is capable of further reaction with an NCO group to form an allophanate linkage and this results in crosslinking as described below.



UREA

If an amine or water is reacted with an isocyanate, urea groups are formed in the following manner.

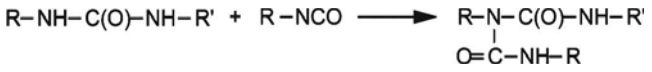
$$R'-NH_2 + R-NCO \rightarrow R-NH-C(O)-NH-R'$$

$$H_2O + R-NCO \rightarrow R-NHCOOH \rightarrow R-NH_2 + CO_2$$

$$R-NH_2 + R-NCO \rightarrow R-NH-C(O)-NH-R$$

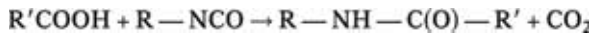
BIURET

If a urea group is reacted with an isocyanate, the biuret compound is formed.



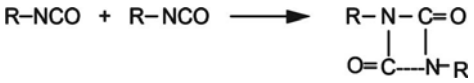
AMIDE

When carboxylic acids react with an isocyanate, amides are formed.



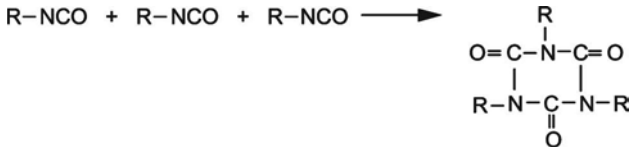
URETDIONE OR ISOCYANATE DIMER

Isocyanates can react with themselves to form isocyanate dimers or uretdione.



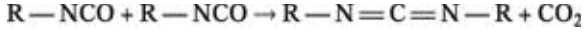
ISOCYANURATE OR ISOCYANATE TRIMER

A six-member ring structure is formed when three isocyanate groups react to form an isocyanurate or isocyanate trimer.



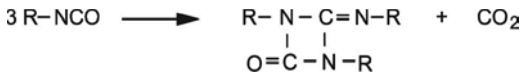
CARBODIIMIDE

Carbodiimides are formed when two isocyanates groups react and carbon dioxide is eliminated.



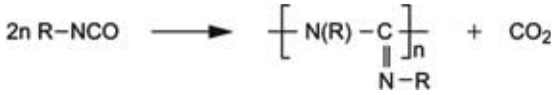
URETONE-IMIME

Three isocyanate molecules can react and form the Uretone-imime molecule.



POLYCARBODIIMIDE

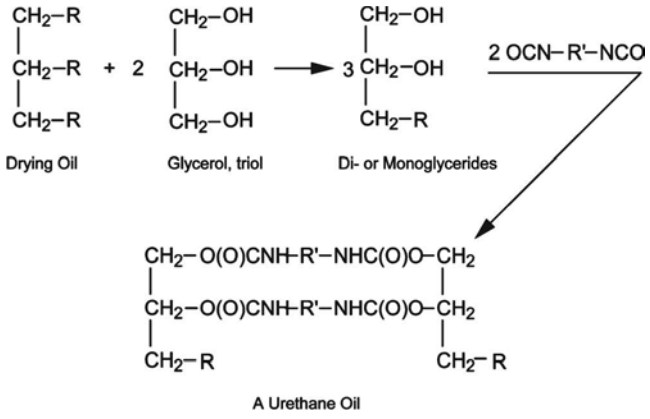
Polycarbodiimide molecules can form when multiple isocyanates react with themselves.



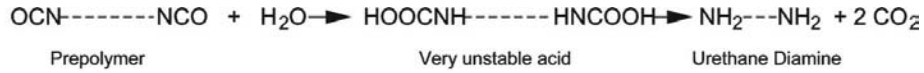
Six ASTM Conventional Type Polyurethane Coatings

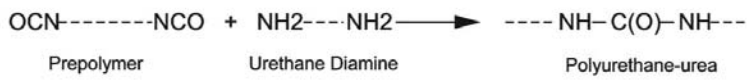
The major chemical reactions that take place with the six types of polyurethane coatings that are defined by ASTM [8] are as follows.

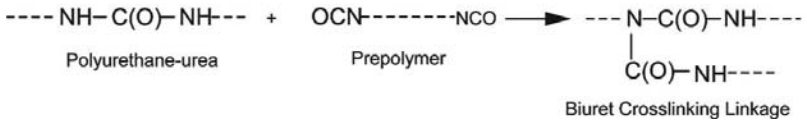
Type I polyurethanes involve a transesterification that introduces the hydroxyl group and yields the di- or monoglycerides that subsequently will be reacted with diisocyanates at NCO/OH ratios equal or greater than 1.0/1.0. This forms urethane modified drying oils—the generalized urethane oil described below wherein R is an unsaturated, aliphatic chain of drying oil and R′ is the aromatic diisocyanate.



Type II polyurethanes involve isocyanate terminated prepolymers that are reacted with moisture (water) in the presence of catalyst to form amines and carbon dioxide. The resultant amines then react with other isocyanate groups to form ureas that also can further react with isocyanate groups to form biuret linkages (crosslinks) as described in the following reactions of prepolymer.







Type III ASTM polyurethanes are prepared by blocking the isocyanate groups with a blocking agent that has an active hydrogen atom, BA-H in the following scheme, and then blending this blocked isocyanate with a polyol, fillers, pigments, and additives. The polyurethane system prepared is a stable one-package system that is cured by deblocking and freeing the isocyanato groups at elevated temperature. These freed groups then react with the hydroxyl groups and form the final polyurethane.

$$\underset{\text{Diisocyanate}}{OCN-R-NCO} + \underset{\text{Blocking Agent}}{2BA-H} \rightarrow BA-(O)C-NH-R-NH-C(O)-BA$$

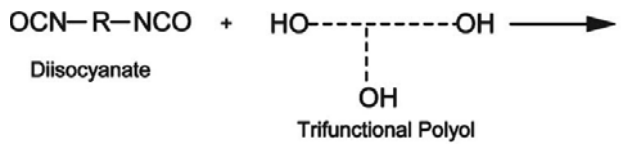
Blocked Diisocyanate

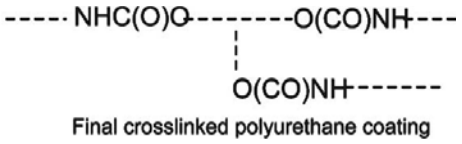
$$BA-(O)C-NH-R-NH-C(O)-BA \xrightarrow{\Delta} OCN-R-NCO + 2BA-H$$

Free NCO for reaction with polyol

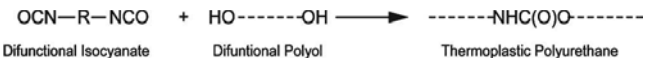
Type IV ASTM polyurethanes are produced with the same chemistry as was used for Type II polyurethanes.

Type V ASTM polyurethanes with or without multifunctionality isocyanates (greater than two) are cured with polyols or urethane/urea linkage-containing polyols with or without multifunctionality (greater than two); however, one of the components with have a functionality greater than 2. The following is one example of the urethane-formation reaction.





Type VI ASTM polyurethanes are high molecular weight, thermoplastic polyurethanes that are formed with an NCO/OH ratio at 1.0 or very close to this value. If this ratio exceeds 1.0 by any amount, there is the possibility of producing a polyurethane that will contain gel particles when dissolved.

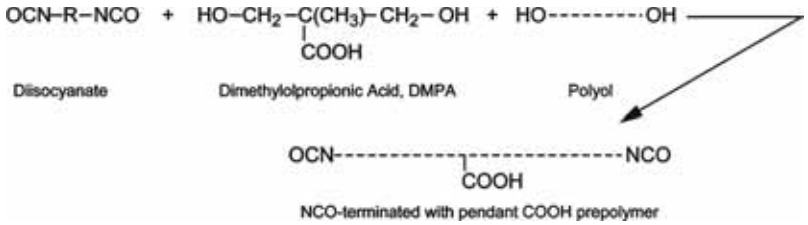


Thermoplastic polyurethanes are used in type VI lacquers as well as in many industrial end uses that require solid polyurethanes. The solid polyurethanes have a similar chemistry except that short chain diol extenders, such as 1,4-butanediol or 1,6-hexanediol, are used and these can form blocks of hard segments with the polyol portion known as the soft segment. In effect, these useful polyurethanes are block copolymers of the $(AN)_n$ type. Thus, one of the blocks is a relatively long, number-average molecular weight of 300 to 3,000, polyether or polyester that forms the soft or flexible segment. The other block is formed by the reaction of a diisocyanate and the chain extender and is termed the hard segment. Again, the overall ratio of isocyanate to hydroxyl is maintained at 1.0 to allow thermal forming. The hard segments act as pseudo cross-links and the result is a tough, strong, elastomeric macromolecule.

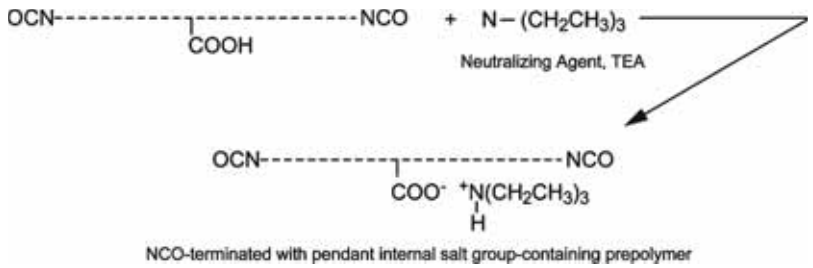
In a mole sense, these polyurethanes can be viewed as polyol/diisocyanate/short-chain extender formed in an equivalents ratio of $1/X/(X-1)$. The number X can vary from 1 or less to as much as 20 or more, though more typically in coatings, X has a value of one or less to about 3 or 4 [32,33,78]. Because of solubility characteristics, a ratio of about 1/2/1 is often used. A small excess of hydroxyl groups is used to keep final free isocyanate content and storage reactivity at a nil level. When the wide range of X values, the types of isocyanates, the types and molecular weight of polyols are considered, it is readily apparent that a myriad of polyurethanes can be prepared and that a broad range of mechanical and chemical properties can be achieved. The chemistry is basically that of isocyanates reacting with hydroxyl groups to form urethane linkages.

Waterborne Polyurethane Coatings

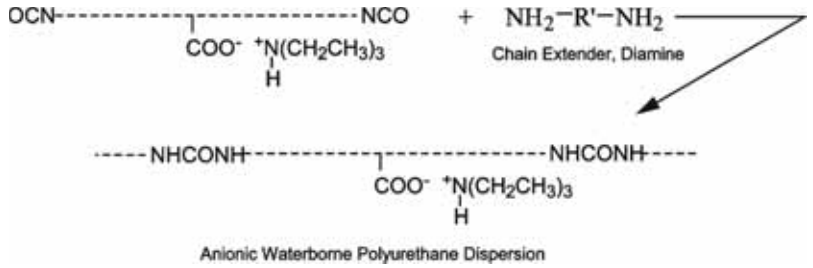
Anionic waterborne polyurethane coatings or WPUDs [34–59,78] are prepared by means of four main chemical reactions as described below. Preparation of NCO-terminated and pendant COOH-containing prepolymer:



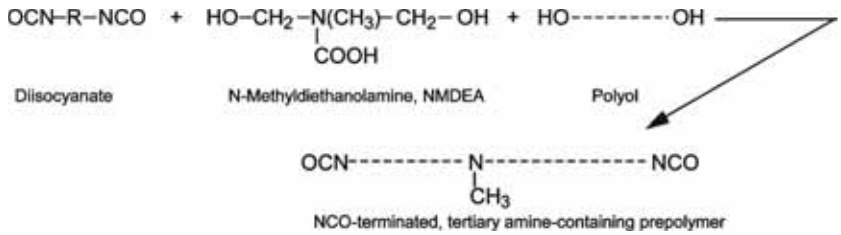
NEUTRALIZATION WITH TRIETHYLAMINE (TEA)

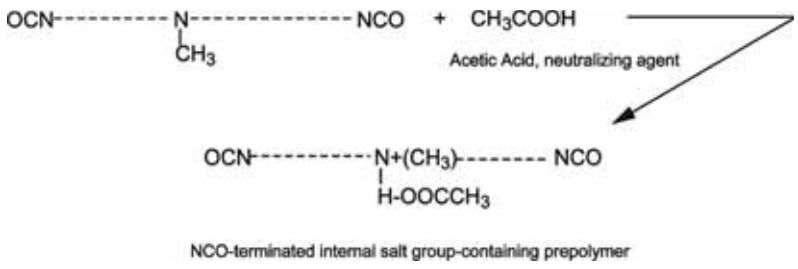


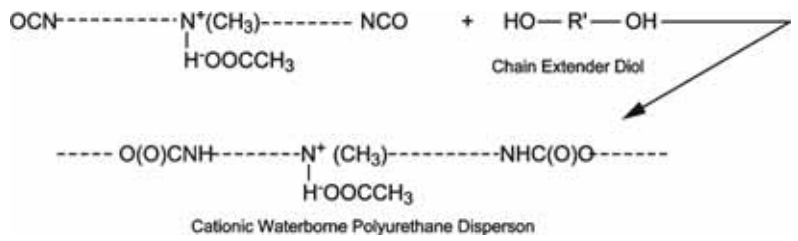
DISPERSION WITH WATER FOLLOWED BY CHAIN EXTENSION WITH DIAMINE



The chemistry involved in cationic WPUDs is similar to that used for anionic WPUDs except that dimethylolpropionic acid is replaced with N-methyldiethanolamine followed by neutralization with an acid such as acetic acid. The prepolymer is then dispersed in water and chain extended with a diol.





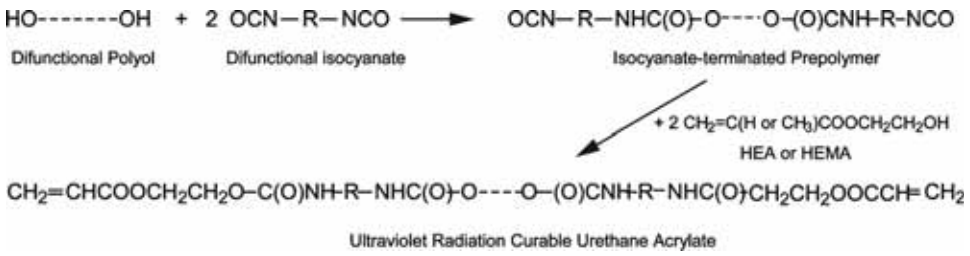


Radiation-Curable Coatings

Radiation-curable polyurethane coatings, in particular the ultraviolet radiation-curable polyurethane-acrylate coatings, are prepared by combination of urethane and acrylate chemistry [79–90]. Acrylate-terminated polyurethanes are used in a number of ultraviolet radiation and electron beam curable formulations. The products are commonly termed "urethane-acrylates" or "acrylated urethanes." They are prepared by first forming an isocyanate terminated prepolymer from a difunctional polyol, and then end-capping the prepolymer with a hydroxy acrylate such as 2-hydroxyethyl acrylate or 2-hydroxyethyl methacrylate.

Powder Coatings

Polyurethane powder coatings are usually urethane-modified polyesters and polyacrylates that cure at high temperatures [40,41]. High temperatures are required for the powdered polymer to flow and level to the extent needed for a particular end use. The key to successful powder coatings is related to a balance between molecular weight and related viscosity as well as a cross-linking mechanism that is stable under storage conditions and not effected to any significant degree until flow and leveling have taken place at the cure temperature. Another requirement is that the glass transition temperature be sufficiently high that the powder does not block during shipping and storage. The polyurethanes used as powder coating are usually of the ASTM Type III. The main end use for powdered polyurethanes is in the major appliance market—refrigerators, dryer drums, range cabinets, etc.



These reactions that lead to urethane acrylates are almost always carried out in an inert solvent. The reactions, as depicted above, have been idealized. In all commercial and laboratory preparations, there is a significant amount of reaction between the ingredients and as a result chain extension and accompanying molecular weight increases take place. This causes the final products to have a markedly higher than expected viscosity. Oligomeric compounds such as these are formulated with triacrylates such as trimethylolpropane triacrylate and various multifunctional acrylates to provide cross-linking, with monomeric acrylates, N-vinyl pyrrolidone and other low molecular weight compounds to provide viscosity reduction. In effect, 100 % solids systems that will rapidly cure when exposed to actinic radiation. In most formulations, the urethane acrylate is considered as the main ingredient that contributes to mechanical properties in the cured film. When the actinic radiation is ultraviolet in nature, a photoinitiator (for example, 2,2-diethoxyacetophenone or benzophenone in combination with an amine synergist) is added as a free-radical source. Electron beam curable formulations do not require a photo-initiator.

Acrylated polyurethanes can be prepared as water-based coatings [88]. The anionic and cationic oligomeric materials are prepared by introducing an internal salt in the backbone similar to the procedures described above for conventional waterborne polyurethane dispersions.

Radiation-cured polyurethanes are often used on plastic substrates that will tolerate only low or moderate temperatures such as clear overprint lacquers on vinyl decals, electronic circuit boards, "no wax" vinyl flooring, tile, wood flooring, packaging, and a host of other end uses. Although radiation-cured, colored, and pigmented coatings and inks are widely used in the marketplace, it should be readily appreciated that radiation penetration is more difficult than in clear coatings.

RAW MATERIALS

Isocyanates

Two types of isocyanates are used to prepare polyurethanes for coating end uses—aliphatic and aromatic [33]. Polymers prepared from either type of isocyanate have excellent chemical and physical properties. Aromatic isocyanate-based products are used in places where weathering resistance, particularly sunlight or ultraviolet radiation resistance, is not important, since these isocyanates will cause discoloration, which almost always manifests itself as yellowing. Yellowing in itself causes a loss of an aesthetic property, but its cause and result do not deleteriously affect mechanical properties. Ultraviolet radiation attacks the labile hydrogen atoms on the aromatic ring structure. When non-yellowing polyurethanes are required, it is necessary to use an aliphatic isocyanate since their structure yields excellent sunlight and ultraviolet radiation resistance. However, it should be kept in mind that aliphatic isocyanates are less reactive and more costly than aromatic isocyanates, and while these factors should be considered, aliphatic isocyanates are very widely used for both interior and exterior applications.

The two main aromatic isocyanates currently used are 4,4′-diphenylmethane diisocyanate (MDI) and toluene diisocyanate (TD), which is a mixture of 2,4- and 2,6-isomers. Moisture-cure urethanes and urethane alkyds usually employ TDI, though MDI has some use due to its low vapor pressure. The extensive use of TDI has been gradually, but markedly, reduced because of its toxicity. Xylylene diisocyanate (XDI) is a mixture of aromatic and aliphatic structures in which there are methylene groups between the aromatic

ring and the isocyanate groups. It is used to some extent, but mainly in Japan. MDI has been modified into a liquid form that has a functionality between 2.0 and 2.5, and it has been used in some coating areas [75]. Recently, Dow Chemical Co. has produced a liquid isomer of MDI that comprises a mixture of 4,4′- and 3,4′-diphenylmethane diisocyanate, and it also has been used in coatings. Crude MDI, polyarylpolyisocyanate (PAPI) that has functionalities between 2.0 and 2.7, is dark brown in color and is low in cost. PAPI in combination with poly(oxypropylene) diamines (Jeffamine™) is used for two-package, solvent-free polyurea coatings. Other aromatic diisocyanates, such as naphthalene diisocyanate, have also been used.

Aliphatic isocyanates are more costly than aromatic isocyanates, and they are used for urethane coatings that require excellent sunlight resistance with no discoloration. These coatings are used on plastics, automobile signs, and similar outdoor end-use products. The main aliphatic isocyanates are hydrogenated MDI (4,4′-dicyclohexylmethane diisocyanate, H_{12}MDI), HDI particularly in a biuret or trimer form for improved vapor pressure, tetramethylxylylene diisocyanate (TMXDI), isopropenyldimethyltoluene diisocyanate (TMI), mixtures of 2,2,4- and 2,4,4-trimethyl hexam-ethylene diisocyanate (TMHDI), 1,4-cyclohexane diisocyan-ate, and isophorone diisocyanate (3-isocyanatomethyl-3,5,5-trimethylcyclohexyl isocyanate (IPDI) [9]. The HDI trimer and adducts are major raw materials together with acrylic polyols for two-package, solvent-based polyurethane coatings used in automobile applications. The three significant isocyanates in the above listing are H_{12}MDI, IPDI, and TMXDI.

BLOCKED ISOCYANATES

ASTM Type III polyurethane coatings, including powder coatings, employ blocked isocyanates that provide room-temperature-stable, one-package systems that are activated at elevated temperatures. At such temperatures, the molecules dissociate and the blocking agent leaves freeing the isocyanate functionality that then readily reacts with available active hydrogen-containing molecules. The reaction is rapid due to its nature and to the kinetic effect of elevated temperature. Blocking groups are proton donors such as ε-caprolactam, malonic and acetoacetic esters as well as other enolizable esters, ketoximes, phenol, etc. For example, trimethylolpropane (TMP) can be reacted with a diisocyanate and then blocked by reacting the free isocyanate group with a blocking agent, BA-H, such as phenol.

ACTIVE HYDROGEN-CONTAINING COMPOUNDS

Isocyanate functionality readily reacts with active hydrogen-containing groups such as OH, NH2, NH, COOH, and SH [33]. Polyfunctional compounds such as glycols, triols, tetraols, polyester polyols, polylactone polyols, polyether polyols, acrylic polyols, and hydrocarbon polyols usually supply hydroxyl groups. Low molecular weight compounds or short-chain extenders, such as 1,4-butanediol, in combination with isocyanates, are termed "hard segments" that function as pseudo cross-links in the final polyurethane [13]. In high molecular weight polyurethanes, such as those used for ASTM Type VI products, these chain extenders represent only a few percent of the total polymer molecular weight yet play a significant role in final physical properties. Glycols and low molecular weight triols require relatively large amounts of isocyanates, usually the most costly ingredient, and impart hardness and rigidity to the coating. The long chain polyols function as "soft segments" and impart flexibility.

There are four major types of polyols—polyether, polyester, polyacrylic, and hydrocarbon. Polyether polyols are of three many types—poly(ethylene glycol), poly(oxypropylene) glycol, and poly(tetramethylene oxide) glycol with different functionalities and molecular weights. Copolymeric glycols of ethylene oxide and propylene oxide are also available and used. The polyester polyols are aliphatic (both diol and dimer acid used are aliphatic), aliphatic from ε-caprolactone via ring opening of the cycloaliphatic ring, or aromatic (either diol or dimer acids or both are aromatic). These polyols are also available with different functionalities and a variety of molecular weights. Acrylic polyols are various acrylates copolymerized with 2-hydroxyethylmethacrylate or 2-hydroxyethylacrylate. The equivalent weight based on hydroxyl functionality is dependent on the concentration of hydroxy-acrylate used, and in addition to a distribution of molecular weights, these polyols have a distribution of hydroxy-functional acrylate within the various molecules. Hydrocarbon polyols are homopolymers or copolymers of butadiene, isobutene, and isopentadiene with special initiators. Coatings based on these polyols have excellent water resistance and electrical insulation, but they have lower adhesion to polar surfaces because of their very low backbone polarity than the other classes of polyols. However, hydrocarbon-based polyols may have potential as intermediates for primers on thermoplastic polyolefins used in the automotive industries.

As would be expected, primary hydroxyl groups react much more rapidly than secondary hydroxyl groups and tertiary hydroxyl groups react slower than either other type. For example, primary hydroxyl groups reacted about 3.5 times faster with phenyl isocyanate than secondary hydroxyl groups and about 200 times faster than tertiary hydroxyl groups [11]. It was also found that n-butanol reacted five times faster with the isocyanate group in the para- or 4-position than with the isocyanate next to the methyl group in 2,4-toluene diisocyanate. This demonstrated that neighboring groups can significantly affect isocyanate reactivity.

Polyfunctional amines, which form urea linkages with isocyanates, are also used as chain extenders. Low molecular weight compounds, such as ethylenediamine, are used for this purpose when waterborne polyurethane dispersions are prepared. Amine terminated oligomers based on alky-lene oxides such as poly(oxypropylene)diamine are also available.

Catalysts

There are two main types of catalyst used to promote the urethane formation reactions. One type is tertiary amine-containing compounds and the other is metal salts or metal oxides—in particular organic metal salts. These catalysts most often are used to promote the reaction between isocyanates and active-hydrogen-containing compounds. Only small amounts, on the order of 10 to 100 parts per million, are needed to cause marked increases in reaction rate. Popular catalysts that have been used are dibutyltin dilaurate, stannous octoate, diaza(2.2.2)bicyclooctane, dibutyltin diacetate, bismuth stearate, and zirconium octoate [91].

Additives

Many additives are used in polyurethane coating formulations, and the particular ones used depend on the final

TABLE 1—Examples of polyurethane end uses	
Home Furnishing	Optical Fibers
Drum Dryers	Printed Circuit Boards
Furniture	Sheet Molding Compound
"No Wax" Flooring and Tile	TPO Bumpers
Range Cabinets	Recreational Products
Refrigerators	Baseball Bats
Wood Flooring	Golf Balls
Industrial Maintenance	Golf Clubs
Bridge	Gym Floors
Industrial Buildings	Playground Equipment
Marine Coatings	Toys
Plant Equipment	Golf Balls
Roof Coatings	Textiles
Windows	Apparel
Miscellaneous	Fabric Coatings
Aerospace	Leather
Luggage	Tarpaulins
Magnetic Tape	Upholstery
Mast and Spar Varnishes	Transportation
Medical Equipment	Aircraft and Aerospace
Safety Glass	Automotive, OEM
Shoes	Automotive, Refinish
Vinyl Decal Overprints	Bed Liners
Wire Coatings	Golf Carts
Plastic Substrates	Motorcycles
Fascia	Railroad Cars
Electronic Parts and Equipment	Vans

applications. Some of the important additives include are anti-oxidants, UV absorbers, wetting agents, anti-sagging agents, dispersants, defoamers, thixotropic agents, adhesion promoters, flatting agents, etc. [92].

MARKETS

The various types of polyurethanes are used in a number of market areas and end uses [33]. A number of these have been mentioned above. Two features of polyurethane coatings that often have been looked on as disadvantages are cost and special handing of the potentially hazardous isocyanates that are used in manufacturing or as curing agents. However, various industry segments have been able to develop safe handling and use methods that overcome one objection. The very high performance characteristics of polyurethanes, their ability to cure at low baking temperatures, and improved total coating solids, i.e., decreased volatile-organic-compound content, that can be obtained are factors that offset cost factors. For example, polyurethanes are replacing poly(vinyl chloride) plastisols as undercoatings and sealants in the automotive and other transportation markets. The ability to use lower coating thickness at equivalent or improved performance makes the applied cost of polyurethane competitive with the vinyl plastisols [93].

The textiles represent a moderate growth area for thermoplastic polyurethane lacquers with their excellent combination of properties as the main driving force for use. These include good elasticity at low temperatures, abrasion resistance, solvent and water resistance, dry cleansability, machine washability, and an ability to be manufactured with a broad variety of tensile/elongation properties [94]. In addition, high performance can be achieved with very thin coatings that do not markedly increase fabric weight or change styling factors such as drape. To decrease volatile organic content, new low viscosity, aliphatic isocyanates [95] and polyurethane polyols [96] are being developed. Although it is not a complete listing, Table 1 is a summary of many end uses for polyurethane coatings.

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Silicone Coatings[1]

D. J. Petraitis[2]

UNIQUE PROPERTIES OF SILICONES THAT MAKE THEM USEFUL AS COATINGS

SILICONE-BASED COATINGS ARE AMONG THE MOST useful materials for a wide variety of applications. Because the basic bond energies of Si–C and Si–O bonds are high, the chemical processes usually associated with aging of coated surfaces are often much slower and in many situations virtually eliminated for silicone coatings. Also, because the Si–C and Si–O bonds are not present in the natural organic world, biocompatibility and resistance to degradation via biochemical and biophysical processes are significantly reduced. In a similar manner, some silicone polymeric coatings and fluorosilicone-based coatings, in particular, have excellent solvent resistance.

Silicone coatings based on trifluoropropylmethyl polysiloxanes have resistance to swelling from such agents as gasoline, jet fuel, solvents, and various other reagents. Chemically, highly branched polymeric silicone coatings begin to approach the properties of silica surfaces as the organic pendant content is reduced. As the organic pendant groups are reduced, the $SiO_{4/2}$ content increases and the chemical resistance increases. Such polymeric coatings can provide physical scratch resistance as well as chemical resistance. Elastomeric silicone coatings, however, do not provide good resistance to strong acids and/or bases. Strong acids or bases, in particular at elevated temperatures, can cause depolymerization of the siloxane backbone, resulting in failure or, in the case of silicone elastomeric coatings, dissolution of the coating.

In a similar manner, silicone coatings are resistant to virtually all frequencies of the electromagnetic spectrum. For compliant coatings, silicones are unsurpassed in resistance to hard radiation, such as that from a Cobalt-60 source for doses in excess of 20 Mrd, as well as from the ultraviolet, visible, and infrared frequencies. When combined with their hydrophobicity, oxygen, and ozone resistance properties, silicones provide excellent weatherability characteristics, and when these properties are combined with the resistance to atomic oxygen encountered in low earth orbit conditions, silicone coatings provide protection for organic substrates in various spacecraft applications.

Coating various medical devices is another applications area that utilizes the high quality chemical and biochemical performance characteristics associated with silicone coatings. Such coatings are used to encapsulate and seal permanent implants such as heart pacemakers. They have also been used to coat temporary implants such as catheters and surgical drains. Thin elastomeric silicone coatings are used to provide soft tissue replacements by forming an envelope to encapsulate gels and/or normal saline solutions. Recent applications for biocompatible silicone coatings include drug delivery devices for both transdermal and long-term implantable, controlled-release drug delivery.

A final characteristic that makes silicone coatings useful is their inherently low or nonflammability. Typically, silicone elastomeric coatings have been rated SE-l when tested via Underwriters' Laboratories Flame Test (UL-94). This property makes silicone coatings ideal for conformal coating of various electrical circuits and devices. In the event of catastrophic thermal degradation, the silicone coatings can and do provide a SiO_2 "ash" coating that may permit the emergency operation of the electrical device on a short-term, temporary basis. Lynch et al. [1] have investigated silicone and other coatings as thermal barrier coatings. They found that the only system that met their requirements of protecting a thin steel plate during a direct flame impingement test and withstanding low temperature flexure tests was a fiberglass-polysilicone composite. Other investigators have studied the effect of silicone fabric coatings on mechanical properties when used in glass fabric/polyester composites [2] and on water absorption of such fabrics [3].

FORMS OF SILICONE COATINGS

Silicone coatings are available in various forms ranging from hard, rigid polymers, to compliant elastomeric products, to soft, almost gel-like, character materials. The rigid polymers are typically supplied in a solvent solution and are mixed with curing agents prior to application. Lead and zinc octoates are among the most common curing agents used. The cure process usually requires approximately 1 h at 250°C to attain complete cure. The cross-linking mechanism involves the condensation of silanol groups

$$\equiv SiOH + HOSi\equiv \rightarrow \equiv Si - O - Si\equiv + H_2O$$

Specific coating applications include jet engine components, furnace parts, incinerators, high-temperature appliances, and missile coatings. In addition, specific silicone polymers have been designed to mix with organic coatings and paints, providing improved performance under moderate heat environments than are realized by the organic materials alone.

[1] *This chapter is from the previous edition. The ASTM documents have been updated and/or added to, selected references have been added, and in certain instances the editor has added small amounts of information.*

[2] *Nusil Technology, 1050 Cindy Lane, Carpinteria, CA 93013.*

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By varying the R-group to Si ratio, the hardness of the final coatings can be changed. As the R:Si ratio is decreased, the cross-link density of the polymeric mass effectively increases. Similarly, variation of the R group itself can result in somewhat different flexibility and other physical properties. Properly designed and condensed resins can be formulated to provide hard, silica-like, abrasion-resistant coatings. Such coatings often involve the condensation of alkoxy groups with silanol groups as well as condensation between silanol groups alone. Technology to minimize shrinkage and maximize adhesion during the cure needs to be incorporated to prevent cracking and subsequent flaking of the coating from the substrate. Amino-functional alkoxy silanes are often incorporated into the formulation to simultaneously optimize cure rate and adhesion.

Silicone elastomeric coatings incorporate the use of polymeric siloxanes with appropriate cross-linking agents to provide compliant, flexible coatings. Among the cure mechanisms that result in elastomers are the following:

1. $\equiv SiOH + HSi\equiv \rightarrow \equiv Si–O–Si\equiv + H_2$ (Sn catalyst)
2. $\equiv SiOH + CH_3COOSi\equiv \rightarrow \equiv Si–O–Si\equiv + CH_3COOH$ (Sn catalyst and presence of water)
3. $\equiv SiOH + ROSi\equiv \rightarrow \equiv Si–O–Si\equiv + ROH$ (Sn catalyst)
4. $\equiv Si–CH=CH_2 + HSi\equiv \rightarrow \equiv SiCH_2CH_2Si\equiv$ (Platinum catalyst)
5. $\equiv SiOH + R_2NOSi\equiv \rightarrow \equiv Si–O–Si\equiv + R_2NOH$ (Sn catalyst and presence of water)

These elastomeric coatings can range from extremely tough, high-strength elastomers to soft gel-like coatings. Typically, the elastomers will have properties within the following ranges:

Durometer:	Type 00 = 10
	Type A = 70
Tensile strength:	0.34 to 13.8 MPa
Elongation:	50 % to 1500 %
Tear strength:	0.88 to 43.8 kN/m

The properties and the cure systems that are chosen for these elastomeric coatings depend, to a large extent, on the end use and the method of application. For instance, the SiOH + HSi (reaction 1) mechanism is often used to provide release coatings for backing paper used with pressure-sensitive adhesives. The actual coating itself has poor strength but attains its properties by simply impregnating the substrate and imparting its nonadhesive properties. Such coatings are repellent to tacky substances and a high level of repellency is achieved when the coating contains a considerable proportion of diorganosilicone units. Depending on particular end uses, various degrees of repellency are needed and this can be achieved by replacing methyl groups with alkenyl groups in the cross-linked coating [4]. Systems with slight adherent qualities have been developed using radiation-cure systems [5–7].

The acetoxy cure system (reaction 2) is used where one-package convenience is desired, where relatively slow cure is acceptable, and where the acetic acid given off during the cure is not a problem.

The oxime (reaction 5) cure system provides many of the properties of the acetoxy cure system, but results in an oxime-leaving group instead of an acetic acid-leaving group. Among the applications for the oxime cure systems are coatings for electronic components and protection for organic composites to prevent atomic oxygen degradation, and coating of quartz blankets to provide adequate emissivity and reflectivity characteristics for certain thermal protection surfaces on the space shuttle. The alkoxy 2-part (reaction 3) cure system, when combined with certain thermal enhancing fillers, such as iron oxide, glass microballoons, and various fibers, is often used to provide ablative and thermally insulating coatings. Various products incorporating the alkoxy two-part cure system are used to protect surfaces and components exposed to plume radiation from various rocket motors and jet engines.

The addition cure system (reaction 4) has characteristics that permit rapid heat-accelerated cure, tough physical properties, virtually nil shrinkage; and, due to the platinum catalyst, the best overall flame resistance. Applications include solar cell protection, particularly for satellites, and bum-through protection for the liners of solid rocket motors. The only negative characteristic of the addition cure system is its susceptibility to inhibition. Because the system contains parts-per-million levels of platinum catalyst, it can be readily "poisoned." Among the most common inhibitors are sulfur-containing organic rubbers and organo-tin compounds that are often used as plasticizers in plastics and also as catalysts for other silicone coatings.

There are other silicone elastomeric cure systems, and one of the most significant applications is to coat fiberglass blankets for fire resistance. Spark protection welding blankets are a common application for peroxide-cured silicone coatings. Since peroxide-cured silicones require higher temperature cures, their usefulness is constrained by the substrate upper temperature limits. Also, selectivity of the specific peroxide is critical to prevent poor cures due to the oxygen inhibition; a characteristic of many peroxides.

Another novel silicone elastomeric coating that has been developed is a combination cure involving the ultraviolet photoinitiation via free radical formation to provide cross-linking. This ultraviolet radiation mechanism is often combined with a standard cure mechanism to provide a combination cure. This system provides quick surface cure followed by a slower room temperature cure of unexposed, shadowed areas to ultimately provide a fully cured conformal coating important to the electronic applications area. Processes using the combination cure can be used to minimize the time and space required to hold the coated parts until cure is completed before downstream assemblies can take place.

Other cure systems have been developed for silicone elastomers, but they find limited use as coating materials and were generally developed for specific applications such as building sealants or glazing compounds. ASTM C1564, Standard Guide for Use of Silicone Sealants for Protective Glazing Systems, deals with the use of the sealants for building construction. Protective glazing includes applications that are subject to natural disasters, such as earthquakes, hurricanes, and windstorm, as well as forms of forced entry, such as blasts, burglary, and ballistic attack.

The most common form for silicone coatings is a dispersion of the silicone in an organic liquid. If the coating is based on a tough elastomeric silicone, the uncured elastomer base is most commonly described as a "dispersion" because it contains insoluble components such as

high surface area fumed silica for reinforcement and often other solid components such as titanium dioxide pigments for coloration or reflectivity properties. The carrier liquid for these dispersions may include chlorinated hydrocarbons, fluoro-chlorohydrocarbons, and both aromatic and aliphatic hydrocarbons. The dispersions also often include organic liquid blends to provide the proper combinations of flow, evaporation, and application ease. Among the most common liquids for silicone dispersions are 1,1,1-trichloroethane, VM&P naphthas, and xylene. Low-molecular-weight alcohols, such as ethanol and isopropanol, and ketones, such as acetone, are not suitable because silicones are generally incompatible with these lower-molecular-weight oxygen-containing solvents. Fluorosilicones require the use of such solvents as methyl ethyl ketone and methyl isobutyl ketone for adequate dispersion. Fluorosilicone-dimethyl copolymer-based silicones can be dispersed adequately in 1,1,1-trichloroethane for thin layer application.

True solutions can be made if the silicone contains no insoluble components. For example, true solutions can be made for unfilled silicones or for silicones that are polymer reinforced. These coatings have limited use, however, because the final cured elastomeric coating lacks the overall toughness of filled materials.

Recent developments have resulted in silicone coatings that have not involved the use of solvents. Because of environmental concerns, the use of solvent carriers for dispersions and solutions has become less desirable. In particular, fluorochlorocarbons and chlorinated hydrocarbons, despite their low toxicity and nonflammability, are being phased out because of international agreements. Similarly, hydrocarbon solvents are undesirable because of their flammability, toxicity, and environmental effects. Silicone-based conformal coatings have been developed without solvent carriers. However, thin layer applications are difficult unless the viscosity is low enough to permit proper coating. Unfortunately, the technology for high-strength, low-viscosity, 100 % solids silicone coatings does not exist. The current products, therefore, when cured, are very low strength and do not provide coatings that are resistant to handling. Research is ongoing to develop water-based dispersions, but to date, the demonstrated physical properties, although higher than the 100 % solids coatings, are significantly less than the solvent-based silicone coatings.

METHODS OF APPLICATION

The method used for application of silicone coatings to substrates depends on the article being coated and the specific type of silicone being used. Dipping, spraying, and brush painting are the most common types of application. The thinnest coatings result from spraying of two-solvent dispersions utilizing standard aerosol spray guns. Needless to say, experience involving aerosol spraying is critical for acceptable coatings. Among the variables to consider are viscosity, solvent, percent solids, pot life, and cure system choices.

The most securely sealed surface layer is accomplished by dip coating. Again, variables including solvent, bath life, and cure systems must be optimized. Additionally, the evaporation of solvent during the dip processing needs to be compensated for by periodically or continuously adding make-up solvent to maintain optimal dip-bath viscosity. If a one-part, humidity-actuated cure system is used for film formation, consideration must be given to provide a dry, inert blanket over the bath to prevent a partially cross-linked elastomeric skin from forming. Dry argon is often utilized to prevent moisture in the air from reacting with the silicone base coating. Another consideration for the dip coatings is the possibility of air bubble inclusion. Again, several variables need to be considered. Low viscosity, controlled immersion and withdrawal rates, and vibration of the bath and/or object to be coated can be used to minimize bubble entrapment. Similarly, two distinct liquids with different rates of evaporation are often used to ensure uniform coating with minimal drip regions and minimal bubble formation.

Painting or brush coating substrates is yet another method to apply a uniform silicone coating. Painting, however, is usually not applicable for either large areas or mass production coatings. For brush application, virtually all of the variables discussed in the above dipping and spraying also apply.

Regardless of the methods of application, the cure parameters demand significant considerations. Vacuum exposure may be used to remove air bubbles and to ensure flow under surface irregularities or impregnation of porous substrates. Vacuum treatment may also be used to enhance removal of the solvents, but care should be taken to prevent evaporation of the reactive volatile components that would prevent cure even after removal from the vacuum. Of course, most commonly, the vacuum removal of solvent is unwarranted and therefore solvent is merely evaporated at ambient pressures. The solvent evaporation can also be enhanced by air circulation and by the use of thermal energy. However, the application of heat should be limited or applied in a step-wise manner to prevent solvent entrapment below the surface resulting in bubble formation. Also, for one-part silicone coatings that are cured through moisture activation, it is ineffective to use heat acceleration because humidity is obviously reduced in a normal air circulating oven. If accelerated cure is required for one-part coatings, a steam autoclave may be used, but only after all of the carrier solvent is removed.

TESTING CONDITIONS

The test requirements for silicone coatings include MIL-I-46058C, Insulating Compound, Electrical (for Coating Printed Circuit Assemblies), for qualifying silicone coatings as insulating compounds for electrical coating applications of printed circuit board assemblies. MIL-I-46058C includes the following tests:

Curing Time and Temperature
Appearance
Coating Thickness
Fungus Resistance
Insulation Resistance
Dielectric Withstanding Voltage
Leakage Current Testing
Q Resonance
Q Resonance after Immersion
Thermal Shock
Flexibility
Thermal Humidity Aging
Flammability

Materials are used in spacecraft applications are evaluated by means of ASTM E595, Standard Test Method for

Total Mass Loss and Collected Volatile Condensable Materials from Outgassing in a Vacuum Environment. This test is used to determine the amount of collected volatile condensable material and total mass loss that leave the specimen from a material when exposed to 125°C for 24 h at a vacuum less than 7×10^{-3} Pa (5×10^{-5} torr) and condense on a collector set at 25°C. Basically, the maximum CVCM value for coatings intended for space applications is 0.1 % and the maximum TML is 1.0 %. The coatings intended for satellite applications require these high levels of purity to prevent the contamination of solar cells, optical surfaces, and other sensitive instrumentation. For most silicone materials, extended devolatilization is required for the polymeric components prior to compounding into the finished product.

For silicone elastomeric coatings, the physical properties of the cured elastomer are critical parameters. The tensile strength, elongation, and modulus are defined in ASTM D412, Standard Test Methods for Vulcanized Rubber and Thermoplastic Elastomers-Tension. Kim et al. [8] have investigated the interaction of thickness, modulus, and shear rate on adhesion forces involved in silicone coatings. Durometer and tear strength measurements are defined in ASTM D2240, Standard Test Method for Rubber Property-Durometer Hardness, and ASTM D624, Standard Test Method for Tear Strength of a Conventional Vulcanized Rubber and Thermoplastic Elastomers, respectively. The viscosity, nonvolatile content, and specific gravity tests are defined in ASTM D1084, Standard Test Methods for Viscosity of Adhesives, ASTM D2288, Standard Test Method for Weight Loss of Plasticizers on Heating, and ASTM D792, Standard Test Methods for Density and Specific Gravity (Relative Density) of Plastics by Displacement, respectively.

Other tests have been developed for silicone coatings to meet the requirements of specific applications. Included among these is the "blocking" test to determine the propensity of silicone coatings to cause "sticking" to contacted surfaces after application and cure. This test involves contact between the silicone-coated surface and the surface to be tested by subjecting the interface to an applied pressure for a fixed time followed by measurement of the force needed to separate the surfaces. A variety of tests have been developed to measure the adhesive force of the coating on the substrate. Again, a number of tests that are oriented toward the specific application have been developed and revised.

SPECIFIC APPLICATIONS FOR SILICONE COATINGS

Among the various applications for silicone coatings is the conformal coating of electronic circuit boards. Because of their previously described stability properties, silicones make ideal conformal coatings. Silicone coatings typically have stiffening points of 65°C, and can be formulated with stiffening points as low as 115°C. This makes them ideal for electronic device protection under extreme environmental conditions.

Investigators have developed a thermoformable coating comprised of a thermoplastic film containing microencapsulated silicone that can be vacuum formed onto an object as a removable protective coating for packaging electronic components or equipment [9]. During vacuum forming or melting onto, say, a printed circuit board, there is a release of the silicone from the microcapsules and a film of silicone with a protective thermoplastic top layer is formed. If desired, as in repair, the protective films may be removed by peeling. Removal is complete since the silicone will adhere more tightly to the thermoplastic film than the electronic equipment.

Recently, there have been a number of studies that deal with ship-hull and other fouling [10–14] and how silicone coatings can play a role in alleviating the problem. The studies are concerned with the release properties of silicone coatings and how these can eliminate or reduce fouling by barnacles, barnacle larvae, and other organisms or materials that cause fouling.

Silicone coatings are used almost exclusively to provide protection from atomic oxygen degradation in low earth orbit (approximately 100–500 miles high). Atomic oxygen degradation is sufficiently significant to cause rapid erosion and degrade organic substrates including epoxides, urethanes, and polyester-based thermoset coatings. Coating protection permits the use of composite materials in space applications where the advantages of high strength and low weight associated with composite materials would be unusable due to their atomic oxygen degradation.

The high-temperature stability and excellent dielectric properties of silicone polymers make them ideal impregnate coatings for high-energy capacitors used in jet engine ignitions. The inherent stability of silicone coatings when combined with specific fillers including zinc oxide, titanium dioxide, and zinc orthotitanate are often used to provide the specific emissivity and reflectance required for thermal-control coatings. Similarly, silicone elastomeric coatings that provide ablation protection are produced by the addition of iron oxide, glass or ceramic microballoons, or graphite fibers to the polymeric matrix. Launch vehicles launch equipment, and thrust reversers are often coated with specially formulated silicone ablative coatings. The incorporation of phenyl siloxanes into the basic silicone polymeric species provides increased ablative properties, and various copolymers—including silicone-boranes and silylphenylenes—have been and are being evaluated to provide protection from impingement of high-energy lasers.

As previously discussed, the biocompatibility of silicones makes them ideal for medical applications. Coating permanent implants as well as temporary implants with silicones provides improved safety and efficacy. Foley catheters coated with silicone elastomers result in less patient discomfort and reduced infection rates. For similar reasons, temporary pressure-sensitive silicone adhesive coatings are used to provide adhesion directly to the skin. Combinations of silicone coatings are being investigated for use in various drug delivery devices. Specifically layered coatings of silicones impregnated with drugs can be used for transdermal drug delivery. When combined with a silicone pressure-sensitive adhesive, a complete system of controlled drug delivery devices can be fabricated.

NEW REQUIREMENTS FOR SILICONE COATINGS

Research and development efforts continue to provide silicone coatings with even more stringent requirements and specifications. Electrical coatings with semiconducting properties for electronic applications and elastomeric coatings with volume resistivities in the 10^4–10^5 Ω cm range have been studied. Silicone coatings with variable electric properties are also being researched.

Similarly, silicone coatings that provide specific biological properties are also being developed. Specifically, hydrophilic silicone coatings are being developed for reduced

thrombogenicity, and microporous coatings are under development for controlled tissue in-growth response.

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Vinyl Polymers for Coatings

Joseph V. Koleske[1]

PREFACE

IN PREPARATION OF THIS CHAPTER, THE CONTENTS of the 14th edition of this manual were drawn upon. The author acknowledges the author of the chapter in the 14th edition, Richard J. Burns. The current edition will review, alter, and update the topics as addressed by the previous author and ensure that any ASTM documents cited are current.

VINYL POLYMERS FOR COATINGS

Definition

The vinyl polymers used in solvent-based coatings, inks, and adhesives are low to- medium molecular weight copolymers of vinyl chloride, vinyl acetate, or other monomers to improve solubility. Functional monomers contribute specific properties; thus, carboxylic acid-containing monomers provide adhesion, while hydroxyl-containing monomers contribute to reactivity, compatibility with other polymeric species, or adhesion to specific surfaces. These modified vinyl chloride copolymers are most often used as thermoplastic, solvent-soluble lacquers, though by formulating with appropriate cross-linking agents and modifiers, air-dry or baking finishes can be produced having thermoset-like properties.

Special techniques have been developed that enable the use of high molecular weight vinyl chloride homopolymers as dispersions in organic media called plastisols or organosols that require a heat fusion step to form films or coatings. Vinyl chloride homopolymers and copolymers are also compounded for use as powder coatings that can be applied by either electrostatic spray or fluidized bed techniques. Water-based vinyl chloride polymers and copolymers include high-molecular-weight polymer latexes that require heat to fuse, and also aqueous dispersions of low-molecular-weight polymers that utilize coalescents to form films at room temperature.

General

Important characteristic features of vinyl polymers/coatings are: (1) relatively high glass transition temperature; (2) excellent resistance to water, alcohols, aliphatic hydrocarbons, vegetable oils, dilute acids, and alkali; and (3) inertness in contact with foods [U.S. Food and Drug Administration (FDA)-listed polymers or copolymers only]. Vinyl copolymer films can be degraded by exposure to high temperatures or by long-term exposure to ultraviolet radiation, with a resultant change in color from clear to amber, red, and, with sufficient exposure, black. Suitable thermal stabilizers are employed to permit the processing of vinyl coatings at high temperature, and proper pigmentation helps to protect vinyl coatings from attack by ultraviolet radiation. Some stabilizer systems can provide limited protection to clear vinyl chloride copolymer films.

History

Between 1912 and about 1929, Ostromislensky pioneered investigations into the polymerization and properties of vinyl polymers, and he also made other valuable contributions to the development of poly(vinyl chloride) [1–4]. Early studies with this polymer showed that it was difficult to process and is thermally unstable. These factors hindered its early commercialization, and it was the development of thermal stabilizers as well as internal (comonomeric) and external plasticizers that opened the commercial door and has led to the wide usage of vinyl chloride polymers. Reid invented the copolymers of vinyl chloride and vinyl acetate [5,6]. In 1933, Davidson and McClure described various applications for vinyl polymers and copolymers including their use as swimming pool coatings [7].

Commercial production of vinyl chloride–vinyl acetate copolymers began in 1936. Carboxyl-modified copolymers were introduced in 1939 and hydroxyl-modified copolymers in 1945. The first commercial use of these vinyl copolymers was in 1936 as a coating used as the sanitary interior lining of beer cans.

In general, the above described copolymers are of relatively low to moderate molecular weight. The viscosity requirements of spray and roll coating applications do not permit the use of very high molecular weight vinyl chloride polymers. In about 1943, organosol and plastisol coating technology that allowed use of such very high molecular weight polymers was developed [8,9].

Polymerization

Vinyl chloride monomer is a gas at standard conditions with a boiling point of –13.9°C. Polymerization is carried out in an autoclave under moderate to high pressure. The reaction is typically initiated by free radical-generating compounds such as peroxides. The polymerization is exothermic, and reaction temperature regulation is necessary to control the growth (molecular weight increases) of the polymer. The use of high pressure and low temperature generally favors the formation of very high molecular weight polymers. To control molecular weight, chain transfer agents are commonly employed. The number-average molecular weight (M_n) of commercially available solvent-soluble vinyl chloride homopolymers and copolymers ranges from a low of a few thousand to about 45,000. The M_n of vinyl chloride

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polymers used for plastisol and organosol coatings ranges between about 60,000 to 110,000 [10].

Manufacture

Vinyl polymers manufactured for the coatings market are made by several processes. Polymerization by the solution and suspension processes is used to make solvent-soluble polymers, while emulsion or dispersion polymerization is used to make much higher molecular weight polymers for plastisols and organosols. Some solvent-soluble grades are also made by the emulsion process. Post-polymerization processes are applied to some copolymers to achieve special properties. The following are brief descriptions of the manufacturing processes. Detailed information is available in many books dealing with vinyl and in particular vinyl chloride-containing polymers In addition, a relatively detailed, but still concise, description of the processes including flow diagrams is available in a government publication [11].

Bulk Process

In the bulk polymerization of most monomers, the monomer acts as a solvent for the initiator and the forming polymer with the end product being a solid mass of polymer. However, in the case of vinyl chloride, polymerization takes place in solution only during the early stages. As the polymer particles grow and reach a sufficient size, they precipitate as a fine powder and polymerization continues in the solid phase of these particles. A slurry results and when the reaction is about 50 % completed, it becomes necessary to separate and remove the polymer particles from the slurry. If this is not done, an extremely rapid, dangerous reaction takes place because of poor heat transfer and autoacceleration [12].

Solution Process

Polymerization is carried out in a solvent in a batch or continuous process. The viscosity of the reaction medium increases as monomer is converted to polymer, and the extent of polymerization can be monitored and controlled by viscosity measurements. When the appropriate viscosity is attained, the autoclave polymer solution is stripped of unreacted vinyl chloride monomer, and the polymer is precipitated in a controlled manner by the addition of water, water/alcohol mixtures, or other precipitant. The slurry is next centrifuged to remove most of the liquid, and the co-polymer is dried in fluid-bed dryers. The particle size of the dried polymers produced by this process ranges from about 75 to about 200 μm. Final particle shape is irregular in nature.

Suspension Polymerization

Suspension polymerization involves the mechanical dispersion of monomer in an aqueous medium. High-molecular-weight, water-soluble colloidal polymers are used in small amounts to stabilize the droplets of suspended monomer(s) and to control particle size. The stabilizer used remains with the polymer during and after polymerization and final polymer recovery. The monomers and associated materials (initiator, stabilizer) exist as discrete, small droplets before and during polymerization and form the final polymer particles after polymerization. The initiator is soluble in the monomer mixture.

Usually, when solutions of suspension vinyl polymers are prepared, mild heating is required to achieve maximum solution clarity at minimum viscosity. Particles of suspension vinyl polymers are characterized as spherical in shape with a size between 100 and 300 μm.

Emulsion Polymerization

Like the suspension process, emulsion polymerization is also carried out in aqueous media, but in place of water-soluble polymers as stabilizers, surfactants are normally used to form and stabilize the very small monomer droplets associated with this process during polymerization. Another differentiation from the suspension process is that in the emulsion process the initiator is soluble in the media rather than in the monomer droplets. A special form of emulsion polymerization called "dispersion polymerization" uses an oil-soluble rather than water-soluble initiator and produces polymer particles that range from about 0.2 to 2 μm in size. These high molecular weight powdered products are used in plastisol and organosol coatings.

Post-Polymerization Process

Some vinyl-alcohol modified polymers are prepared in a two-step process. The first step consists of the preparation of a vinyl chloride-vinyl acetate copolymer by either a solution or suspension process. Next, the copolymer is dissolved in a suitable solvent and a reactant is added to partially hydrolyze the pendant acetoxy groups and yield a vinyl alcohol moiety.[2] The modified polymer is then precipitated from solution and dried as described for the solution process. The vinyl chloride/vinyl alcohol/vinyl acetate or vinyl chloride/vinyl alcohol copolymer thus formed has only secondary hydroxyl groups. These polar groups account for the copolymers' unique solubility/compatibility properties.

These vinyl-alcohol-containing polymers differ from those prepared directly using other hydroxyl-containing monomers in their compatibility with alkyds and in the rate of reactivity with co-reactants such as polyfunctional isocyanates or amino-formaldehyde cross-linking agents.

Applications for Vinyl Chloride-Based Copolymer Coatings

The main solvent-soluble vinyl chloride copolymers available in industry are described in Table 1. These copolymers produced by the solution polymerization process are based on vinyl chloride/vinyl acetate copolymers, and they have the following generalized compositions.

1. Vinyl chloride/vinyl acetate copolymers.
2. Carboxyl-modified vinyl chloride/vinyl acetate copolymers.
3. Hydroxyl-modified copolymers of two types:
   a. Hydroxyalkyl acrylate modified vinyl chloride/vinyl acetate copolymers via direct polymerization.
   b. Vinyl alcohol-modified copolymer derived from vinyl chloride-vinyl acetate copolymer in a post-polymerization reaction process.
4. Carboxyl/hydroxyl modified vinyl chloride/vinyl acetate copolymers
5. Sulfonate modified vinyl chloride/vinyl acetate copolymers.

[2] It is well known that vinyl alcohol does not exist as a monomer and thus its use in a direct polymerization step is not possible.

TABLE 1—Typical (i.e., not specifications) properties of vinyl chloride copolymers for coatings [13,14]. Specific Gravity of the copolymers vary from 1.34 to 1.39 [determined by ASTM D792, Standard Test Methods for Density and Specific Gravity (Relative Density) of Plastics by Displacement].

Copolymer Composition, wt %			Reactive Functionality			Solution Viscosity			Molecular Weight Number Average[b]	Glass Transition Temperature°C
Vinyl Chloride	Vinyl Acetate	Other Monomer	Type	wt %	Inherent Viscosity[a]	Centipoise	Solids, wt %	Solvent, MEK/ toluene		
90	10	. . .	None	. . .	0.74	250	15	67/33	44 000	79
86	14	. . .	None	. . .	0.50	200	20	50/50	27 000	72
86	14	. . .	None	. . .	0.40	175	25	33/67	22 000	72
80	13	1[c]	Carboxyl	1.0	0.50	150	20	50/50	27 000	74
83	16	1[c]	Carboxyl	1.0	0.38	250	25	25/75	19 000	72
81	17	2[c]	Carboxyl	2.0	0.32	370	30	25/75	15 000	70
90	4	6[d]	Hydroxyl	2.3	0.53	350	20	50/50	27 000	79
90	4	6[d]	Hydroxyl	2.3	0.44	400	25	50/50	22 000	77
81	4	15[e]	Hydroxyl	1.8	0.56	171	20	50/50	33 000	70
81	4	15[e]	Hydroxyl	1.9	0.44	184	30	50/50	24 000	65
81	4	15[e]	Hydroxyl	2.0	0.30	340	30	25/75	15 000	65
82	4	14[c,e]	Hydroxyl/ carboxyl	2.0	0.56	170	20	50/50	35 000	72
85	13	2[f]	Sulfonate	1.0	0.33	500	20	50/50	17 000	72

[a] Determined by ASTM D1243, Standard Test Method for Dilute Solution Viscosity of Vinyl Chloride Polymers.
[b] Based on a polystyrene standard.
[c] Maleic Acid.
[d] Vinyl Alcohol.
[e] Hydroxyalkyl acrylate.
[f] Sulfonate-containing monomer.

Soluble polymers similar to those described in Table 1 and prepared by either a solution or suspension process are available from various suppliers.

Food and Drug Administration Considerations

FDA regulations for various end uses list vinyl chloride copolymers by chemical identity. Designations for adhesives and coatings used on food contact surfaces are listed in Table 2. Particular copolymers are listed in these documents by chemical identity are for use on metal and paper substrates that are used as food contact surfaces of articles used in processing, manufacturing, packing, producing, heating, packaging, holding, or transporting food, or as components of closures with sealing gaskets for food containers. Vinyl chloride/acetate copolymers, hydroxyl-modified vinyl chloride-acetate copolymer, and several other vinyl chloride copolymers made with monomers having acid or ester functionality are commercially available. Regulations such as these are subject to change or expansion, so users should always search for up-to-date FDA information.

Vinyl Chloride Copolymers—Analysis

There are many references to chemical methods for identifying and characterizing vinyl chloride copolymers [15]. Infrared spectra of vinyl polymers are very useful for qualitative and quantitative purposes. Spectra of neat vinyl polymers can be found in a variety of sources such as atlases, encyclopedia of plastics, or specific papers dealing with the subject [16–18]. Also, several ASTM documents deal with the identification and characterization of vinyl polymers used in coatings materials.

ASTM D2621, Standard Test Method for Infrared Identification of Vehicle Solids From Solvent-Reducible Paints, details the qualitative characterization of separated paint vehicle solids by infrared spectroscopy. An analysis spectrum for an ortho-phthalic alkyd, vinyl chloride-acetate modified vehicle is detailed.

ASTM D2124, Standard Test Method for Analysis of Components in Poly(Vinyl Chloride) Compounds Using an Infrared Spectrophotometric Technique, presents methods through which vinyl systems can be separated into components including polymers, copolymers, plasticizers, stabilizers, and fillers. Each component can then be analyzed by infrared techniques.

A particularly useful document was ASTM D4368, Standard Guide for Testing Poly(Vinyl Chloride) Resins. Unfortunately, this standard guide was withdrawn in 2005. The ASTM website indicates that a working document

TABLE 2—United States Food and Drug Administration (FDA) regulations [14]	
FDA Regulation[a]	**Intended Use**
21CFR 175.105	In adhesives used in articles intended to be used for holding, packaging, or transporting food
21CFR 175.300(b)(3)(XV)	In polymeric coatings used as continuous films for food contact surfaces intended for use in heating, holding, manufacturing, packaging, packing, processing, producing, or transporting food.
21CFR 175.320	As coating components for coatings to be applied as a continuous film on one or both sides of a base polyolefin film that is in compliance with 21CFR 177.1520.
21CFR 176.170(b)	Component of coatings on food contact surfaces of paper and paperboard used to package aqueous and fatty foods.
21CFR 176.180	Component of coatings on food contact surfaces of paper and paperboard that will be in contact with dry food.
21CFR 177.1210	Components of coatings used on closures with sealing gaskets used for food containers.
[a] Regulations such as these are found in the Code of Federal Regulations (CFR) and users should be aware that they can be and are revised from time to time.	

exists, so there may be a replacement in the future. ASTM D4368 described methods for testing homo- and copolymer vinyl chloride-containing polymers to determine important characteristics such as total chlorine content of the composition, dilute solution viscometry to assess polymer molecular weight, and high and low shear viscosity measurements to characterize vinyl dispersion polymers that are used for plastisols and organosols.

Formulation of Solution Coatings

Typical vinyl coatings formulations consist of copolymer, solvent(s), plasticizer, pigments (required for exterior exposure), and optional ingredients such as stabilizers, modifying polymers(s), and cross-linking agent(s).

The polymer, almost always a copolymer, is normally selected on the basis of its ability to provide adhesion to the substrate. While, in most cases, strong adhesion is desired, there are special coatings such as strippable or peelable coatings where adhesion is not wanted. Table 3 contains the relative adhesion of a few vinyl copolymers to various polymers and substrates. The copolymer selection may be made on the need for reactive functionality to produce cross-linked coatings that change the nature of the coating from thermoplastic to thermoset a factor that is characterized by improved solvent and/or stain resistance in the final coating.

Solubility

Variation in the ratio of vinyl chloride to vinyl acetate, the degree of polymerization, and the modifying third monomer results in a wide variety of vinyl copolymers with different solubility characteristics. Highest solubility is favored by low vinyl chloride content and low molecular weight. This relationship in terms of copolymer solution viscosity is apparent from the viscosity data given in Table 1.

Vinyl solution-polymerized copolymers can be dissolved in ketones, esters, certain chlorinated solvents, and some nitroparaffins. As a class, ketones are the best solvents in terms of the ability to dissolve large amounts of solids with minimal solution viscosity. Hydrocarbons are chiefly used as diluents primarily to lower cost. Both aromatic and aliphatic hydrocarbons can be used as diluents. Aromatic hydrocarbons, particularly toluene and xylene as well as higher boiling fractions such as Aromatic 100 or 150, are preferred because they can be used at high levels, in the range of 50 %–65 % of the solvent blend depending on the copolymer composition, molecular weight, and desired solids. The Aromatic 100 and 150 are usually used only in baking finishes.

Aliphatic hydrocarbons can be used in limited amounts, up to about 30 % of the solvent blend. Higher levels can lead to viscosity instability, and only low boiling aliphatic hydrocarbons, those with boiling points up to 117°C, are suitable. The use of higher boiling aliphatic hydrocarbons can cause

TABLE 3—Adhesion of vinyl copolymers to various substrates. Rating: 10 = pass scotch tape test, no loss of adhesion; 5 = some loss of adhesion, not recommended; 0 = no adhesion

	Vinyl Chloride/Vinyl Acetate Copolymer		
Substrate	**No modification**	**Carboxyl modified**	**Hydroxyl modified**
Steel	0	10	0
Galvanized	0	10	0
Paper (glassine)	10	10	10
Aluminum Foil	0	10	10
Polyethylene, treated	0	0	0
Polypropylene, treated	0	0	0
Polysulfone	7	10	10
Acrylic	10	10	10
PVC Plastic	10	10	10
ABS Plastic	10	10	10
Polycarbonate	10	10	10
Poly(phenylene oxide)	4	10	0
Poly(ethylene terephtalate)	0	0	0
Impact Polystyrene	0	0	0
Inked Surface	0	5	5

TABLE 4—Typical solvent mixtures for spray applied coatings, compositions in wt %

Non Regulated Mixture		Rule 66 Compliant Mixture		Rule 66/EPA 33/50 Initiative Compliant Mixture	
Methyl isobutyl ketone	50	Methyl ethyl ketone	14	Methyl ethyl ketone	7
Toluene or xylene	50	Butyl acetate	46	Acetone	3
	100 %	Cyclohexanone	9	Methyl isoamyl ketone	15
		Toluene	12	Butyl acetate	40
		Xylene	7	Cyclohexanone	9
		VM&P Naphtha	12	Toluene	6
			100 %	VM&P Naphtha	20
					100 %

precipitation of the copolymer during film formation and final drying. Alcohols are strong precipitants for vinyls and generally are not used in unmodified vinyl copolymer lacquers. However, in some cases vinyl copolymers, usually hydroxyl-modified versions, are readily formulated with other polymers, oligomers, or copolymers that are alcohol soluble. With these, up to 15 %–20 % alcohol may be used in the solvent blend. Careful attention must be paid in vinyl coating formulations that contain alcohols to ensure that problems do not develop during application and drying of the coatings. Glycol ethers and glycol ether esters are sometimes used in vinyl coatings to improve "flow out" of baked coatings.

In response to regulations restricting the type and amount of solvents used in coatings, such as the early forerunner regulation known as the "Los Angeles Rule 66" and later versions,[3] vinyl coatings were reformulated as compliant systems by reducing the amount of branched ketones and aromatic hydrocarbons and making up the difference with esters and aliphatic hydrocarbons [19]. Though it was necessary to use more oxygenated solvents, the performance requirements of compliant coatings remained the same. Table 4 has some typical solvent blends that had been used for spray applications and the reformulated compliant systems. These particular mixtures are for demonstration purposes to illustrate how regulations can markedly change formulations.

Solution Characteristics

From the time a vinyl polymer is dissolved, the viscosity of solutions increases with time until equilibrium is reached, after which the viscosity remains constant. This behavior is believed to be due to the formation of regions of microcrystallinity or other strong association between polymer molecules in solution. The extent of the viscosity increase is dependent on (a) polymer molecular weight, (b) solids content of the solution, and (c) the "strength"[4] of the solvent blend. The viscosity increase may be small or so large that the solution sets to a gel. Properly formulated vinyl polymer solutions usually reach an equilibrium viscosity in about 3–5 weeks. Guidelines for the preparation of viscosity-stable solutions for polymer of varying molecular weight are shown in Table 5.

Vinyl chloride copolymer solutions also exhibit what is known as the "memory effect." When a vinyl chloride copolymer solution is heated to about 60°C, the effect of microcrystallinity is eliminated. If the solution is then cooled to its original temperature, the viscosity will not immediately return to its original value because of the time lag needed for the effect of the microcrystallinity to redevelop. With time, the viscosity of the solution will return to the same value as it had before the heating process. The converse relationship holds when vinyl chloride copolymer solutions are cooled below the original storage temperature and then returned to the original condition. A graphical representation of the memory effect is given in Fig. 1.

Plasticizers

Internal plasticization of vinyl chloride polymers is achieved by copolymerization of vinyl chloride with monomers such as vinyl acetate. The comonomer reduces softening and processing temperatures and markedly improves solubility. However, such copolymerization often cannot achieve all of the desired physical flexibility and toughness characteristics required in many end uses. Plasticizers are often used with vinyl chloride copolymers to improve flexibility, formability, and impact resistance of the coating. Monomeric as well as polymeric plasticizers or compatible polymers with low glass transition temperature (T_g) may be used to plasticize a vinyl coating.

Phthalate, phosphate, and glycol ester plasticizers are typically used. Plasticizers are selected to meet the requirements of the coating that may include low-temperature flexibility, resistance to extraction by solvents, resistance to migration, to humidity, etc. Blends of plasticizers may be required to meet specific requirements. FDA regulations as well as other health considerations must be taken into account when selecting these additives.

Table 6 presents a listing of plasticizers that have been commonly used with vinyl copolymers.[5] Care must be exercised in choosing the level of plasticizer since excessive amounts tend to make the film soft and prone to dirt retention and can lead to oozing from the surface under certain conditions. Ordinarily, a level of 25 phr (parts per hundred

[3] See chapters in this manual that deal with regulations and with solvents.

[4] "Strength" in this case refers to the quality of the solvent and its ability to alter the size, configuration, and conformation of the dissolved molecules.

[5] Also see the chapter in this manual that deals with plasticizers in general.

TABLE 5—Guidelines for viscosity stable solutions

Composition[a]	Third Monomer	M_n[b]	Maximum Solids	Typical Solvent Blend, wt %[c]
90/10/0	None	44 000	15	MEK/toluene, 67/33
86/14/0	None	27 000	25	MIBK/toluene, 50/50
86/14/0	None	22 000	28	MIBK/toluene, 50/50
86/13/1	Maleic acid	27 000	25	MIBK/toluene, 50/50
83/16/1	Maleic acid	19 000	28	MIBK/toluene, 50/50
81/17/2	Maleic acid	15 000	33	MIBK/toluene, 33/67
90/4/6	Vinyl alcohol	27 000	25	MIBK/toluene, 50/50
90/4/6	Vinyl alcohol	22 000	28	MIBK/toluene, 50/50
81/4/15	Hydroxyalkyl acrylate	33 000	25	MIBK/toluene, 50/50
81/4/15	Hydroxyalkyl acrylate	24 000	28	MIBK/toluene, 50/50
81/4/15	Hydroxyalkyl acrylate	15 000	33	MIBK/toluene, 33/67

[a]Vinyl chloride/vinyl acetate/third monomer, weight percentages.
[b]Number average molecular weight, polystyrene reference standard.
[c]MEK is methyl ethyl ketone and MIBK is methyl isobutyl ketone.

parts polymer) plasticizer is considered about maximum for use with coating polymers.

Pigmentation

Vinyl copolymer coatings are pigmented (1) to achieve the desired colors and other aesthetic characteristics and (2) to prevent degradation of the vinyl copolymer caused by ultraviolet radiation when they are to be used outdoors [20]. Most organic and inorganic pigments can be used. However, basic pigments must be avoided with carboxyl-modified copolymers since these pigments can and probably will react with the copolymer to form irreversible gel and may alter the desired color.

Prime or color pigments that absorb ultraviolet radiation must be used at a level sufficient to protect the vinyl copolymer. Extender pigments or fillers do not absorb ultraviolet radiation and can only be used in combination with an ultraviolet-radiation adsorbing pigment, such as titanium dioxide (TiO_2). A minimum level of about 75 phr TiO_2 is required to provide resistance to ultraviolet radiation. Other inorganic pigments can be used to replace TiO_2 by substituting on an equal volume basis. Organic pigments that are manufactured with very small particle size are used at a lower concentration, and blends of inorganic

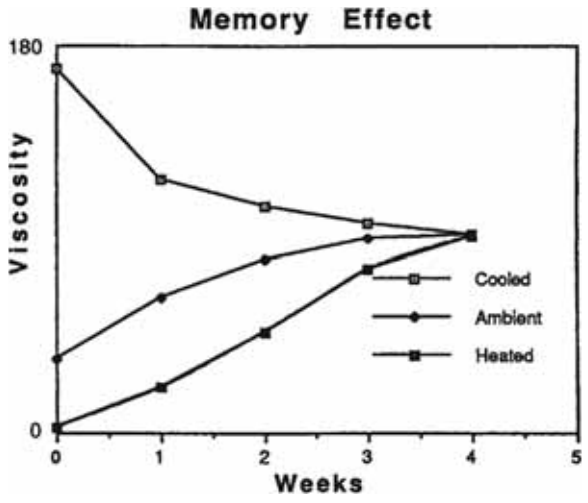

Fig. 1—Memory effect in vinyl chloride copolymer solutions.

TABLE 6—Typical plasticizers that are compatible with solution vinyl chloride-based copolymers. Note—some of these plasticizers may be out of favor for health reasons, but all are compatible with solution vinyl chloride copolymers. Any users should check with suppliers regarding health considerations.

Phthalates	Linear Dibasic Acid Esters
Butyl benzyl phthalate (BBP)	Di-n-butyl sebacate (DBS)
Di-2-ethylhexyl phthalate (DOP)	Di-2-ethylhexyl adipate (DOA)
Di-isooctyl phthalate (DIOP)	Di-isononyl adipate (DINA)
Di-isononyl phthalate (DINP)	Di-2-ethylhexyl azelate (DOZ)
Di-isodecyl phthalate (DIDP	
Citrates	Phosphates
Acetyl tri-n-butyl citrate	Tri-2-ethylhexyl phosphate (TOP)
	Isodecyl diphenyl phosphate
Epoxides	Polymerics
Epoxidized soybean oil (ESO)	Adipic acid polyesters
2-Ethylhexyl epoxytallate	Azelaic acid polyesters

and organic pigments are often used to achieve the desired color. Excessively high pigment concentrations can lead to early chalking.

Organosols and Plastisols

A plastisol is a dispersion of discreet particles of high molecular weight vinyl chloride homopolymer in plasticizer. The combination almost always contains a low level of thermal stabilizer in sufficient quantity to prevent degradation during the baking or fusing process. Plastisols normally require a minimum amount of about 55–60 parts plasticizer per hundred parts of polymer to form a fluid mixture. The viscosity of the dispersion is dependent on particle packing effects, the volume of dispersed polymer relative to the volume of liquid plasticizer, the size and shape of the suspended particles, solvating or swelling effect of the plasticizer on the polymer particles, and the viscosity of the liquid plasticizer. The relatively high levels of plasticizer needed to produce a flowable liquid mix results in the formation of fused films that are too soft for use as coatings.

Plastisol coatings are usually formulated from the addition of coarse particle-size poly(vinyl chloride) called extenders to the mix. These extenders are obtained from suspension or bulk (mass) polymerization and allow the use of less plasticizer and useful films with improved hardness result. Additionally, small amounts of thinner, usually aliphatic hydrocarbon are used (up to about 10 wt %) to reduce viscosity and provide better flow and leveling of the plastisol coating. Plastisol coatings do not adhere well to most substrates and most often require the use of a suitable primer before application.

An organosol differs from a plastisol in that much lower levels of plasticizer are used. Combinations of weak solvents that are termed "dispersants" in combination with hydrocarbon solvents, termed "diluents," are used to provide sufficient liquid to make a fluid dispersion. Because lower levels of plasticizer are used, films with much greater hardness can be obtained.

Commercial organosols are usually modified with a solvent-soluble polymer to prevent mud cracking or film splitting during the bake used to fuse the film. The modifier polymer at times contains carboxyl functionality to make the coating self-adherent. In other instances, it may be a hydroxyl-containing copolymer to provide functionality for reaction with cross-linking agents, such as amino or phenol/formaldehyde oligomers and thus achieve a degree of thermoset properties. Though vinyl chloride copolymers are usually the preferred modifier for organosols, other polymers, such as acrylic polymers, are used.

Careful consideration must be given to the selection of the solvent/diluent mixture for organosols, if one is to attain the highest solids coupled with good viscosity stability. Commercial organosols of 50 %–55 % non-volatiles by weight are typical.

Plastisols and organosols require a high baking temperature of about 350°F (177°C) to fuse the films. At elevated temperatures, the plasticizer or plasticizer diluent mixture exerts a strong solvating or swelling effect on the dispersed poly(vinyl chloride) particles. At fusion, the polymer no longer exists in discreet particle forms, but rather as a continuous homogeneous film. Films of plastisols or organosols need to only reach fusion temperature, and they do not need to be held at the fusion temperature for a long time period to form the final film. Undercuring or baking at temperatures lower than that required for fusion will yield films deficient in tensile strength, elongation, abrasion resistance, and other properties.

Plastisols and organosols also require the use of thermal stabilizers to protect the vinyl polymer against degradation during the fusion/bake operation. Thermal stabilizers are usually combinations of metal salts of organic acids in combination with epoxidized oils or liquid epoxy compounds. Special attention must be given to the selection of thermal stabilizers for organosols modified with solvent-soluble polymers, especially when carboxyl-modified polymers are used. In such cases, metallic salts must be avoided as these will usually cause gellation; typically, mercapto tin or tin ester compounds are used in combination with an epoxy stabilizer.

The type pigment and pigment concentration used in pigmented organosols follow the guidelines given for solution vinyl copolymers. It is, however, more difficult to prepare pigmented plastisols because there is generally little solvent used to control viscosity. Low oil absorption pigments must be used to avoid excessively high viscosity and difficult-to-work-with formulations.

Primers for Plastisols and Organosols

To develop good adhesion when used on metal substrates, plastisol coatings require a primer. An organosol coating may also require a primer if it is not modified with an adhesion-promoting modifier. Suitable primers can be formulated from carboxyl-modified vinyl copolymers and may require employing thermoset technology for best results. This is accomplished by using cross-linking agents such as amino-formaldehyde or phenolic compounds to provide resistance to excessive softening from highly plasticized plastisol or organosol coatings.

MAJOR MARKET AREAS FOR VINYL COPOLYMER COATINGS

Rigid Packaging

LINERS FOR INTERIOR SURFACE COATINGS, CANS, CAN ENDS, CLOSURE/CAPS AND CROWNS

The first commercial use for vinyl chloride copolymer coatings was as the topcoat lacquer used on the inside of beer cans. As beverage cans evolved from three- to two-piece construction, the vinyl coating also changed from lacquer to hydroxyl-functional vinyl chloride copolymers in combination with amino-formaldehyde cross-linking agents. Thermoset coatings, such as these, were needed to meet the need for greater corrosion conditions encountered. Thermoset coatings of epoxy-modified vinyl chloride copolymers with carboxyl-modified vinyl copolymers were used to coat coil stock. The coated coil stock is then formed into the stay-on-tab can ends, an application that requires excellent mechanical properties to withstand the forming steps without cracking. Organosol coatings containing a solution vinyl copolymer component, usually carboxyl-type for adhesion, have also been used on precoated stock for can ends. Vinyl organosols are further modified with amino-formaldehyde or phenolic compounds to upgrade chemical resistance and permit the use of such coatings for packaging food that will be autoclaved to sterilize the contents [21].

Vinyl lacquer and vinyl thermoset coatings are used as size coats for metals that are formed in caps and closures for jars or as crowns for beverage bottles. These systems serve as the primer coat for gasketing compounds made with plastisol or vinyl copolymer dry blends.

Flexible Packaging

Solvent-soluble carboxyl-modified vinyl chloride copolymers have good adhesion to most materials used in flexible or semi-rigid packaging including aluminum foil, paper, and plastic films, such as poly(ethylene terephthalate), polycarbonate, poly (vinyl chloride), and cellophane. This type copolymer is used for its adhesion characteristics, ease of heat sealing, and resistance to attack by the packaged product. The vinyl copolymer may be used alone or modified with plasticizers or other compounds and polymers to formulate heat-sealable coatings for applications requiring varying degrees of force needed to open the container. This could range from applications such as blister packaging where the bond needs to be strong enough to cause substrate failure when the package is opened, to items such as jellies or cream containers found in restaurants where a tight but readily peel-able bond is required.

Vinyl coatings are also used to coat collapsible metal tubes for packaging materials such as pharmaceutical preparations, toothpastes, and the like where the need is for a very flexible coating that will not crack nor be attacked by the contents of the package even though high stresses from collapsing and rolling up the tube are encountered multiple times.

Other applications include decorative coatings for aluminum foil/paper laminates used in cigarette packaging, food wrappers for fast food restaurant items, for butter, margarine, soups, and so on. Decorative foil for floral wrappings, decorative labels, and coatings for aluminum foil used on vapor barrier insulation in construction applications are also coated with vinyl copolymers.

Inks and Overprint Coatings

The major markets for vinyl copolymer-based inks are for products that have a vinyl surface such as floor and wall coverings, swimming pool liners, vinyl upholstery, and garment fabrics. The main reason for use on these substrates is related to excellent adhesion as well as the toughness, elongation, and stain resistance that are obtained with overprint lacquers—usually transparent wear layers. Other areas of importance include treated poly(ethylene terephthalate) and polyolefin films, aluminum, paper composites, and metalized substrates. Ink formulation is quite similar to that used when formulating coatings except solvent choices are somewhat narrowed and higher pigment or other colorant loadings are needed to achieve hiding in the thin films typical of inks.

Vinyl inks are often reverse printed on a clear vinyl or other polymeric film, and the printed film is then laminated to substrates such as wood or metal to make articles having simulated wood finish. Vinyl inks are also printed by the gravure or screen process because these presses are compatible with the strong solvents needed for vinyls. Flexographic printing is not suitable for vinyls because the plates are susceptible to solvent attack. Inks for highly plasticized vinyl surfaces are usually formulated with ester solvents to avoid excessive softening of calendered films and puckering of the films.

Dry Film Printing (Hot-Stamp Transfer Process)

Dry film printing involves printing vinyl inks onto a carrier film such as poly(ethylene terephthalate), polyethylene, polypropylene, or other suitable surfaces to which the ink will not strongly adhere. The inks are applied and dried usually in web form. When ready for use, the printed carrier film is placed with the inked side on the surface to be decorated. A heated die presses the composite to make intimate contact with the surface so that when the die is removed, the ink is firmly bonded to the substrate and the carrier is cleanly peeled away.

Maintenance and Marine Finishes

Heavy duty marine finishes were developed in the mid-1940s. These systems were comprised of a poly(vinyl butyral) wash primer, vinyl chloride copolymer red lead anti-corrosive intermediate coatings (based on vinyl alcohol modified copolymers, which were needed to provide adhesion to wash primer), and vinyl copolymer/wood rosin/cuprous oxide anti-foul top coats. Such systems have become the subject of numerous specifications. Many United States government agencies as well as agencies of other governments have written specifications with such a coating system specified for use below the waterline of marine vessels.

Because of their good water resistance, weathering qualities, flexibility, fast drying characteristics, ease of application, and repair, vinyl chloride-based copolymers quickly became established as maintenance finishes. This application area includes coatings for locks, dams, appurtenant structures for waterways, interior linings for potable water tanks, steel structures such as bridges, electrical towers, equipment in chemical plants, dams and locks, storage tanks, and the like. Many specifications have been written that require the use of vinyl copolymers as maintenance paints [22,23].

Air atomizing spray guns at low solids were used for application of vinyl maintenance and marine coatings in the early usage days. The low solids required several coats to attain coverage sufficient for good corrosion protection. High-build airless spray-applied vinyl coatings were developed in the 1970s to fill the need for coatings systems that could be applied in fewer coats at less expense [24].

Wood Finishes

Reactive heavy-duty vinyl finishes, coatings and sealants for wood have been developed. These consist of a hydroxyl-modified vinyl chloride copolymer cross-linked with amino/formaldehyde compounds. Alkyd copolymers were often added to improve film build. Such finishes became established as the standard for kitchen cabinets because of their retention of excellent adhesion and water resistance, particularly when the coated wood becomes wet from high humidity or water splashing. These finishes also have excellent resistance to a variety of household chemicals, solvents, and stains and have been used as fine furniture finishes [25].

Magnetic Recording Media

Vinyl chloride copolymers, especially hydroxyl-modified copolymers, have been used as binders for magnetic iron oxide tapes since the beginning of the development of tape recording. The vinyl copolymers are used because of their good adhesion, abrasion resistance, and pigment wetting properties. The early binder formulations used alkyd

copolymers as plasticizers, and later polyesters were used. The polyesters were followed by polyurethanes as the plasticizer as the technology of tapes advanced and placed more stringent requirements on the performance of magnetic tape for audio and video [26].

Powder Coatings

Vinyl powder coatings are formulated with vinyl chloride homopolymers and copolymers for application by fluidized bed, powder spray, or electrostatic powder spray. Powder coatings are prepared by dry compounding the polymers, plasticizer, pigments, and additives in ribbon blenders followed by attrition or dispersion to powder in mixers such as a Henschel mixer. Some powder coatings are prepared by a melt mix technique followed by cryogenic grinding. This latter technique produces powders of smaller particle size [27].

Powder coatings prepared by dry compounding are usually applied by fluidized bed or by spray techniques. For fluid bed powder application, the metal parts are heated so that the powder will adhere to the part, begin to coalesce, and start film formation. An oven bake after the powder application is needed to complete the film-forming process by fusion or melting.

Cryogenically ground powder coatings are applied by electrostatic powder spray. With the electrostatic method, it is not necessary to preheat the parts, but an oven bake is necessary after application to fuse the powder to a coherent film. The finer particle size allows deposition of and thinner and smoother films than is attainable from the fluidized bed process.

Poly(vinyl chloride) powder coatings are used to coat products such as metal pipe, fencing, and metal furniture.

Poly(Vinyl Chloride) Latex

Emulsion polymerized vinyl chloride homopolymers and copolymers are used in the latex form not so much to make finished coatings, but rather as substance coated onto a base or support and thereby providing the substrate for items such as wall coverings, backing for carpeting, and the like. In a sense, such use could be considered analogous to a waterborne version of an organosol coating. The vinyl chloride homopolymers need to be modified with a substantial loading of plasticizer, and some grades are sold as preplasticized latexes. These water-based materials require a high temperature bake to fuse the polymer plasticizer mix into a continuous film.

By varying the type and amount of co-monomer used to make emulsion polymerized copolymer latexes, products with a decreased glass transition temperature and lower film-forming temperature are available. These allow lower temperature bakes for film formation.

Waterborne Vinyl Dispersions

Waterborne vinyl dispersions made from solution-polymerized vinyl copolymers became available in the 1980s. These colloidal aqueous vinyl dispersions are of medium molecular weight and have high glass transition temperatures of about 80°C. Coalescents are needed with these products to form a film. Some dispersions are available with a glycol-ether coalescent already present in the product, and a co-solvent free variety is also available. With the latter, the formulator can choose whichever coalescent, glycol-ether, glycol-ether ester, plasticizer, or blend of coalescents that best meets performance requirements.

Waterborne vinyl dispersions are used in many adhesive, ink, overprint lacquer, industrial coating, and heat-sealable coating applications where solvent-based vinyl coatings had been used and still are used.

Trends in Vinyl Coatings

New and modified regulations of concern to vinyl chloride copolymers have been requiring improved volatile organic solvent content—that is, lower volatile organic content (VOC). Studies over the recent past have centered on high solids and waterborne systems. In the case of high solids formulations, reductions in copolymer molecular weight have allowed viscosity stable solution at twice and more the solids content. While higher solids can be achieved, the reductions in molecular weight have affected the performance of coatings made from such copolymers—decreases in chemical resistance and physical properties were noticed in films formed from low molecular weight lacquers.

To overcome such decreases in properties caused by lower molecular weight copolymers, the copolymers designed for high solids vinyl copolymers are modified to contain hydroxyl functionality and to allow for reaction with added co-reactant materials to build molecular weight through the thermoset process of cross-linking. Here difficulties can be encountered in trying to achieve a minimum of one functional group on each oligomeric molecule. Thus, the high solids lacquer designed copolymers can be used alone for applications that do not have very demanding requirements, but the copolymers are best used when they contain functionality for cross-linking with amino-formaldehyde or isocyanate cross-linking agents or as modifiers for alkyds, polyester-isocyanate, or epoxy-amine coatings to improve initial drying or set-to-touch rate, or to improve recoatability [27]. Modification of the vinyl copolymers to improve specific characteristics such as the copolymer containing sulfonate groups for improved pigment dispersion provides new tools for formulators [28].

The waterborne vinyl dispersions previously described represent an alternative to high solids vinyls as a way to formulate low VOC coatings. The waterborne vinyls are compatible with a wide variety of other waterborne polymers that have low VOC content, such as acrylics, alkyds, urethanes, and amino-formaldehyde cross-linking agents. Investigators are looking into the interactions that take place between poly(vinyl chloride) and poly(vinyl acetate) in various solvents [29]. The results indicate that the solvent has a marked effect on the interactions that take place in solution and these in turn have an effect on films prepared from the mixtures. There may be ramifications from these studies with homopolymers as to copolymer interactions.

Although this chapter deals with polymers and oligomers prepared from vinyl chloride, it should be pointed out that vinyl chloride (that is, the monomer) is a hazardous chemical and a known human carcinogen. Thus, precautions should be taken by anyone who comes in contact with the monomer. It is beyond the scope or intent of this chapter to deal with all of the details and ramifications of the health hazards associated with vinyl chloride monomer and readers are directed to information available from organizations such as the United States

Occupational Safety and Health Administration, from Europe's Restriction on Hazardous Substances (RoHS), from Waste Electronic and Electrical Equipment, as well as other groups. Of course, manufacturers' Material Safety Data Sheets, for both the monomer and polymers derived from it, should always be consulted when dealing with these materials. The internet contains an abundance of information about these and other organizations, vinyl chloride monomer, and polymeric species derived from vinyl chloride.

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Miscellaneous Materials and Coatings

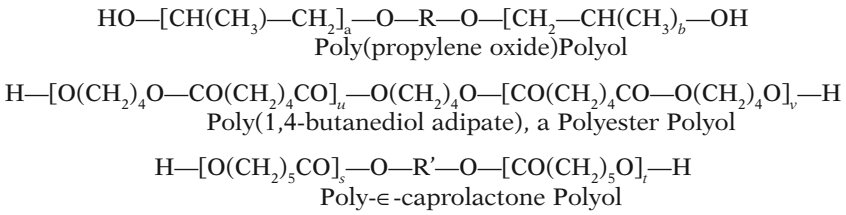
Joseph V. Koleske[1]

THIS CHAPTER IS CONCERNED WITH A VARIETY OF products that are not discussed elsewhere in the manual. Some topics are mentioned only briefly to indicate that the area has not been forgotten and that the topic is not within the scope of the manual.

POLYOLS

Polyols, or polyalcohols as they are sometimes known, are compounds containing one or more, but usually two or more, free hydroxyl groups. Most definitions, and particularly those over 10 years old, list typical polyols as compounds such as ethylene glycol, propylene glycol, neopentyl glycol, glycerol or glycerin, trimethylolpropane, pentaerythritol, and sorbitol that were used in the preparation of alkyds and polyesters. Today the word "polyols" is far more encompassing and more often than not refers to alkylene oxide [1] and ∈-caprolactone [2] adducts of the above-mentioned and other monohydric or polyhydric alcohols, low-molecular-weight polyesters prepared from the above mentioned as well as other polyhydroxyl compounds and dicarboxylic acids (particularly adipic acid) [3–5], polytetrahydrofurans prepared by a cationic ring-opening polymerization of tetrahydrofuran [6,7], and low-molecular-weight polycarbonates [8–10]. Ortho-phthalate based polyesters used in the manufacture of polyurethanes have hydrolytic stability advantages based on the aromatic ingredients in high solids and cationic photocure systems, as well as in a number of other end uses including elastomeric fibers, dentistry, artifact preservation, and pharmaceutical preparations. The two main classes of polyols used in coatings are the polyether polyols, which are typified by the poly-(propylene oxide) polyols (PPO), and the polyester polyols, which include both poly(glycol adipates)(PEA) and poly-∈-caprolactone polyols (PCP). Both classes of polyols are available as difunctional and trifunctional hydroxyl compounds though the adipates are almost always difunctional in nature. Higher functional polyols are known and available, but their usage is less common than that of the di- and trifunctional products. In the above structural formulas, R and R′ may be the same or different and –O–R–O– and –O– R′–O– are the residues of the polyhydric alcohol initiators.

Difunctional and trifunctional PPOs are usually initiated with 1,2-propylene glycol and glycerol, respectively. The adipate polyols are usually prepared with an excess of diol, so most end groups are hydroxylic rather than carboxylic in nature. Since these polyols are prepared by a condensation reaction, there is no need for an initiator. Caprolactone polyols are initiated with a variety of diols and triols such as diethylene glycol, ethylene glycol, 1,4-butanediol, trimethylol propane, glycerol, etc. The above structure for PPO indicates that the hydroxyl



$$HO—[CH(CH_3)—CH_2]_a—O—R—O—[CH_2—CH(CH_3)_b—OH$$

Poly(propylene oxide)Polyol

$$H—[O(CH_2)_4O—CO(CH_2)_4CO]_u—O(CH_2)_4O—[CO(CH_2)_4CO—O(CH_2)_4O]_v—H$$

Poly(1,4-butanediol adipate), a Polyester Polyol

$$H—[O(CH_2)_5CO]_s—O—R'—O—[CO(CH_2)_5O]_t—H$$

Poly-∈-caprolactone Polyol

substitution pattern within the polyol [11,12]. There are other compounds that meet the above definition, but they are not usually termed polyols. Compounds such as these are certain acrylic oligomers [13], vinyl chloride copolymers, hydroxyl-containing glycidyl ether compounds, vinyl alcohol copolymers, and so on. This chapter will not be concerned with these latter compounds since they are dealt with elsewhere in the manual.

Polyols are important compounds used in the manufacture of alkyds and polyurethane coatings, of intermediates used in radiation curable formulations, as copolymerizable groups are both secondary, which is the usual case. However, from time to time, a primary hydroxyl group will be found due to an unexpected opening of the propagating 1,2-epoxide. The subscripts *a*, *b*, *u*, *v*, *s*, and *t* in the above structural formulas can be the same or different, and they can take on a wide variety of values with the number average molecular weight ranging from about 150 to 3,000 for polyols usually used in coatings. Details about preparation of urethane coatings based on polycaprolactone polyols for rigid substrates [14] and flexible substrates [15] are available.

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A variety of other specialty polyols also exist, such as poly(butylene oxide) and polybutadiene polyols, which are useful when very high levels of barrier hydrophobicity are needed [16]. Poly(tetramethylene oxide) polyols also have good hydrophobic character. New polyols are also being developed, including polyols based on lactose that have flame-retardant characteristics as well as polyols with different end capping, etc. [17]. Poly(phenylene ether) has been made into low-molecular-weight polyols that are effective in enhancing high temperature performance of products [18]. Hydroxyl terminated, low-molecular-weight polysulfides have been prepared by splitting a relatively high-molecular-weight polysulfide in aqueous latex form with a dithiodialkylene glycol and sodium sulfite [19]. Such polyols have been used as polysulfide-based polyurethane glass sealants. Although new polyols such as these are often designed for use in the manufacture of polyurethane foams and elastomers, they can be and are used in coating formulations.

Recently, there has been a noticeable interest in highly branched and highly functional polyols that are hyperbranched or dendritic and polydisperse in nature [20–22]. Perfect dendrimers have a uniform distribution of branches and functional groups around a central core molecule and are monodisperse or substantially monodisperse in character [23]. At present, such molecules are more of academic than practical interest due to the multistep procedures required for their preparation. In contrast, hyperbranched dendritic polyols, which contain a nonuniform distribution of branches and functional groups around a central core, have a certain or definite degree of polydispersity that can have a M_w/M_n ratio of about 1.5 or more [24]. Such polyols are of commercial interest since they can be prepared by a one-step process. The polyols are most conveniently prepared from glycerol in molecular weights of about 1,000 to 35,000 g/mol. The molecules have a functional group on the end of every branch, and a molecule with a molecular weight of about 5,000 has about 68 hydroxyl end groups and a 1,500 molecular weight product will have 24 functional groups. With such high degrees of branching the compounds are amorphous in nature and soluble in a variety of organic solvents as well as with water in the case of polyglycerol. They have low solution viscosities because chain entanglements are nil, low vapor pressure, and high reactivity. The polyglycerol polyols have been further reacted by copolymerization with glycidyl ethers [25] and propylene oxide [26], esterification [27], and condensation with suitable acrylates to form radiation-curable products [28]. The hyper-branched polyols can be cross-linked with a variety of cross-linking agent and formed into useful products such as high solids, thermoset binders [29] and radiation-curable printing inks [30]. Such cured products have improved scratch and abrasion resistance, adhesion, hardness, and flexibility.

End capping polyols can provide adducts with different properties. For example, poly(propylene oxide) polyols, which contain terminal secondary hydroxyl groups, can be end-capped with ethylene oxide to provide polyols with more reactive primary hydroxyl groups [1,7]. Ways to apply nuclear magnetic resonance to measure the ethylene oxide content of these and other propylene oxide/ethylene oxide copolymers are detailed in ASTM D4875, Test Methods of Polyurethane Raw Materials: Determination of the Polymerized Ethylene Oxide Content of Polyether Polyols. Also described in the literature [1,7] are polyols modified to have amine, allyl, carboxyl, cyano, and vinyl ether end groups. Glycols that are solid and/or that have subliming characteristics, as 2,2′-dimethyl-3-hydroxypropyl 2,2′dimethyl-3-hydroxypropionate, can be modified with a few ethylene or propylene oxide groups to yield new polyols that are liquid, have low viscosity, and do not sublime with even a few molecules of ethylene oxide having nil or very little effect on moisture resistance [31]. Polyols can be end-capped with an anhydride to form adducts that have free carboxylic acid functionality or a mixture of it and hydroxyl functionality as has been done with the poly-∈-caprolactone polyols [32] or the alkylene oxide capped glycols [33]. In other instances, poly(propylene oxide) polyols have had carboxyl groups grafted to their backbone with acrylic or methacrylic acid. These grafted polyols retain their original hydroxyl end groups and are used in coating formulations [34].

Polyols can be incorporated into alkyds, made into moisture-curing urethanes, can be cross-linked with aminoplasts, and can be cross-linked with cycloaliphatic epoxides when terminated with carboxylic acid end groups. In using the polyols, the hydroxyl number [35] is their most important physical characteristic to be measured and used. Five wet chemical methods and two nuclear magnetic resonance methods for determining the hydroxyl number are given in ASTM D4274, Test Methods for Testing Polyurethane Polyol Raw Materials: Determination of Hydroxyl Numbers of Polyols and in ASTM D4273, Test Methods for Testing Polyurethane Raw Materials: Determination of Primary Hydroxyl Contents of Polyether Polyols, respectively. An infrared method can be found in ASTM D6342. Standard Practice for Polyurethane Raw Materials: Determining Hydroxyl Number of Polyols by Near Infrared (NIR) Spectroscopy. The equivalent weight or combining weight of a polyol is determined from the hydroxyl number by the following relationship

Equivalent Weight = 56 100/Hydroxyl Number

when potassium hydroxide is used as the titrating agent. Of course, if functionality is known, polyol molecular weight can be calculated by multiplying the equivalent weight by the functionality. Manufacturers provide information about hydroxyl number and usually about methods for analytically determining it.

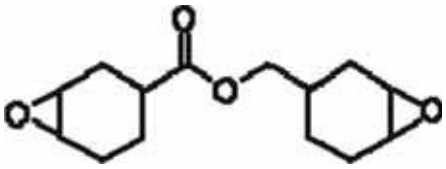
Another important reactivity parameter is the acid number described in ASTM D4662, Test Methods for Polyurethane Raw Materials: Determination of Acid and Alkalinity Numbers of Polyols. Acidity and alkalinity in polyols can affect reactivity, shelf life, color, and hydrolytic stability of coatings prepared from polyols. Polyethers and poly-∈-caprolactone polyols usually have very low acid numbers. However, due to the nature of the condensation reaction coupled with transesterification used to produce polyester polyols, these polyols have relatively high acid numbers. The alkalinity in polyols with low alkalinity content can be determined with ASTM D6437, Test Method for Polyurethanke Raw Materials: Alkalinity in Low-Alkalinity Polyols (Determination of CPR Values of Polyols). Color, which has obvious implications, can be determined with ASTM D4890, Test Methods for Polyurethane Raw Materials: Determination of

Gardner and APHA Color of Polyols. Other factors such as ethylene oxide content, specific gravity, suspended matter, unsaturation content, and water content can be determined with various ASTM Test Methods, D4875, D4669, D4670, D4671, D4672, respectively.

CYCLOALIPHATIC EPOXIDES

Although the topic of epoxides in coatings is the subject of a separate chapter in this manual, that chapter deals with glycidyl or 1,2-epoxides that are not attached to a ring structure. Such epoxides are the largest volume products of all epoxides used, and the main products in this class are the diglycidyl ethers of bisphenol A. However, there is a special class of epoxides, termed "cycloaliphatic epoxides," that are used in specialty coatings and in cationic radiation-cure coatings. These epoxides are characterized by a saturated ring structure that imparts a high degree of weatherability and excellent electrical properties such as dielectric constant, dissipation factor, dielectric breakdown voltage, etc., to coatings and other products made from them. The good weatherability of the cycloaliphatic epoxides is apparent from the fact that they have been used for decades to make the large electrical insulators used in substations [36]. These compounds react well with carboxylic acids, as evidenced by their time-honored use as acid scavengers, and this reactivity often forms the basis for their use in coating formulations.

The main commercial cycloaliphatic epoxide is 3,4-epoxycyclohexylmethyl 3,4-epoxycyclohexane carboxylate that has the structure



Cycloaliphatic Epoxide

This epoxide is well known by the familiar name designation ERL-4221. Table 1 contains the properties of this epoxide and other cycloaliphatic epoxides that are commonly known in the industry. Epoxide equivalent weight can be determined with ASTM D1652, Test Methods for Epoxy Content of Epoxy Resins. Manufacturers can also be helpful in supplying information about methods of analysis for specific products. Usually these epoxides are reacted with polyols that function as flexibilizing agents for the highly cross-linked polymeric network that results. These epoxides polymerize by nucleophilic attack on the epoxide ring to form an ether linkage and a hydroxyl group on the ring. The hydroxyl group that is formed on the ring is quite acidic in character and will readily open other cycloaliphatic epoxide groups.

Recently, a variety of new cycloaliphatic epoxides have been prepared by a transesterification process involving methyl-3,4-epoxycyclohexanecarboxylate and a variety of hydroxyl-terminated compounds [38]. The hydroxyterminated compounds included 1,4-butanediol, 1-8-octanediol, 1,4-cyclohexanediol, and others. The new epoxides provided tougher films when cross-linked with ultraviolet radiation in the presence of cationic photoinitiators than conventional cycloaliphatic epoxides.

In the coatings industry, cycloaliphatic epoxides are used as a major formulating ingredient in cationic, photocurable formulations [39]. Usually they are formulated with polyols, onium-salt photoinitiators, and other ingredients. The onium salts photolyze in the presence of ultraviolet radiation to form strong protic acids that cause rapid polymerization of the epoxides as well as their copolymerization with active hydrogen compounds such as polyols. The presence of alkalinity including even very weak bases can result in neutralization of the protic acids formed by photolysis. Since the protic acids function as initiators, their neutralization will cause a marked decrease in polymerization rate. It may even result in nil reactivity. Coatings such as these are used as conformal coatings [40–42] in the electronics industry because of their excellent electrical (MIL-I-46058C approved, QPL Type ER) flammability (UL QMJU2 at a 2-mil thickness) and water permeability properties, as exterior can and other packaging coatings, overprint varnishes, printing inks for paper and metal, etc.

Cycloaliphatic epoxides have been reacted with the free carboxylic acid groups on anhydride adducts of polyols [43]. Such coatings are characterized by pot lives of less than 8 h, high solids, and low-temperature curing capabilities with very high gloss and depth of image, high hardness, excellent solvent resistance, adhesion, and toughness. In other instances, the epoxides have been reacted with polyols in the presence of triflic acid salts (as diethylammonium triflate, 3M Co.). In this case, shelf lives of more than 8 months have been obtained and the formulated systems have high solids coupled with low viscosity and low temperature-cure characteristics. Cured coatings have an excellent balance of properties similar to those described above.

TABLE 1—Commercial cycloaliphatic epoxides and their physical properties [36,37]

Chemical Name	Viscosity, cP at 25°C	Specific Gravity 25/25°C	Color, 1993 Gardner (max)	Epoxide Equivalent Weight	Boiling Point, °C (mm Hg)	Vapor Pressure at 20°C, mm Hg	Solidification or Glass Point°C
3,4-Epoxycyclohexylmethyl 3,4-epoxycyclohexane carboxylate	350–450	1.175	1	131–143	354 (760)	<0.1	–20
Bis(3,4-epoxycyclohexylmethyl) adipate	550–750	1.15	1	190–210	258 (10)	<0.1	9
2-(3,4-Epoxycyclohexyl-5,5-spiro-3,4-epoxy) cyclohexane-m-dioxane	7,000–17,000 at 38°C	1.18	2	133–154	>250 (760)	<0.01	>0
1-Vinyl-epoxy-3,4-epoxycyclohexane	<15	1.18–1.10	1	70–74	227 (760)	0.1	–55

TABLE 2—A partial listing of polymeric films available for coating or other uses [46].

Type Polymer	Available As	
	Conventional Film	Shrink Film
Cellophane	Yes	No
Cellulose acetate	Yes	No
Cellulose acetate-butyrate	Yes	No
Cellulose triacetate	Yes	No
Ethylene/vinyl acetate copolymer	Yes	No
Fluorocarbon	Yes	No
Ionomer	Yes	No
Nylon	Yes	Yes
Polycarbonate	Yes	No
Polyester	Yes	Yes
Polyethylene	Yes	Yes
Polyethylene linear low density	Yes	No
Polypropylene, nonoriented	Yes	No
Polypropylene, oriented	Yes	Yes
Polyurethane	Yes	No
Poly(vinyl alcohol)	Yes	No
Poly(vinyl chloride)	Yes	Yes
Polyvinylidine chloride	Yes	Yes

With the use of cycloaliphatic epoxides in radiation-curable coatings gaining importance, new tests to monitor the photocuring process involving these materials are being developed. In one instance, optical pyrometry is being used as a rapid, reproducible, and inexpensive way to continuously monitor such polymerizations [44]. In another case, in-situ dielectric analysis and real-time Forrier transform infrared spectroscopy are being used to monitor the cure of such systems [45]. In either of these cases, the techniques work equally well for the free-radical cure of acrylate systems initiated with radiation.

COATING FILMS

Films of many different polymers are available in different forms for use as functional and decorative coatings, adhesive backings, and other uses. Some of these materials [46,47] are listed in Table 2. A directory of film manufacturers that lists the manufacturer product name or number and a short description of the product is available [48]. Full description of these films and their uses is beyond the intent and scope of this manual.

METALLIC COATINGS [47,49,50]

Metallic films are used in a variety of ways. Some metallic coatings are described elsewhere in this manual. The previously described coatings are formulations wherein powdered or flaked metals [51] are combined with a binder. However, solid metallic films are used as coatings in other ways familiar to us. Such films are both functional and decorative in nature, and they form a layer that changes the surface properties of the substrate to those of the metal being applied. The coated product becomes a new material that has a corrosion-resistant outer layer provided by the metal while the load-bearing characteristics are provided by the core material. A variety of metals are used and these include aluminum, cadmium, chromium, copper, gold, nickel, silver, and zinc.

Metals can be applied to plastics and glass by a variety of processes including the physical vapor deposition processes known as vacuum metallizing by thermal evaporation, cathode sputtering, and ion plating of aluminum, copper, chromium, gold, silver, and silicon monoxide [52]. Many special effects can be produced including multilayers for cost and protection, iridescent effects by using compounds with high (CeO_2, ZnS) and low (MgF_2, SiO) refractive index, dyeing—particularly of aluminum to achieve a gold color and other colors—and glass coatings on plastic optical parts. Coatings formed by such vacuum deposition processes are most often applied to plastic substrates with end uses for the coated parts including automotive parts; plastic and paper webs for decorative and functional packaging of cosmetics, drugs, clothing, foods, etc.; household fixtures; data storage systems; optical components; semiconductor devices; and glass for automotive and architectural applications. As indicated above, the packaging industry has a very large use for thin metallic films on paper and plastic substrates.

A plasma technique [53] known as unbalanced magnetron sputtering (UBM) has advantages over conventional balanced magnetron sputtering, which is usually used to metallize silicon wafers and architectural glass. In such techniques, an argon plasma is used to remove atoms from a negatively charged target, and magnets are then placed at the outer edges of the target, which is made the cathode. Each of the magnets produces a field of the same strength, and because of this the system is termed "balanced." This conventional system works well when the substrate is silicon and the coating is thin. However, in certain end uses, thick, dense coatings with excellent adhesion are required, and it is herein that UBM has significant advantages for applying coatings of hard, wear-resistant alloys, such as TiN, NbN, TiC, CrN, TiNbN, and the like, to metal-cutting saw blades and other tools, cams, and gears.

Metallic and ceramic coatings are also applied to metals by a thermal spray technique in which a metallic or ceramic wire, rod, or powder is melted and driven through air or a vacuum at high velocities [54,55]. The molten material, which can range from soft, abradable nickel-graphite to hard ceramic zirconia, is deposited on a surface of base metal to which it bonds through chemical and mechanical processes. Thermally sprayed coatings are used as abrasion, corrosion, and heat barriers for expensive machined components, castings, and other parts used in hostile chemical, mechanical, and thermal environments encountered in automotive, spacecraft (including aerospace and

TABLE 3—ASTM specification for electrode-deposited coatings of various metals.

Chemical Symbol	ASTM Designation	Title, Specification for Electrodeposited Coatings of . . .
Ag	B700	Silver for Engineering Use
Au	B488	Gold for Engineering Uses
Cd	B766	Cadmium
Ch	B650	Engineering Chromium Coatings on Ferrous Substrates
Cu	B734	Copper for Engineering Uses
Cu–Ni–Ch	B456	Copper Plus Nickel Plus Chromium and Nickel plus Chromium
Pb, Pb–Sn	B200	Lead and Lead-Tin Alloys on Steel and Ferrous Alloys
Pd	B679	Palladium for Engineering Use
Pd–Ni	B867	Palladium for Engineering Use
Rh	B634	Rhodium for Engineering Use
Sn	B545	Tin
Sn–Ni	B605	Tin Nickel Alloy
Sn–Pb	B579	Tin-Lead Alloy (Solder Paste)
Zn	B633	Zinc on Iron and Steel
Zn–Co	B840	Zinc-Cobalt Alloy Deposits
Zn–Fe	B842	Zinc-Iron Alloy Deposits
Zn–Ni	B841	Zinc-Nickel Alloy Deposits

aircraft), and industrial applications. The special protection provided by these coatings is needed to improve reliability and durability.

Other metal deposition processes for protective, cost savings and/or decorative coating metal, glass, and plastics include electrodeposition by electroplating (Cu, Ni, Cr) and electroless plating (Ni, Cu), galvanizing (Zn), and pack cementation (Al). Electroplating is carried out by passing an electrical current through a solution of the dissolved metal that is to be plated. In this process, the object to be plated functions as the cathode of an electrochemical cell. It attracts metal ions from the solution, and they are deposited as a metallic film on the substrate. Process control is achieved by controlling factors such as additives, amperage, applied voltage, bath solution purity, residence time, and temperature. Additives, often trade secrets, can play an important role in development of smooth, adherent films. Cleaning and rinsing are important process steps. The metals that can be plated include Al, Cd, Cu, Ch, Fe, Ph, Ni, Sn, and Zn. The index in the Annual Book of ASTM Standards (Section 0.0) lists in the neighborhood of 100 standards that deal with electrodeposition. Those that deal with specifications for particular metal deposition are listed in Table 3.

Electroless plating involves similar steps as electroplating except there is no use of an external or applied electrical current. Nickel is the primary metal deposited by this process. Basically, it is a chemical reduction process in which dissolved nickel ions are chemically reduced by means of a chemical reducing agent present in the plating bath. Since the driving force for deposition is constant within the bath when agitation is proper, the metal deposits are very uniform in nature even over complex-shaped objects such as screws, internal areas such as holes, and the like.

Hot dip galvanizing is the process in which an iron or mild steel product is zinc coated by dipping it into a molten zinc bath. It is widely used in the automotive and transportation industry where it imparts corrosion protection to the coated parts. The zinc coating acts as a sacrificial material and thereby provides cathodic protection to the ferrous, strength-providing substrate. Various ASTM standards for galvanizing technology are listed in Table 4.

Pack cementation in which diffusion coatings are formed by simultaneously depositing aluminum, chromium, or silicone and heat-treating the metal to be coated. Shaped ferrous substrates are packed into the appropriate metal powder and heated. The process takes place in a furnace over a programmed time and temperature period during which there is migration of the aluminum (or other metallizing element) and the substrate metal atoms as they diffuse into each other. As a result, oxidation resistance is given to ferrous alloys. In the aluminizing process, a chemical activator is used to facilitate the diffusion process. ASTM documents dealing with aluminum and chromium diffusion coatings applied by this process are ASTM B875, Standard Specification for Aluminum Diffusion Coating Applied by Pack Cementation Process, and ASTM B874, Standard Specification for Chromium Diffusion Coating Applied by Pack Cementation Process.

The Association of Industrial Metallizers, Coaters and Laminators, AIMCAL, is a global, nonprofit, trade association that represents converters of metallized, laminated, and coated flexible substrates as well as their suppliers (www.aimcal.org). They provide a Source Book that is a useful guide for those in the metallized products area. It provides information about the capabilities of the

TABLE 4—ASTM practices, preparation, specifications, and test method for galvanized materials/structures/surfaces.

ASTM Designation	Title
A896	Practice for Conducting Case Studies on Galvanized Structures
D6386	Practice for Preparation of Zinc (Hot-Dip Galvanized) Coated Iron and Steel Product and Hardware Surfaces for Painting
D2201	Practice for Preparation of Zinc-Coated and Zinc-Alloy-Coated Steel Panels for Testing Paint and Related Coating Products
A123/A123M	Specification for Zinc (Hot-Dip Galvanized) Coatings on Iron and Steel Products
A394	Specification for Steel Transmission Tower Bolts, Zinc-Coated and Bare
A641/A641M	Specification for Zinc-Coated (Galvanized) Carbon Steel Wire
A653/A653M	Specification for Steel Sheet, Zinc-Coated (Galvanized) or Zinc-Iron Alloy-Coated (Galvannealed) by the Hot-Dip Process
A740	Specification for Hardware Cloth (Woven or Welded Galvanized Steel Wire Fabric)
A854/A854M	Specification for Metallic-Coated Steel Smooth High-Tensile Fence and Trellis Wire
B852	Specification for Zinc Alloys (CGG) Continuous Galvanizing Grade for Continuous Hot-Dip Galvanizing of Sheet Steel
D2251	Test Method for Metal Corrosion by Halogenated Organic Solvents and Their Admixtures

approximately 200 member companies, profiles of the companies, products, equipment, and service.

SPECIALTY ORGANIC COATINGS

Polysulfides

Polysulfide coatings [56] have excellent barrier properties due to low permeability, good abrasion, chemical, and weather resistance, good adhesion, low shrinkage, and low-temperature flexibility coupled with good stress relaxation characteristics. These coatings are based on polysulfide polymers prepared

$$HS—(C_2H_4O—CH_2OC_2H_3—S—S)_xC_2H_4OCH_2OC_2H_4SH$$

from bis(2-ethyl)formal, 1,2,3-trichloropropane and sodium polysulfide. The polymers are available in a molecular weight range of 1,000–8,000. The thiol or mercaptan end groups of this polymer provide sites for curing in an oxidative manner with manganese dioxide, dicumene hydroperoxide and organic peroxides in general, *p*-quinonedioxime, by reaction with glycidyl epoxides in the presence of tertiary amines, or by reaction with multifunctional isocyanates. The polymers are used as rubbery coatings and sealants in buildings and civil engineering projects requiring excellent ultraviolet radiation resistance and other general weatherability properties. Polysulfide coatings have been commercially used for over 50 years. The most recent use of the polymers is to provide chemically resistant barrier coatings on chemical-containment storage-tank dikes that protect the environment from chemicals that could cause serious pollution problems. Their elongation properties make them especially useful for bridging of concrete cracks.

Studies with polysulfides include development of roofing compositions that comprise bituminous materials that have crumb rubber and an elastomeric polysulfide as major components [57]. Anther roofing systems involve a glass filter-fiber roofing mat that is coated with an elastomeric polysulfide and crumb rubber composition [58]. Non-slip, non-abrasive coatings have been prepared from polysulfide compositions [59]. Such coatings maintain sufficient traction in wet and dry environments as are encountered around swimming pools and similar wet areas. Polysulfides have also been used as toughening agents in primer and topcoat coating compositions that provide durable, non-skid surfaces as are needed on aircraft carrier and other ship decks as well as on oil well drilling platforms [60]. As mentioned in the section dealing with polyols above, polysulfides have been converted into polyols, and these have been used to make polyurethane insulated glass sealants [19].

The odor level of polysulfides has been reduced by contacting the polysulfide with a hydrocarbyl acrylate or methacrylate [61]. Both mono(meth)acrylates and poly-(meth)acrylates have been used for this purpose. Although a wide variety of these inhibitors can be used, the preferred inhibitors are n-dodecyl acrylate and glycidyl methacrylate or mixtures of these compounds.

It is worth pointing out that poly(phenylene sulfide) is used as a high performance engineering thermoplastic. Its utility is derived from its excellent heat and flame resistance, good mechanical properties, and chemical resistance coupled with easy processability. The polymer's high temperature performance properties make it useful as a thermo-set phenolic replacement in electrical/electronic applications.

ASTM B866, Test Method for Gross Defects and Mechanical Damage in Metallic Coatings by Polysulfide Immersion and ASTM E1773, Standard Practice for Sealing Rigid Wall Tactical Shelters with Polysulfide Based Sealants are useful for examining particular aspects of polysulfide materials.

Phenoxy

Polyhydroxyethers, which are commonly known as phenoxy polymers or merely phenoxy, are high-molecular-

weight, high-performance thermoplastic materials that are similar in character to the diglycidyl ethers of bisphenol A that are described in Fig. 1 of Chapter 10 in this manual, entitled "Epoxy Resins in Coatings." However, there are significant differences that make the phenoxy polymers separate and unique polymers [62–64]. These polymers have the structure

$$—[O—C_6H_4—C(CH_3)_2—C_6H_4—O—CH(OH)—CH_2]_n—$$

where n is about 100, indicating a molecular weight of about 30,000 compared with a molecular weight of about 300–10,000 for the diglycidyl ethers of bisphenol A. In addition, phenoxy polymers do not have active epoxide end groups and are thermally stable materials with no limit on shelf life, are tough and ductile, and can form useful, resistant films by solvent evaporation without cross-linking. The hydroxyl functionality associated with phenoxy polymers provides a site for cross-linking with isocyanates, epoxides, or aminoplasts. Films from these polymers are considered to have excellent physical and chemical resistance properties when the polymer is in a thermoplastic form, but if improved resistance to certain solvents is needed, the polymers may be cross-linked. The high molecular weight of these polymers results in relatively low solids (~ 20 %) coating systems, and this might be a restriction to their use in today's climate for high solids. The excellent properties of these polymers has led researchers into investigations of ways for advancing molecular weight of the diglycidyl ethers of bisphenol A during the curing stages [65].

Phenoxy is still used in a variety of ways with and without powdered zinc or other metals in the composition. Coatings that withstand substantial deformation without losing continuity have been compounded from compositions comprised of phenoxy and modifier, polymeric materials [66]. The modifier polymeric materials are softer than phenoxy and are, for example, poly(alkylene oxides), polyesters, caprolactone polyols, polyester urethanes, and polyether urethanes. Phenoxy has found utility on steel that is coated with zinc or zinc-based alloy and used as fuel tanks [67]. Tin-plated steel that is used in the manufacture of gas tanks can be coated with a mixture containing phenoxy and powdered tin and zinc dust to provide corrosion resistance [68].

Parylene Coatings [69,70]

Parylene coatings are applied by exposing a substrate to a gaseous atmosphere of *p*-xylylene. The gaseous monomer is stable, but when it is condensed on a substrate it spontaneously polymerizes to form high-molecular-weight, linear, poly(*p*-xylylene), which is commonly known as parylene [71]. The resultant coating of crystalline polymer provides a pinhole-free coating with an outstandingly uniform thickness and conformance even over pointed objects such as a needle. The polymer has excellent electrical properties, including high dielectric breakdown voltage, low dielectric constant and dissipation factor, and high-volume resistivity due to low moisture absorption and freedom from ionic impurities. Parylene is used for coating printed wiring assemblies, semi-conductors, capacitors, electrets, contamination and corrosion control, medical and surgical devices, medication delivery devices, solder masks for printed circuit boards, as well as similar end uses that require an inert coating that can be uniformly applied in an extremely thin film [72–76].

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Part 4: Plasticizers

17

Plasticizers

Peter Tan[1] and Leonard G. Krauskopf[2]

PAINT AND COATING FORMULATIONS OFTEN incorporate high boiling fluids as plasticizers where rigid or brittle resins fail to meet toughness and flexibility requirements. The primary function of the plasticizer is to impart flexibility to the resin, thus minimizing film cracking. Depending on resin and other ingredients used in the system, plasticizer choice may affect compatibility, toughness, flammability, smoke generation, heat and light stability, and other aging or permanence-related performances. Plasticizers are primarily employed in heavy gage coatings and/or when improved toughness is required for industrial, automotive, and appliance applications.

Plasticizers function by reducing the glass transition temperature of the resin to a point below its application temperature. The chemical mechanism of plasticization involves a strong polar association of polymer-plasticizer molecules, but not a chemical reaction between them. Plasticizers fundamentally reduce van der Waals forces between polymer-polymer molecules in the amorphous regions and do not penetrate crystallites [1–3]. The plasticized morphological phase is then of a different nature than that of the neat polymer and has unique mechanical properties.

The absence of a chemical bond between the plasticizer and the polymer impairs permanence; plasticizer molecules are free to leave the polymeric coating by means of extraction and volatility. Plasticizer loss, however, is minimal in most applications except for very low molecular weight plasticizers and/or exposure to very severe thermal conditions. Thus, plasticized coatings products have high durability and long service life in most applications. Plasticizers are liquids of molecular weight greater than that of solvents—to limit volatility—but are not solids, such as alloying polymers, etc. It should be noted that cross-linked resinous coatings significantly reduce plasticizer loss due to diffusibility and volatility. Several thousand high boiling fluids are potential plasticizers for coatings applications. The choice of plasticizer is dependent on compatibility with the resin in use, cost, and other desired attributes.

Plasticizers may be classified by both chemical structure and performance characteristics, as shown in Table 1 [4]. Typical plasticizers are liquid esters of molecular weight between about 200 to 800, with specific gravities between 0.75 and 1.35 at 20/20°C, viscosities between 50 to 450 cSt, vapor pressure of less than 3.0 mm of mercury at 200°C, and flash points greater than 120°C (248°F). They are generally stable and innocuous and should not be considered a significant threat to humans or the environment [5,6].

Plasticizer extenders are commonly used in extruded or molded flexible plastic shapes. Extenders are low-cost organic oils that may be subdivided as groups of aliphatic, aromatic, or chlorinated hydrocarbons. They are seldom used in coatings due to their relatively high volatility and limited compatibility in polar resins.

This chapter lists the basic properties of plasticizers and methods for their determination. Methods for the isolation, identification, and quantitative determinations of these plasticizers are also included.

PHYSICAL AND CHEMICAL PROPERTIES

Acidity

Plasticizer acidity may be due to improper processing, degradation during storage, contamination, presence of byproducts, or residual catalyst. ASTM D1613, Test Method for Acidity in Volatile Solvents and Chemical Intermediates Used in Paint, Varnish, Lacquer, and Related Products, may be used for determination of acidity. Either ethyl or isopropyl alcohol may be used as diluent for the plasticizer, which is titrated with aqueous sodium hydroxide or potassium hydroxide to the phenolphthalein end point. Results may be expressed in weight percent, as weight equivalents of acetic acid, acid number (milligrams potassium hydroxide consumed per gram of sample), or if the plasticizer is an ester, as weight percent of the parent acid of the ester (see section entitled "Ester Value").

Color

The majority of plasticizers are colorless. As a class, esters are very stable chemical reagents. However, exposure to abnormal conditions, such as high thermal or ultraviolet energy, moisture, or chemically active surfaces, may induce development of color bodies and/or chemical decomposition of the plasticizers. Higher molecular weight phthalates, polymeric plasticizers, and chlorinated paraffins may range in color from light to bright yellow. Although ASTM D1209, Test Method for Color of Clear Liquids (Platinum-Cobalt Scale), has been a standard color measurement method for plasticizers, it was withdrawn by ASTM in 1987. However, the test method can be obtained from a third party. ALPHA is a scale that is likewise used for liquids of low color. The standards are based on platinum solutions without cobalt

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TABLE 1—Plasticizer family/performance grid. Note: × = primary performance function

Family	General Purpose	Strong Solvating	Low Volatility	Low Temperature	Low Diffusibility	Flame Resistant	Stabilizer
Phthalates	×	✓	✓	✓	✓	. . .	. . .
Trimellitates	. . .	. . .	×	✓	✓	. . .	. . .
Aliphatic dibasic esters	. . .	. . .	. . .	×	. . .	. . .	. . .
Phosphates	. . .	✓	. . .	✓	. . .	×	. . .
Epoxides	. . .	. . .	✓	✓	. . .	. . .	×
Polyesters	. . .	. . .	✓	. . .	×	. . .	. . .
Extenders	×	. . .	. . .	✓	. . .	. . .	. . .

Source: Society of Plastics Engineers, Regional Technical Conference (SPE, RETEC) Vinyl I; 1992; reprinted with permisson

and are described in ASTM D2849, Standard Method of Testing Urethane Foam Polyol Raw Materials.

ASTM D1 544, Test Method for Color of Transparent Liquids, employs the Gardner Color Scale for amber and dark-colored plasticizers, which cannot be read on the platinum-cobalt (Pt-Co) or APHA scales. Gardner standards are colored disks held in a "Hellige" gage. Gardner values of "1" and "2" are approximately equivalent to 250 and 400, respectively, on the APHA scale. The Gardner scale goes up to "18" for use with increasingly darker amber and brownish color liquids.

The platinum-cobalt scale is also known as the Hazen scale, but readers should be aware of potential confusion with APHA; APHA adopted a version of this scale in which a hazel color of one is the same as APHA 100. To avoid confusion, it is recommended that only the Pt-Co scale be used when referring to Procedure D1209.

The APHA color scale in ASTM D2849 (see Footnote 3) reflects a slightly greenish hue for APHA versus the Pt-Co scale, which is slightly yellowish. The scale readings are similar in the 25 to 50 range, but in the vicinity of 100 Pt-Co, the APHA scale (Pt only) reads 10 to 20 units lighter (lower). Both the Pt-Co and APHA scales cover a range from "3" up to "500," but are recommended for use for liquids having colors ≤250 units.

An instrumental method (Hunter Colorimeter) that is five to seven times more precise may also be used for color measurement, replacing the subjective comparisons of the above methods using Nessler tubes; while commonly used in commercial practice, the Hunter Colorimeter is not yet defined as an ASTM method.

Copper Corrosion

ASTM D130, Test Method for Corrosiveness to Copper from Petroleum Products by the Copper Strip Test, and ASTM D849, Test Method for Copper Strip Corrosion by Industrial Aromatic Hydrocarbons, which is normally applied to hydrocarbon solvents, may be used to evaluate the copper corrosive tendencies if suspected to be sourced in plasticizer. The appearance of a copper strip, which has been immersed in the test fluid, under standard conditions, is compared with twelve special standard strips classified as follows:

1. Slight tarnish (1a,b) light orange, dark orange.
2. Moderate tarnish (2a,b,c,d,e) claret red, brassy, or gold.
3. Dark tarnish (3a,b) magenta, multicolored.
4. Corrosion (4a,b,c) transparent black, jet black.

The historical application of copper corrosion testing to plasticizers was an attempt to measure effects contributed by residual sulfur compounds due to sulfur-based catalysts, which may hydrolyze to acidic *p*H in the presence of moisture. Current commercial grade plasticizers do not typically contribute to copper corrosion. Commercial grade alkyl sulfonate esters of phenol [7] are plasticizers in which the sulfur is organically "combined" and not readily susceptible to hydrolyses.

Distillation Range

Most plasticizers have high boiling points or boiling ranges. This property can be used as a measure of its degree of permanence or resistance to loss through volatilization. Presence of lighter components can also be detected. The measurement of vapor pressure is a costly and time-consuming procedure. Thus, commercial liquids of high molecular weight—low vapor pressures—are typically characterized by boiling ranges in which one determines initial, mid, and final (or dry point) boiling point temperatures. For fluids with dry point >140°C, ASTM D86, Test Method for Distillation of Petroleum Products at Atmospheric Pressure, is used. Fluids with dry point <140°C are measured using ASTM D1078, Test Method for Distillation Range of Volatile Organic Liquids. For very high boiling fluids or where decomposition may occur, distillation may be done under vacuum regulated at 5 mm Hg. The initial and final boiling points or the mid boiling point are typically reported.

Gas chromatographic (GC) techniques are commonly applied as a fundamental measure of plasticizer chemical purity and isomer distribution. Direct relationships between GC traces and boiling ranges have not yet been established for plasticizers.

Both distillation range and GC analyses are means to relate vaporization characteristics of plasticizers to practical needs. The fundamental characteristic of vapor pressure may be measured by ASTM D2879, Test Method for Vapor Pressure-Temperature Relationship and Initial Decomposition Temperature of Liquids by Isoteniscope. The log of plasticizer vapor pressure varies linearly with the reciprocal absolute temperature (Kelvin) according to the Clausius-Clapeyron equation [8]

[3] ASTM withdrew this method in 1987 and it cannot be downloaded from the ASTM website. However, the document can be obtained from a third party.

$$\ln \frac{P_1}{P_2} = \frac{\Delta H}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \quad (1)$$

where

P_1 and P_2 = vapor pressure, g cm^2 s^{-2},
T_1 and T_2 = respective temperatures, K,
ΔH = molar heat of vaporization, cal—g^{-1}, and
R = gas constant, 1.99 cal°C^{-1} mol.

Vapor pressure values are useful to estimate normal boiling points at 760 mm mercury and solubility parameters [1]. Sears and Darby have reported that the vapor pressure of binary plasticizer blends may be expected to fall between the values of the neat plasticizers, but cannot be predicted from knowledge of the blend ratio and the neat vapor pressures.

Ester Value

Esters are the largest group of materials that are commercially useful as plasticizers. This is a result of reasonable costs and broad utility in a wide range of polymers having moderate to high polarity characteristics. Ester value can be used to estimate the purity or ester content of the plasticizer. ASTM D1617, Test Method for Ester Value of Solvents and Thinners, or ASTM D1045, Test Methods for Sampling and Testing Plasticizers Used in Plastics, may be used for this determination. The methods involve saponification of the ester in a known excess amount of KOH. The excess amount of KOH is then determined by titration with standard sulfuric acid. The amount of KOH consumed in the saponification process is a measure of the ester content of the plasticizer.

A gas chromatography method, ASTM D3465, Standard Test Method for Purity of Monomeric Plasticizers by Gas Chromatography, may also be used to determine the purity of monomeric plasticizers. The GC method does not provide "ester values." It is useful to characterize major isomers present versus known standards and to ascertain trace quantities of nonparent organic compounds. GC instrumentation is costly and requires comparison of output traces against a library of known materials that have been characterized under a specific set of conditions using specific GC instruments and columns.

Flash Point

Most plasticizers are high flash materials. Either ASTM D92, Test Method for Flash and Fire Points by Cleveland Open Cup Tester, or ASTM D93, Test Methods for Flash Point by Pensky-Martens Closed Cup Tester, may be used. Preference should be for the closed cup method; this yields a more conservative number and is consistent with Department of Transportation (DOT) regulations in the United States. DOT has revised the definitions and classifications of hazardous materials, effective 1 Oct. 1993, as follows:

Flash Point	
Not Regulated	≥93°C (200°F)
Combustible	61–92.5°C (142–199°F)
Flammable	≤60.5°C (141°F)

The "flash point" is defined as the minimum temperature at which a liquid gives off vapor within a test vessel in sufficient concentration to form an ignitable mixture with air near the surface of the liquid as determined by ASTM D56, Test Method for Flash Point by Tag Closed Cup Tester, or ASTM D3278, Test Methods for Flash Point of Liquids by Small Scale Closed-Cup Apparatus. In industry, all four methods are used for flash point determination.

Flash point values are reported for commercially significant monomeric plasticizers in E. J. Wickson's *Handbook on PVC Formulating* [7]. While not a very good analytical tool, flash points will reflect presence of nonparent, low-flashpoint contaminants.

Pour Point

Due to the high molecular weight and isomeric mixtures of plasticizers, few have distinct freezing points. The pour point can be useful information for handling plasticizers during cold seasons. Method of measurement is described in ASTM D97, Test Method for Pour Point of Petroleum Products, and ASTM D5950, Standard Test Method for Pour Point of Petroleum Products (Automatic Tilt Method). Plasticizer pour point temperatures may also be estimated from viscosity/temperature plots as the temperature at which kinematic viscosity is 50,000 cSt. Most plasticizers have pour points of less than –30°C [7]; no known relationship exists between pour point and plasticizer performance properties in polymers under low-temperature conditions [9].

Refractive Index

The refractive index of a plasticizer is measured using ASTM D1218, Test Method for Refractive Index and Refractive Dispersion of Hydrocarbon Liquids. Refractive index is often thought of as a means of identifying the plasticizer. This is an erroneous assumption. It may be used, however, to differentiate between classes of plasticizers, as, for example, between phthalates and adipates [10]. When used with other physical measurements, refractive index may be used as a supplemental test. Refractive index can also be used to check for product contamination, but it is only useful to distinguish commercial materials having very widely different refractive indices.

Residual Odor

Residual odor may be contributed by reaction by-products from manufacturing or by residual raw ingredients, which are often more volatile and odorous than the plasticizer. When ASTM D1296, Test Method for Odor of Volatile Solvents and Diluents, is used, tests at elevated temperatures (about 150°C) can be considered to improve detection. Since odor is a subjective characteristic, generalizations for plasticizers are limited to terms such as "mild and characteristic." ASTM D6165, Guide for Comparison, Detection, and Identification of Odors of Paints, Inks, and Related Materials, is also useful for ascertaining and differentiating odors.

Sampling

To obtain representative samples of plasticizers for evaluation, ASTM D1045, Methods for Sampling and Testing Plasticizers Used in Plastics, may be followed. ASTM E300, Standard Practice for Sampling of Industrial Chemicals, can also be used.

Density and Specific Gravity

Density is an important characteristic for design engineering of plasticizer storage and building facilities. Specific gravity is the density of the given reagent relative to that of water at the specified temperature; it is generally used in the characterization of plasticizers or as a means to detect gross contamination. Specific gravity at 20/20°C is measured with ASTM D891, Test Methods for Specific Gravity, Apparent, of Liquid Industrial Chemicals, and is commonly employed in industry. Commercial plasticizers typically fall within the range of 0.92–1.50 sp gr at 20/20°C. ASTM D4052, Test Method for Density and Relative Density of Liquids by Digital Density Meter, is the recommended procedure to measure specific gravity of fluids that lie between 0.68 and 0.97; this method is applicable to hydrocarbons that are commonly used as plasticizer extenders. Another standard method used in the paint and coatings industry is ASTM D1475, Density of Liquid Coatings, Inks, and Related Products.

Viscosity

Viscosity measures the fluid's resistance to flow; the thicker the fluid, the higher its viscosity and the greater its resistance to flow under gravity. In ASTM D445, Test Method for Kinematic Viscosity of Transparent and Opaque Liquids (and Calculation of Dynamic Viscosity), time is measured in seconds for a fixed volume of the fluid to flow under gravity through the capillary of a calibrated viscometer at constant temperature. The kinematic viscosity of a plasticizer varies as a log log function versus the log of absolute temperature according to the following equation

$$\log\log\eta \cong A - B\log T \tag{2}$$

where

η = kinematic viscosity, centistokes,
T = temperature, degrees Kelvin, and
A and B = constants.

This reflects the tremendous influence of temperature on viscosity and allows one to interpolate viscosity values at specified temperatures. The kinematic viscosity (centistokes) can be converted to its dynamic viscosity (centipoise) by multiplying by the true density of the fluid at the specified temperature: dynamic viscosity, cP = kinematic viscosity, cSt, times density.

Water

Residual water from manufacturing processes and moisture absorbed from the atmosphere can affect the quality and clarity of coatings. Water content can be measured using ASTM D1364, Test Method for Water in Volatile Solvents (Karl Fischer Reagent Titration Method). Plasticizers are hydrophobic liquids and typically have a limited capacity to take up water and/or be dissolved into water. Higher-molecular-weight phthalates are practically insoluble in water with solubilities in the 0.1 to 1.2 mg/L (ppm) range with even less solubility in salt water [6].

Typical Properties

As shown in Table 1, commercial plasticizers fall into about seven chemical family groups (eight if we were to add a "miscellaneous" grouping). The major plasticizer types in use are phthalates, trimellitates, and aliphatic dibasic esters such as adipates. The families of esters are formed by reacting the parent acid with monomeric alcohols ranging from C4H9OH (butanol) to $C_{13}H_{27}OH$ (tridecanol); the alcohol may also vary in isomeric structure ranging from normal (un-branched) to very specific and/or randomly branched structures. Two alcohols have found wide usage in synthesis of commercial plasticizers—2-ethylhexanol and isononanol—a mixture of randomly branched (primarily methyl branched) nonyl isomers. Table 2 is a summary of typical properties of plasticizers derived from these two alcohols with the major parent acids—phthalic, trimellitic, and adipic [11].

METHODS OF IDENTIFICATION

A plasticizer may initially be characterized by its functional groups. While absolute identification is complicated without sophisticated chemical or instrumental methods, it is possible to identify the type of plasticizer by functional groups or presence of elements associated only with the plasticizer by the use of infrared analyses or wet chemistry. Most plasticizers are a member of one of the following families:

Plasticizer Type/Functional Group
Adipates
Chlorinated compounds
Epoxides (oxirane)
Phosphates
Phthalates
Polyesters
Trimellitates

Isolation of Plasticizers

Plasticizers may be separated from a lacquer or dried film by solvent extraction if it is to be analyzed. The lacquer is first dried to remove all solvents present. The dried solid is then solvent extracted (in an appropriate apparatus) with hot ethyl ether or another appropriate solvent that will extract the plasticizers while leaving most of the resins behind. The extractant is concentrated, and a small amount of methyl or ethyl alcohol is added. This will cause some of the dissolved resin to precipitate out. Next, filter and concentrate the extractant. ASTM D494, Test Method for Acetone Extraction of Phenolic Molded or Laminated Products, may be applied.

Instrumental Methods

Modern instrumental analytical methods are able to separate, identify, and quantify components in composite mixtures. Rapidly falling costs of such instruments have enabled instrumental methods to be more widely available. These include gas chromatography (GC), high-performance liquid chromatography, infrared spectroscopy (FTIR), and other emerging analytical instruments such as supercritical fluid chromatography, GC/FTIR, and GC/mass spectrometry.

Infrared Spectrophotometry

An infrared scan of the isolated plasticizer is by far the best way to identify the functional groups in the molecule. Mixtures of plasticizers can present problems due to masking effects. If one or more of the component plasticizers is known and its IR scan available, subtracting it from the IR scan of the mixture may aid in identification of the other component. Other chromatographic techniques could be used to separate the components before scanning.

TABLE 2—Selected physical properties of plasticizers prepared with 2-ethylhexyl (2-EH) and i-nonyl (iso-N) alcohols. Note: Health information about these and other plasticizers can be found by searching the CAS number on the Internet.

	Adipate		Phthalate		Trimellitate	
Abbreviation[a]	DOA	DINA	DOP	DINP	TOTM	TINTM
CAS No.	103-23-1	33703-08-1	117-81-7	28553-12-0	3319-31-1	53894-23-8
Alkyl group	2-EH	iso-N	2-EH	iso-N	2-EH	iso-N
Boiling point	214°C at 5 mm Hg	406°C	384°C	>400°C	414°C	300°C at 4 mm Hg
Density, 25°C	0.925	0.920	0.985	0.972	0.988	0.978
Flash point[b]	181°C, OC	180°C, COC	207°C, CC	221°C, CC	263°C, CC	280°C, COC
Formula MW	371	399	391	419	547	589
Pour point, °C	<–60	<–60	–47	–54	–44	–46
Refractive Index, n_{20}^{D}	1.447	1.449	1.486	1.486	1.486	1.485
Vapor pressure, mm Hg at 200°C	2.4	1.5	1.32	1.0	0.5	0.45

[a]DOA—di(2-ethylhexyl)adipates; DINA—di(iso-nonyl)adipates; DOP—di(2-ethylhexyl)phthalate; DINP—di(iso-nonyl)phthalate; TOTM—tri(2-ethylhexyl) trimellitate; TINTM—tri(iso-nonyl)trimellitate.
[b]COC = Cleveland open cup; CC = closed cup; OC = open cup.

Liquid Chromatography

Column chromatography involves distribution of substances between liquid (mobile phase) and substrate (solid phase). Column and thin layer chromatography can be used. Instrumental methods using high-performance liquid chromatography with ultraviolet detection can be used for separation, identification, and quantification of plasticizers that possess a suitable chromophore.

Gas Chromatography

By comparing relative retention times and peak shapes with known samples, a plasticizer or mixture can often be identified and quantified. When coupled with IR (i.e., GC/FTIR), the IR spectrum of each chromatographic peak can assist in the identification of functional groups and hence plasticizer identity, ASTM D3465, Standard Test Method for Purity of Monomeric Plasticizers by Gas Chromatography.

Qualitative Methods

For the detection of nitrogen, chlorine, sulphur, or phosphorus, the sample needs to be fused with metallic sodium. This preparation should be carried out in a fume hood and caution observed when handling metallic sodium. A small amount (about 3 mm^3) of metallic sodium is placed in a dry 6 in. (15.24 cm) test tube. The test tube should be held vertically by clamping it at the open end. The test tube is then heated until a cloud of sodium vapor begins to form. Remove the flame immediately. Add two to three drops of the plasticizer sample directly to the sodium vapor. When the test tube is cold, carefully break off the end containing the sodium in a mortar. Add several milliliters of alcohol to destroy unreacted sodium. Add about 20 mL of distilled or de-ionized water, grind up the sample, transfer to a beaker, bring to boil, and filter. The filtrate is then used for the chemical detection of the elements.

Sulfur

Add two to three drops of 10 % solution of lead acetate to 2 mL of a 10 % solution of sodium hydroxide. Add this mixture to 5 mL of the filtrate. A black precipitate of lead sulphide indicates the presence of sulphur. Positive identification suggests that the sample is either a sulphonamide or sulphate.

Nitrogen

Bring 2 mL of the filtrate to boil in a test tube. Add five drops of a 10 % solution of NaOH and five drops of 10 % ferrous sulphate solution. When cold, add, drop wise, a 10 % solution of hydrochloric acid until the solution is acidic and the precipitate of ferrous hydroxide has dissolved. Avoid using an excessive amount of acid. A blue or green color or blue precipitate indicates presence of nitrogen. A positive test suggests that the plasticizer could be an amide.

Chlorine

Acidify 5 mL of the filtrate with several drops of dilute sulfuric acid and bring it to boil. Cool and acidify with nitric acid. Add several drops of a 10 % silver nitrate solution. A white precipitate indicates the presence of a chlorinated compound.

Phosphorous

Boil 5 mL of the filtrate with 3 mL of concentrated nitric acid for 1 min. Cool and add twice the volume of 10 % ammonium molybdate solution. Heat to about 60°C and set aside to cool. A yellow precipitate indicates the presence of phosphorous. Phosphate plasticizers will result in a positive test.

Phthalates

Add about 0.05 g of resorcinol and 0.05 g of phenol to separate 6 in. (15.24 cm) test tubes. Add to each test tube two to three drops of the isolated plasticizer and a drop of concentrated sulfuric acid. Heat the contents in an oil bath at 160°C for several minutes. Cool and add 2 mL of distilled water and 2 mL of 10 % sodium hydroxide solution and stir. The presence of phthalate is indicated by a pronounced

TABLE 3—Plasticizers and their compatibility with coating resins. C = compatible, P = partially compatible, and I = incompatible.

Plasticizer	CA	CAB	CN	EC	PMMA	PS	VAc	VB	PVC	VC/VAc
Phthalates										
DOP	I	C	C	C	C	C	I	P	C	C
DIOP	1	C	C	C	C	C	C	P	C	C
DINP	P	C	C	C	C	C	C	P	C	C
DIDP	P	C	C	C	P	C	P	P	C	C
Trimellitates										
TOTM	P	C	C	C	P	C	P	P	C	C
TINTM	P	C	C	C	P	C	P	P	C	C
Phosphates										
TCP	C	C	C	C	P	C	C	C	C	C
TOP	P	P	C	C	I	C	I	C	C	C
Acyclic esters										
DOA	P	C	C	C	P	C	P	P	C	C
DINA	P	C	C	C	P	C	P	P	C	C
DOZ	P	C	C	C	P	C	P	P	C	C
DOS	P	C	C	C	P	C	P	P	C	C
Epoxidized										
Soybean oil	I	P	C	C	I	I	I	I	C	C
(2EH)tallate	I	C	C	C	L	L	L	C	C	C
Polyesters										
Adipic/Diol	P	C	C	C	P	C	P	P	C	C
Phthalic/Diol	P	C	C	C	P	C	P	P	C	C

Resins
CA = Cellulose acetate
CAB = Cellulose acetate/butyrate
CN = Cellulose nitrate
EC = Ethyl cellulose
PMMA = Methyl methacrylate
PS = Polystyrene
VAc = Vinyl acetate
VB = Vinyl butyral; 19 wt % vinyl alcohol
PVC = Vinyl chloride
VC/VAc = Vinyl chloride/vinyl acetate copolymer: 90/10
PLASTICIZERS
Phthalates
DOP = di(2-ethylhexyl)
DIOP = di(isooctyl)
DINP = di(isononyl)
DIDP = di(isodecyl)
Trimellitates
TOTM = tris(2-ethylhexyl)
TINTM = tris(isononyl)
Acyclic Esters
DOA = di(2-ethylhexyl) adipate
DINA = di(isononyl) adipate
DOZ = di(2-ethylhexyl) azelate
DOS = di(2-ethylhexyl) sebacate
Note: Compatibility of plasticizers in specific polymers is a function of relative concentration (PHR), as well as the presence of other formulating reagents and residuals present in polymers. The above ratings are based on plasticizer levels typically used in coatings applications (<40 PHR).

green fluorescence in the tube with resorcinol, and the tube with phenol will be red.

PERFORMANCE PROPERTIES

Compatibility

Compatibility is the ability of two or more substances to mix together without objectionable separation [12]. In the case of plasticizers, it is primarily a measure of the solvency or strength of positive interactions between the plasticizer and the polymer that attract them together.

Solvency is the extent (or amount) of interaction of plasticizer or solvent molecules at the surface of a polymer particle; a solid solution results when the polymer and plasticizer—and possibly additional reagents—become molecularly homogeneous. The degree to which a homogeneous solution, or miscibility, is stable is a function of the plasticizer/polymer interactions when in the presence of other reagents employed in the coating formulation; it must be recognized that the presence of these additional reagents can compete with the polymer/plasticizer interactions. The rule of thumb "like dissolves like" applies, but more specific knowledge is required to avoid results that appear to be anomalous.

Dried polymeric coatings may be considered as solid solutions; the limits of miscibility are impacted by all of the reagents that become components of the coating—those intentionally added, as well as inadvertent contaminates and/or degradation products formed in the coating process. When plasticizers are employed, they have a major effect on compatibility, primarily due to the level, or concentration, used in the polymer. If we accept the definition of a solution as a homogeneous mixture of two or more types of molecules, then "solvency" is a measure of a given solvent or plasticizer to homogenize and interact with a given polymer. Quantification of this "interaction" has been elusive; scales that have been devised are capable of measuring only gross differences. Observations of phase separation of plasticizer/polymer have been more finite than that predicted in many cases; while on the other hand, observations of symptoms (compatibility) are incapable of separating "solvency" from other interfering mechanisms that are concurrent, such as diffusibility.

Hansen publications [13, 14] define the total solubility parameters of polymers, solvents, and other reagents as a function of three component parameters:

$$\lambda_T = (\lambda_d^2 + \lambda_p^2 + \lambda_h^2)^{1/2}, \quad (\text{cal/cm}^3)^{1/2} \tag{3}$$

where

λ_T = total solubility parameter,
λ_d = dispersion parameter,
λ_p = polarity parameter, and
λ_h = hydrogen bonding parameter.

The location of polymers and other nonionic reagents may be defined on this three-dimensional grid. Hansen states that it may be assumed that the closer a plasticizer lies to the center of the polymer solubility space of a polymer, the more compatible it will be with the given polymer. Many materials have been characterized in this fashion. Exxon Chemical Company has developed a computerized capability to define the location of various solvents and plasticizers relative to that of various polymers; it is called the CO-ACT® program and contains information on more than 1,200 resins, solvents, and plasticizers [15].

Compatibility data for different plasticizer resin systems are available in various publications [1, 16, 17]. The plasticizers are usually presented as compatible, incompatible, or partially compatible with the resins. These data are often not useful due to incomplete description of the resin or a lack of standard approach in the test and reporting of observations. Where Hansen parameters are available for the plasticizers and resins, comparison of three-dimensional Hansen solubility parameters provide a better measure of compatibility as described earlier. Table 3 lists generalized examples of plasticizers and their compatibility with various coating resins.

Permanence

"Reactive" plasticizers are specialty types designed to self-polymerize or graft onto the polymeric resin during the curing process. But, in most cases, plasticizers do not chemically react with the polymer. They function by an overall solvating action that is less strong than that of a good solvent, but stronger than that of incompatible reagents such as lubricants. This interaction imparts a slight effect on plasticizer "permanence," or more properly "transience." One of two factors are generally the controlling influence over loss of plasticizer:

- Rate of diffusion of plasticizer from the resin bulk to the surface.
- Rate of loss of plasticizer from the surface.

The slowest rate of the two is the controlling factor under any specific set of conditions. Volatility and extraction by aqueous reagents are generally surface-controlled losses, while rate of diffusion controls loss under oil immersion and similar tests. The subject is very complex [1,2], but one may consider plasticizer vapor pressure as a key predictor of volatile loss, while diffusion-controlled losses are improved with plasticizers of higher molecular weight and branchiness in the chemical structure.

Resistance to washing is typically characterized as a function of thermal and/or humidity cycling exposures. This is a measure of the aging resistance of the plasticized polymeric coating.

Low-Temperature Properties

Some applications require flexibility and impact resistance at low temperatures. This property may be significantly improved at increased plasticizer levels, as well as being a function of the plasticizer type [1]. For example, at approximately 50 PHR, plasticizer in poly(vinyl chloride) phthalates of linear alcohols impart about –10°C improvement in low-temperature brittleness over branched, DOP-type, phthalate plasticizer. Dialkyl adipates, however, impart about –25°C improvement over the brittleness value of DOP-plasticized PVC as measured by ASTM D746, Test Method for Brittleness Temperature of Plastics and Elastomers by Impact. Commercial coatings require the optimum choice of plasticizer type and concentration to meet required costs, hardness or modulus, permanence, and low-temperature properties.

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Part 5: Solvents

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Solvents

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SOLVENTS ARE SUBSTANCES, USUALLY LIQUIDS, which are capable of dissolving other substances to bring them into liquid form. In the paint and coating industry, solvents dissolve the solid or semisolid film-forming resins and reduce viscosity so that the paint can be applied as a uniform, thin film to a surface. Although solvents are transient components of a paint, they significantly affect not only the application characteristics of a paint, but also the appearance, physical properties, and durability of the coating.

The two most important performance requirements that must be considered in selecting the proper solvent for any coating end use are solvency and evaporation rate. These key properties control initial paint viscosity during application, coating viscosity at various stages of drying, and final coating appearance. Solvents must evaporate relatively quickly during initial drying to prevent excessive flow and sag, but they must evaporate more slowly in the later stages to provide good leveling and adhesion.

Solvency and evaporation rate are often measured indirectly since direct measurements are not always feasible or convenient. In addition, there are numerous other solvent properties that must be considered for specific applications. These are often listed as requirements in the solvent specifications and include measures of purity, uniformity, safety, and compliance with air pollution regulations.

There are many different solvents used by the coatings industry. To facilitate their review and comparison, it is convenient to classify them chemically into three general categories: Hydrocarbon solvents, oxygenated solvents, and other solvents. Each category will be discussed separately in the sections that follow.

Solvents may also be classified according to the function they perform: Active, latent, and diluent. An active solvent is a true solvent for the film-forming resin and has the major role in dissolving it. A latent solvent alone will not dissolve the resin, but behaves as an active solvent or has a synergistic effect when used in conjunction with an active solvent. A diluent usually has no solvency for the resin, but is tolerated by it in blends. Diluents are added to reduce cost and vehicle viscosity through dilution.

CLASSIFICATION BY CHEMICAL TYPE

Solvents can be broadly classified by chemical type into three categories:

1. *Hydrocarbon solvents*—organic compounds comprised of molecules consisting of hydrogen and carbon atoms.
2. *Oxygenated solvents*—organic compounds comprised of molecules consisting of hydrogen, carbon, and oxygen atoms.
3. *Other solvents*—organic compounds consisting of hydrogen, carbon, and atoms other than oxygen, such as chlorine or nitrogen, or inorganic compounds such as water or supercritical carbon dioxide.

Hydrocarbon Solvents

The vast majority of hydrocarbon solvents are derived from petroleum, although a few are of vegetable origin. Therefore, hydrocarbon solvents may be regarded as being "natural products." Most are physically separated from petroleum by distillation and other refining processes. As a result, hydrocarbon solvents tend to be mixtures of organic compounds (rather than individual chemicals), and they may vary in composition depending on feedstock source.

Solvency of hydrocarbons is relatively weak compared with oxygenated and other solvents. Being of natural origin, they are good solvents for natural resins and natural-modified resins, such as drying oils, varnishes, alkyds, asphalt, rosin, and petroleum resins. However, they are generally poor solvents for synthetic resins such as vinyls, epoxies, urethanes, acrylics, and nitrocellulose. Hydrocarbon solvents are usually used as low-cost diluents in solvent blends. Other distinguishing characteristics of hydrocarbon solvents are low specific gravity and complete water immiscibility.

Hydrocarbon solvents may be further subclassified into four subcategories: aliphatics, aromatics, naphthenes, and terpenes.

ALIPHATIC HYDROCARBONS

Most aliphatic hydrocarbon solvents are manufactured by distilling the appropriate boiling range fractions from crude oil and subsequently treating them to improve odor and color stability. These saturated organic molecules are generally mixtures of straight chain or *normal-paraffins* and branched chain or iso-paraffins, with perhaps some cycloparaffins [1].

Unique, distinguishing characteristics of commodity aliphatic hydrocarbons are very weak solvency, low odor, low specific gravity, and cost. Although they are active solvents for some varnishes and alkyds, they are used primarily as low-cost diluents in solvent blends. Weak solvency is not necessarily a disadvantage of aliphatic hydrocarbons. They are preferred as carrier solvents in vinyl organosols and as

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reaction diluents in certain polymer syntheses because of their low tendency to dissolve or swell polymers.

Examples of some typical aliphatic solvents used by the coatings industry are shown in Table 1 together with their ASTM specification references. Others are commercially available as aliphatic naphthas having producer-defined distillation ranges. The fastest-evaporating solvents—hexane, heptane, and lacquer diluent—are often used as the diluent component of fast-drying lacquers, where one of their important functions is to reduce cost.

Mineral spirits is the most commonly used aliphatic solvent. (Outside the United States, mineral spirits is often called white spirits.) It is the common "paint thinner" sold in retail stores and is used in architectural paints, varnishes, and stains. It has the right combination of moderate solvency and moderately slow evaporation rate to impart proper brushability, leveling, and wet edge.

Mineral spirits is a distillation fraction boiling between 300°F (149°C) and 415°F (213°C), with a minimum flash point of 100°F (38°C). Four types are defined in ASTM D235, Specification for Mineral Spirits (Petroleum Spirits) Hydrocarbon Drycleaning Solvent [2]. "Low dry point" mineral spirits, referred to as Stoddard solvent, has a faster evaporation rate and is used as a dry-cleaning solvent.

VM&P naphthas have about the same solvency as mineral spirits, but have a much faster evaporation rate. They are distillation fractions having boiling ranges between 235°F (113°C) and 310°F (154°C). ASTM D3735, Specification for VM&P Naphthas [2], defines four types. They are used primarily in spray-applied, industrial finishes.

Several hydrocarbon solvent producers also manufacture and market complete lines of pure, isoparaffinic solvents that are synthetically produced from petroleum components. Unique characteristics of the isoparaffins are that they have very weak solvency and are virtually odorless. Examples are odorless mineral spirits and odorless VM&P naphtha.

AROMATIC HYDROCARBONS

Aromatic hydrocarbons, which are cyclic, unsaturated compounds, are also made from petroleum. However, their manufacture requires additional processing steps. To manufacture aromatic solvents, an aliphatic naphtha distillate from crude oil is typically processed through a catalytic reformer to rearrange the molecules into cyclic and

TABLE 1—Typical properties of selected aliphatic hydrocarbon solvents

Solvent	ASTM Specification	Specific Gravity 60/60°F	Distillation Range, °C	Evaporation Rate n-BuAc=100	Flash Point TCC, °F (°C)	Kauri Butanol Value	Aniline Point °F (°C)
Hexanes	D1836	0.660–0.686	63–71	1500	<0 (<–18)	33 max	135 (57)
Heptane	"	0.73	94–99	600	18 (= 8)	36	129 (54)
Lacquer diluent	"	0.75	93–115	400	20 (–7)	40	120 (49)
VM&P naphthas	D3735						
Type I "Regular"		0.72–0.79	113–154	200	40 (4) min	30–45	117 (47)
Type II "High Flash"		0.72–0.79	138–177	150	74 (23) min	30–45	110 (43)
Type III "Odorless"[a]		0.72–0.76	113–154	210	40 (4) min	30	165 (74)
Type IV "Low Aromatic"		0.72–0.76	113–154	. . .	40 (4) min	30–38	160 (71)
Mineral Spirits	D235						
Type I "Regular"		0.75–0.82	149–215	10	108 (42)	37	130 (54)
Type II "High Flash"		0.76–0.82	177–213	8	142 (61)	36	135 (57)
Type III "Odorless"		0.74–0.77	149–213	10	104 (40)	27	184 (84)
Type IV "Low Dry Point"		0.75–0.81	149–185	15	104 (40)	38	123 (51)
"Stoddard Solvent"		. . .		. . .			
Deodorized kerosene	"	0.81	177-265	2	142 (61)	30	160 (71)

[a] Isoparaffinic hydrocarbon.

TABLE 2—Typical properties of selected aromatic hydrocarbon solvents

Solvent	ASTM Specification	Specific Gravity 60/60°F min/max	Distillation Range, °C	Evaporation Rate, n-BuAc=100	Flash Point, TCC, °F (°C)	Kauri-Butanol Value	Mixed Aniline Point, °F CO
Toluene	D841	0.872	110–111	180	45 (7)	105	48 (9)
Mixed xylenes	D843	0.871	137–142	70	83 (28)	98	51 (10)
ortho-xylene	D5471	0.885	143–145	65	90 (32)	106	51 (10)
meta-xylene	D4076[a]	0.869	139–140	70	81 (27)	97	51 (10)
para-xylene	D5136	0.866	138–139	70	81 (27)	93	52 (11)
Ethylbenzene	D3193	0.872	136–137	74	70 (21)	95	52 (11)
High flash, aromatic naphthas	D3734	. . .	. . .	. . .	. . .	. . .	. . .
Type I "Aromatic 100"	"	0.865/0.882	149–183	20	100 (38)	87	65 (18)
Type II "Aromatic 150"	"	0.880/0.910	177–216	5	142 (61)	85	65 (18)

[a]Specification withdrawn 1995.

polycyclic compounds, which are further dehydrogenated to aromatic hydrocarbons. The aromatic hydrocarbons are typically concentrated and refined through an extraction process and thus separated by distillation [1].

There are four aromatic solvents commonly used by the coatings industry: Toluene, mixed xylenes, and two high-flash aromatic naphthas. Evaporation rates of these four aromatic solvents range from fast to very slow. ASTM specification references and key properties are summarized in Table 2. Distinguishing characteristics of aromatic solvents, relative to hydrocarbon solvents, are stronger solvency and odor, high specific gravity, and higher cost.

Toluene is a pure chemical, methylbenzene. It is a fast-evaporating solvent used as an active solvent for certain resins, as a lacquer diluent, in spray paints, aerosols, and in a variety of industrial coatings.

Mixed xylenes are used as paint solvents and in thinners. Xylene is a mixture of three isomers: *ortho-*, *meta-*, and *para*-xylene, plus ethylbenzene. Xylene solvents from different producers may vary in composition, resulting in slight differences in properties and performance [3]. Xylene has a moderate evaporation rate and is used primarily in industrial coatings.

The individual components of mixed xylene solvent are also isolated and marketed separately as chemical intermediates, which are used by the coatings and chemical industries. Phthalic anhydride, used in the manufacture of alkyd resins, is produced from *ortho*-xylene. Terephthalic acid, also used in the manufacture of resins, is produced from *para*-xylene. Styrene is produced from ethylbenzene.

Two *high-flash aromatic naphthas* as specified in ASTM D3734, Specification for High-Flash Aromatic Naphthas [2], round out the aromatics most commonly used by the coatings industry.

Type I—Aromatic 100 has a flash point not less than 100°F (38°C).

Type II—Aromatic 150 has a flash point not less than 142.5°F (61°C).

Aromatic 100 consists mainly of C_9 aromatics, while Aromatic 150 is a mixture of predominantly C_{10} aromatics. Both are slow evaporating and are used in baked industrial coatings.

NAPHTHENIC HYDROCARBONS

Most of the aliphatic hydrocarbon solvents contain minor amounts of naphthenes, i.e., cycloparaffins or cyclic aliphatics. Properties of naphthenes, with respect to solvency, odor, and specific gravity, are intermediate between aliphatics and aromatics.

Purely naphthenic hydrocarbon solvents currently have very limited commercial availability. Cyclohexane, a pure naphthenic hydrocarbon, finds applications not as a solvent but as a chemical intermediate in the manufacture of nylon fiber and engineering resins, plasticizers, polyurethane, polyester, and epoxy resins. Properties are summarized in Table 3.

TERPENES

Terpene solvents are obtained from pine trees and to a much lesser extent as a by-product of the citrus industry. They are the oldest solvents used in coatings, predating ancient Egyptian civilization [1,4]. The main solvents in this group

TABLE 3—Typical properties of cyclohexane

ASTM specification	D5309; D7266
Specific gravity, 60/60°F	0.782
Distillation range, °C	79–81
Evaporation rate, n-butyl acetate=100	1000 (estimated)
Flash point, °F (°C)	–4 (–20)
Kauri-butanol value	52
Mixed aniline point, °F (°C)	93 (34)

are turpentine, dipentene, and pine oil. Chemically, they are mixtures of C_{10} unsaturated hydrocarbon compounds. A good review of terpenes may be found in ASTM D804, Terminology Relating to Naval Stores, Including Tall Oil and Related Products [5].

Terpene solvents have volatilities similar to mineral spirits. However, they have only minor commercial significance today because they are more expensive than hydrocarbon solvents. Although their solvency is greater than that of aliphatic hydrocarbons, they have a much narrower range of solvency and evaporation rate and a stronger odor. Furthermore, because of their unsaturated structure, they are restricted in some areas by air pollution regulations.

There are four kinds of *turpentine,* as specified in ASTM D13, Specification for Spirits of Turpentine [5], depending on the source and method of production [1,6].

Gum turpentine or *gum spirits* is produced by distilling the crude gum or oleoresin collected from living pine trees. It contains mostly α-pinene with lesser quantities of β-pinene and small amounts of other terpene hydrocarbons.

Steam-distilled wood turpentine is obtained from oleoresin within the wood of pine stumps or cuttings, either by direct steaming of the mechanically disintegrated wood or after solvent extraction of the oleoresin from the wood. It consists primarily of α-pinene, with small quantities of dipentene and other terpenes.

Sulfate wood turpentine is recovered during the conversion of wood to pulp by the sulfate (Kraft) papermaking process. It is a mixture of α- and β-pinene, with small amounts of other terpene hydrocarbons.

Destructively distilled wood turpentine is obtained by fractionation of certain oils recovered from the destructive distillation of pine wood. It is a complex mixture of a wide variety of aromatic hydrocarbons with only moderate quantities of terpenes being present.

Standard methods of sampling and testing turpentine are described in ASTM D233, Methods of Sampling and Testing Turpentine [5].

Dipentene is obtained by fractional distillation from crude oils recovered in the several commercial methods of processing pine wood during the production of turpentine. It has somewhat stronger solvency and a slower evaporation rate than turpentine. Standard test methods for sampling and testing dipentene are described in ASTM D801, Methods of Sampling and Testing Dipentene [6].

Pine oil is a unique material separated during the four commercial turpentine production methods. Unlike the other hydrocarbon solvents, pine oil consists mainly of terpene alcohols, with a variety of small quantities of other oxygenated terpenes. Pine oil has strong solvent power due to the oxygen functionality. However, its evaporation rate is very slow. Pine oil is generally used in additive quantities, i.e., 5 wt % of the total solvent, to provide good coating flow out and wetting properties. Standard methods for sampling and testing pine oil are described in ASTM D802, Methods for Sampling and Testing Pine Oil [5].

d-Limonene is a relatively new commercial terpene hydrocarbon solvent recovered and purified from by-products of the citrus industry.

Typical properties of some selected terpene solvents are summarized in Table 4 [7,8].

Oxygenated Solvents

Oxygenated solvents contain oxygen in the molecule. Unlike hydrocarbon solvents, oxygenated solvents are synthetically produced; as a result, they are somewhat higher in cost. Most are pure, single-component chemical compounds compared with hydrocarbon solvents, which tend to be complex mixtures. Oxygenated solvents generally have very narrow distillation ranges, some as narrow as 1°C.

Relative to the hydrocarbons, oxygenated solvents have much stronger solvency and are used as active solvents for most synthetic resins. Their strong solvency, together with the wide range of volatilities available, makes them an extremely important group of solvents for the coatings industry. Other distinguishing characteristics include higher specific gravity and partial to complete water solubility.

There are four principal types of oxygenated solvents widely used in coatings: ketones, esters, glycol ethers (ether alcohols), and alcohols. Through blending, almost

TABLE 4—Typical properties of selected terpene solvents

	Turpentine					
		Wood				
	Gum Spirits	Steam Distilled	Sulfate	Destructively Distilled	Dipentene	Pine Oil
ASTM specification	D13	D13	D13	D13	. . .	. . .
ASTM test method	D233	D233	D233	D233	D801	D802
Specific gravity, 60/60°F (min/max)	0.860/0.875	0.860/0.875	0.860/0.875	0.860/0.875	0.853	0.923
Distillation range, °C	. . .	. . .	. . .	. . .	170–190	200–225
Evaporation rate, n-butyl acetate = 100	. . .	. . .	. . .	. . .	18	5
Flash point, TCC, °F (°C)	. . .	. . .	. . .	. . .	120 (49)	130 (54)
Kauri–butanol value	. . .	. . .	. . .	. . .	56	>500
Aniline point, °F (°C)	. . .	. . .	. . .	. . .	70 (21)	<–4 (<–20)
Initial boiling point, 760 mm, °C (min/max)	150/160	150/160	150/160	150/157	. . .	. . .

any desired combination of performance properties can be obtained.

KETONES

Ketones are characterized chemically by a carbonyl group (—C═O) bonded to two carbon atoms or alkyl groups in the molecule. This versatile class of solvents has powerful solvency and a wide range of evaporation rates, from very fast-evaporating acetone to slow-evaporating isophorone. Ketones are further characterized by their strong, sharp odors. They have narrow distillation ranges because of their high purity. Acetone is completely water miscible, while other ketones have varying degrees of water solubility. Properties of selected ketones, with their ASTM specification references, are summarized in Table 5. (Diacetone alcohol is included in this category since this ketone alcohol functions more as a ketone than an alcohol.)

Acetone is a very fast-evaporating solvent. It is often used in aerosols and sprayed coatings, particularly in nitrocellulose and acrylic lacquers, to effectively reduce viscosity for spray application and then quickly flash off during the spraying process. Methyl ethyl ketone (MEK) has a fast evaporation rate, and methyl isobutyl ketone (MIBK) exhibits a moderate evaporation rate. MEK and MIBK are extensively used as active solvents in synthetic resin lacquers and paints. The very slow evaporation rate of isophorone makes it useful in baked industrial coatings.

ESTERS

Esters used as solvents are alkyl acetates and propionates and glycol ether acetates. Several other types of ester solvents are also commercially available as specialty products. The alkyl esters cover a wide range of volatilities, mainly methyl through hexyl esters. Glycol ether acetates are slow-evaporating solvents, and they are used as retarder solvents in solvent-based coatings and as coalescents in latex paints.

Esters have strong solvency, although generally slightly weaker than ketones of similar volatility. They are characterized by their pleasant, sweet, fruity odors. All esters have narrow distillation ranges since they are relatively pure compounds.

Typical properties of the most common ester solvents are summarized in Table 6. As with ketones, their solvencies follow a general pattern, diminishing with increasing molecular weight and with increasing branching of the molecule. Evaporation rate also decreases with increasing molecular weight, but increases with increased branching. n-Butyl acetate, one of the most important ester solvents, has a medium evaporation rate. It is used as a reference for expressing evaporation rates of other solvents.

GLYCOL ETHERS

Glycol ethers are ether alcohols having both ether and alcohol functionality. The ethylene glycol ethers, derived from ethylene oxide and alcohols, have been widely used in coatings. However, because of health hazard concerns associated with certain ethylene glycol ethers, they are being replaced in many applications by propylene glycol ethers, which are derived from propylene oxide.

Glycol ethers have a truly unique combination of properties: Strong solvency, slow evaporation rate, complete water miscibility, high flash point, and mild odor. They are often used in small percentages in lacquers and lacquer thinners as retarder solvents to maintain coating flow and leveling after most of the other solvents have evaporated. In these applications, their water miscibility is beneficial in reducing moisture blush. Glycol ethers are also widely used as coupling solvents in water-based coatings to solubilize the water-reducible polymers.

Chemical terminology for the glycol ethers is cumbersome. For example, 2-ethoxyethanol is also referred to as ethylene glycol monoethyl ether. Therefore, they are often identified by their commercial brand names. Typical properties of selected glycol ethers are summarized in Table 7.

TABLE 5—Typical properties of selected ketone solvents

Solvent	ASTM Specification	ASTM Purity Test	Specific Gravity Range, 20/20 °C	Boiling Point, °C	Evaporation Rate, n-BuAc=100	Flash Point, TCC, °F (°C)	Toluene Dilution Ratio
Acetone	D329	D1363	0.792	56	1160	0 (–18)	4.5
Methyl ethyl ketone	D740	D2804	0.806	80	570	20 (–7)	4.3
Type I regular	"	"	0.805–0.807	78.5–81.0	. . .	. . .	. . .
Type II urethane grade	"	"	0.805–0.807	78.5–81.0	. . .	. . .	. . .
Methyl isobutyl ketone	D1153	D3329	0.800–0.803	114–117	165	60 (16)	3.6
Methyl isoamyl ketone	D2917	D3893	0.812–0.815	140–148	50	96 (36)	4.1
Methyl n-amyl ketone	D4360	D3893	0.817	151	40	102 (39)	3.9
Diacetone alcohol	D2627	. . .	0.940	170	12	120 (49)	3.0
Isophorone	D2916	D2192	0.922	215	3	180 (82)	6.2

TABLE 6—Typical properties of selected ester solvents

Solvent	ASTM Specification	ASTM Purity Test	Specific Gravity, 20/20°C	Boiling Point, °C	Evaporation Rate n-BuAc=100	Flash Point, TCC, °F CO	Toluene Dilution Ratio
Methyl acetate	. . .	. . .	0.904	55	1180	0 (–18)	2.9
Ethyl acetate	D4614	D3545	0.901	77	410	24 (–4)	3.1
Isopropyl acetate	D3131	D3545	0.873	88	360	35 (+2)	3.0
n-Propyl acetate	D3130	D3545	0.889	101	230	55 (13)	3.2
Isobutyl acetate	D1718	D3545	0.871	115	145	62 (17)	2.7
n-Butyl acetate	D4615	D3545	0.883	126	100	81 (27)	2.8
n-Amyl acetate	D3540	D1617	0.876	140	40	101 (38)	2.3
Methyl amyl acetate[a]	D2634	D1617	0.858	148	20	96 (36)	1.7
n-Hexyl acetate	D5137	D1617	0.874	165	17	134 (57)	1.8
n-Butyl propionate	. . .	. . .	0.876	145	45	100 (38)	2.1
n-Pentyl propionate	. . .	. . .	0.872	168	18	135 (57)	1.8
2-Ethoxyethyl acetate[b]	D3728	D3545	0.974	156	20	126 (52)	2.5
PM acetate[c]	D4835	D4773	0.969	146	34	114 (46)	2.6

[a] Four grades.
[b] Ethylene glycol monoethyl ether acetate.
[c] Propylene glycol monomethyl ether acetate.

ALCOHOLS

Alcohols are chemically characterized as organic compounds having a single hydroxyl group (–OH). This structure imparts some degree of water solubility to alcohols, complete for the low molecular weight compounds, methanol, ethanol, and propanol, and partial for the higher molecular weight compounds. Alcohols are further characterized physically as having mild, pleasant odors. Typical properties of selected alcohols are summarized in Table 8.

By themselves, alcohols are very poor solvents or non-solvents for most polymers. There are few exceptions; ethanol is a solvent for shellac, poly(vinyl acetate), poly (vinyl butyrate), some phenolics, and natural resins. Alcohols find applications as latent solvents or co-solvents for nitrocellulose lacquers, melamine-formaldehyde and urea formaldehyde resins, and certain alkyds. They are also useful coupling solvents, with glycol ethers, to solubilize water-reducible resins. In addition to their use as solvents, latent solvents, and coupling solvents, they are

TABLE 7—Typical properties of selected glycol ether solvents

Solvent	ASTM Specification	ASTM Purity Test	Specific Gravity Range 20/20°C	Boiling Point Range, °C	Evaporation Rate, n-BuAc=100	Flash Point, TCC, °F (°C)	Toluene Dilution Ratio
2-Methoxyethanol[a]	D3128	. . .	0.963–0.967	123–126	56	103 (39)	4.0
2-Ethoxyethanol[b]	D331	. . .	0.929–0.932	134–136	35	108 (42)	4.9
2-Butoxyethanol[c]	D330	. . .	0.901–0.904	168–173	6	150 (66)	3.5
Propylene glycol monomethyl ether	D4837	D4773	0.922–0.925	117–125	71	94 (34)	5.2
Dipropylene glycol monomethyl ether l	D4836	D4773	0.953–0.956	184–195	3	167 (75)	4.2

[a] Ethylene lycol monomethyl ether.
[b] Ethylene glycol monoethyl ether.
[c] Ethylene glycol monobutyl ether.

TABLE 8—Typical properties of selected alcohol solvents

Solvent	ASTM Specification	ASTM Purity Test	Specific Gravity, 20/20°C	Boiling Point, °C	Evaporation Rate, n-BuAc=100	Flash Point, TCC, °F (°C)	Solubility, 20°C, wt%	
							In Water	Water In
Methanol	D1152	E346	0.793	64	600	52 (11)	Complete	Complete
Ethanol, anhydrous	. . .	. . .	0.790	78	260	55 (13)	Complete	Complete
Isopropanol	D770	. . .[a]	0.786	82	230	54 (12)	Compete	Complete
n-Propanol	D3622	. . .[a]	0.804	97	100	74 (23)	Complete	Complete
sec-Butanol	D1007	. . .[a]	0.808	99	120	74 (23)	20.0	36.3
Isobutanol	D1719	. . .[a]	0.803	107	70	85 (29)	9.5	14.3
n-Butanol	D304	. . .[a]	0.811	117	50	97 (36)	7.9	20.8
n-Amyl alcohol	D319	. . .[a]	0.813	130	30	91 (33)	1.7	9.2
Methyl isobutyl carbinol	D2635	. . .[a]	0.808	131	30	103 (39)	1.6	6.3
2-Ethyl hexanol	D1969	D5008	0.834	182	<1	164 (73)	0.1	2.6

[a] Purity and identity of these pure compounds are determined by a combination of tests of specific gravity (ASTM D268 or D4052), boiling point, and distillation range (ASTM D1078).

used as chemical raw materials for the manufacture of other solvents (e.g., ketones and esters), monomers, and synthetic polymers.

Methanol is the fastest evaporating alcohol. It is the only alcohol that has some solvency for nitrocellulose. Methanol, historically known as wood alcohol, is now rarely used as a solvent because of its relative toxicity.

Pure ethyl alcohol (ethanol) is restricted in use by law to beverages and to scientific and analytical purposes. It cannot be used without a federal government permit. Commercial ethyl alcohol, for solvent and chemical intermediate use, is denatured with any of a large number of government-approved substances to make it unfit for use in beverages. There are close to 100 approved denatured formulations available in both 95 vol % (190 proof) and anhydrous (200 proof) grades. Because of the large multiplicity of grades, ASTM specifications have not been established for ethyl alcohol. Isopropyl alcohol can replace ethyl alcohol in most coating solvent applications.

Butyl alcohols (butanols) differ in volatility and solvency among the four isomers, which are normal, secondary, iso-, and tertiary. All have moderate volatility. Branching increases volatility and decreases solvency. n-Butanol is by far the most widely used isomer. t-Butanol is a solid at room temperature.

The higher-boiling alcohols are used in relatively small amounts in solvent blends, and they find applications mainly in baked industrial coatings.

OTHER OXYGENATED SOLVENTS

Specialty oxygenated solvents include furan solvents and organic carbonates. Currently, they are not specified by ASTM standards. Information about them may be obtained from their suppliers.

Furan solvents of commercial interest include furfuryl alcohol, tetrahydrofuran (THF), and tetrahydrofurfuryl alcohol. These solvents have a cyclic ether structure and are characterized by exceptionally strong solvency for some synthetic resins, especially vinyls.

Ethylene and propylene carbonates are cyclic organic esters, which are good solvents for many organic and inorganic materials. The former is a solid at room temperature. Characteristics of these carbonates include high flash point, very slow evaporation rate, high specific gravity, and very low odor.

Other Solvents

CHLORINATED HYDROCARBONS

Chlorinated solvents contain chlorine atoms in the molecules. This gives them unique features of nonflammability, i.e., most have no flash point, and very high specific gravity. Several chlorinated solvents specified by ASTM standards are summarized in Table 9.

Methylene chloride has long been the active ingredient in many paint removers. It has strong solvency to soften and swell cured paint films and has a very fast evaporation rate.

1,1,1-Trichloroethane (methylchloroform) found solvent applications in coating formulations because it was considered to be nonphotochemically reactive by many regulatory agencies, and therefore did not have to be included in measuring volatile organic compound (VOC) content [1]. However, in the recent Montreal HAZOP accord, it has been banned and is no longer manufactured.

Trichloroethylene is widely used for metal cleaning in vapor degreasing operations. (See ASTM D3698, Practice for Solvent Vapor Degreasing Operations [9].)

Use of chlorinated solvents is declining due to (a) global concerns about their damaging effects on the Earth's protective ozone layer and (b) concerns about the toxicity and carcinogenicity of many chlorinated solvents.

NITRATED HYDROCARBONS

Nitrogen-containing hydrocarbon solvents include nitroparaffins and N-methyl-2-pyrrolidone (NMP). These are not currently specified by ASTM standards.

There are four nitroparaffinic solvents commercially available: nitromethane, nitroethane, 1-nitropropane, and 2-nitropropane (2NP). Of these, 2NP is of most interest to

TABLE 9—Typical properties of selected chlorinated hydrocarbon solvents

Solvent	ASTM Specification	Grade or Application	Specific Gravity, 20/20°C	Boiling Point, °C	Evaporation Rate, n-BuAc=100
Methylene chloride	D3506[a]	Pentachlorophenol solutions	1.366	38	1450
"	D4079	Vapor degreasing	. . .	. . .	. . .
"	D4701	Technical grade	. . .	. . .	. . .
1,1,1-Trichloroethane	D4126	General solvent; vapor degreasing	1.327	72	600
Trichloroethylene	D4080	Vapor degreasing	1.465	86	450
Perchloroethylene	D4081	Dry cleaning	1.625	121	210

[a] Specification was withdrawn in 1993.

the coatings industry. It has an evaporation rate similar to that of *n*-butyl acetate, and it is reported to have fast solvent release from coating films.

NMP is a specialty solvent having strong solvency, high flash point, complete water solubility, and high specific gravity. It is reported to be biodegradable and have a low order of toxicity. Applications include paint strippers, water-based coatings, printing inks, and reaction solvent for high-temperature resins.

SUPERCRITICAL CARBON DIOXIDE [10]

It has long been known that certain gases under supercritical temperature and pressure conditions can behave as solvents. They have become useful in a variety of industrial and analytical separation processes, such as extraction, polymer fractionation, chromatography, and catalyst regeneration, and as a reaction medium.

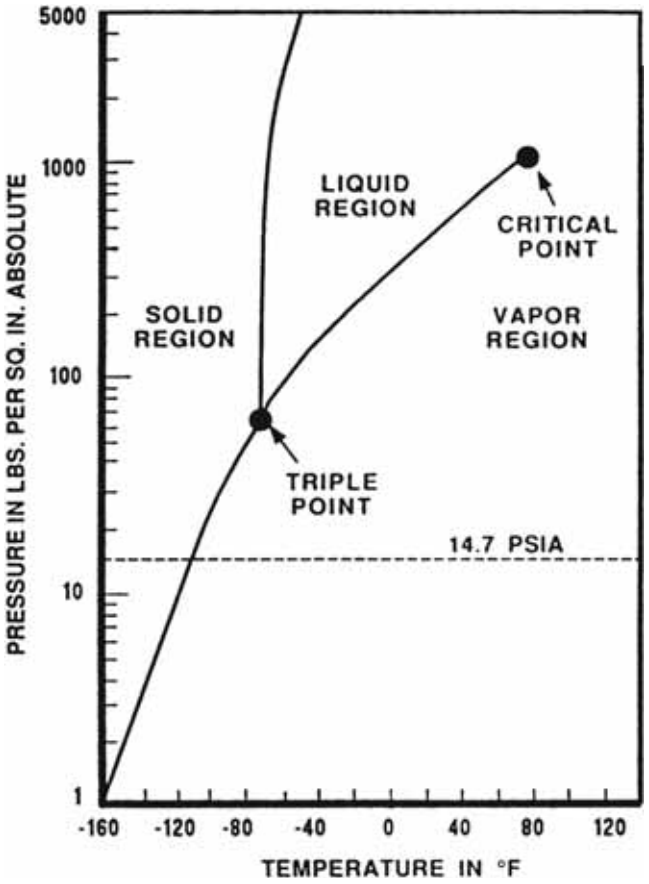


Fig. 1—Phase diagram for carbon dioxide [10].

Supercritical fluids have properties intermediate to those of normal liquids and gases. The supercritical fluid region on a phase diagram corresponds to temperatures and pressures near or above the critical point of the fluid where the properties of the liquid and gas are similar or identical, so that in effect only one fluid phase, which is simultaneously liquid like and gas like, exists (Fig. 1).

Supercritical carbon dioxide has many useful attributes, which make it attractive as a diluent for spray-applied coatings. Carbon dioxide is environmentally compatible because it is not regarded as a VOC. It acts as a hydrocarbon diluent and replaces organic solvents to the extent of 10-30 vol % of a formulation. Low VOC coatings can be formulated with existing high-performance polymer systems, and 70-80 % reductions in VOC are achievable. Using carbon dioxide as a coating solvent effects a net reduction in the amount of "greenhouse" carbon dioxide that is otherwise produced as a result of coating operations.

The UNICARB™[3] process has been developed to utilize supercritical carbon dioxide in airless sprayed coating operations. It has numerous advantages in this application. The temperatures and pressures necessary to use supercritical carbon dioxide are well within the capabilities of present hot, airless spray systems.

Carbon dioxide has low toxicity, is nonflammable, inert, inexpensive, and readily available. Supercritical carbon dioxide has high solubility in most coating formulations, and it is a good viscosity reducer for polymer solutions. In the actual spraying process, it behaves as a highly volatile solvent, producing vigorous atomization that can remedy many of the defects of airless spraying, thereby achieving high quality coatings.

CLASSIFICATION BY FUNCTION

Solvents can be classified according to the function they perform in an end-use application: active solvents, latent solvents, and diluents.

Active Solvents

Active solvents are sometimes called "true solvents." They are the ones that really do the work to dissolve resins and

[3] Union Carbide Corp., a subsidiary of Dow Chemical Co.

other film formers. Active solvents are usually the more expensive ones with strong solvent power: ketones, esters, and glycol ethers. They are essential for dissolving film-forming polymers and for effectively reducing the viscosity of paints, varnishes, and lacquers for application.

Relative solvency of active solvents, particularly for lacquers, may be determined by ASTM D1720, Method for Dilution Ratio of Active Solvents in Cellulose Nitrate Solution [2], and expressed in terms of toluene dilution ratio. Stronger solvents will tolerate more hydrocarbon diluent and still keep resins in solution. High toluene dilution ratio values indicate strong solvency. Typical values for selected active solvents may be compared in Tables 5–7.

Latent Solvents

By themselves, latent solvents are either poor solvents or nonsolvents for most coating resins. However, they possess a hidden or latent solvency that manifests itself when they are used in combination with active solvents. Latent solvents then behave as if they were strong active solvents. This synergism is used to advantage in formulating nitrocellulose lacquers in particular. Latent solvents are often alcohols that are intermediate in cost.

Diluents

Diluents are generally nonsolvents if used alone with synthetic resins. Their function is to participate in solvent blends to provide viscosity reduction through dilution of lacquers and paints and to reduce the cost of thinners and coating solvent blends. Diluents are usually low-cost hydrocarbon solvents.

There is usually a limit to how much diluent will be tolerated by coating resins in a solvent blend. If the limit is exceeded, the resins will start to gel or precipitate from solution. Aromatic hydrocarbon solvents are usually tolerated in greater amounts than are aliphatic hydrocarbons.

ASTM D1720 may be used to determine the relative tolerances for hydrocarbon diluent when *n*-butyl acetate is used as the reference active solvent. In the test, the maximum ratio of hydrocarbon diluent to *n*-butyl acetate that will be tolerated by a solution of 8 g of nitrocellulose in a total of 100 mL of solvent and diluent is determined. This provides a measure of the suitability of the diluent for lacquer solvent fromulations. For example, the toluene dilution ratio of n-butyl acetate is 2.8, while the VM&P naphtha dilution ratio is only 1.2, indicating a much greater tolerance for toluene than for VM&P naphtha.

Solvent Balance

In formulating coating solvents and thinners, careful attention must be paid to the proper balance of solvency and evaporation rate. Generally, expensive active solvents are kept to a minimum amount that is sufficient to provide adequate solvency and viscosity reduction. Diluent content is usually maximized to keep cost low.

Evaporation rate of each component must be considered in selecting appropriate active solvents and diluents depending on the method of coating application. As the applied coatings dry, the balance of active solvents and diluents remaining in the wet coating must be such that solvency for the coating resin remains sufficiently strong throughout the drying process. Otherwise, resin blush, i.e., precipitation or separation of the resin, can occur, resulting in loss of gloss, incompatibility, haze, or other serious coating defects.

KEY PERFORMANCE REQUIREMENTS

Solvency

Solvency is the foremost performance requirement of a solvent. From a practical perspective, the term "solvency" to a coatings formulator refers to the ability of a solvent to (a) dissolve resins, (b) hold those resins in solution in the presence of diluents, and (c) efficiently reduce viscosity of resin solutions, lacquers, and paints. In general, relative solvency is measured indirectly by determining compatibility of specified resins or a chemical reagent with the solvent under test.

Three test methods are most often used for measuring and expressing relative solvent strength: Kauri-butanol value, aniline point, and diluent ratio. The first two test methods are used exclusively for hydrocarbon solvents and the latter test for only oxygenated solvents. Although these methods are somewhat archaic, the values obtained have been found to be useful in estimating general solvency for many coating resins.

Another method, a viscosity reduction test, provides a means of direct measurement of solvent power when a specific resin under consideration is employed. Solvents are directly compared by measuring the viscosities of solutions at different resin concentrations and plotting viscosity versus resin concentration.

KAURI-BUTANOL VALUE

Kauri-butanol value (KBV) is one measure of the solvent power of hydrocarbon solvents. High KBV indicates relatively strong solvency and often relatively high aromatics content as well. Comparative KBVs for selected materials are found in Tables 1–4.

KBV is a continuous scale and is sometimes used as an indicator of aromatics content; low aromatic (aliphatic) hydrocarbons have low KBVs and weak solvency, while highly aromatic hydrocarbons have high KBVs and relatively strong solvency. For example, odorless mineral spirits at the low end of the scale have a KBV of about 27, regular mineral spirits about 37, and aromatic hydrocarbons close to 100.

KBV is defined in ASTM Method D1133, Method for Kauri-Butanol Value of Hydrocarbon Solvents [2], as the volume in milliliters of the solvent at 25°C required to produce a defined degree of turbidity when titrated into a specified quantity of a standard clear solution of kauri resin in *n*-butyl alcohol; Kauri resin, a natural product, now archaic, was once used as a coating polymer. Standard test solutions are available from chemical supply companies. The kauri resin solution is standardized against toluene, which has an assigned value of 105, and a mixture of 75 % *n*-heptane and 25 % toluene on a volume basis has an assigned value of 40.

The procedure is to accurately weigh 20 g of standardized kauri-butanol solution into an Erlenmeyer flask and bring the flask and its contents to 25°C in a water bath. It is then titrated with the solvent being tested to a turbidity end point that occurs when the sharp outlines of ten-point print on a sheet placed under the flask are obscured or blurred but are not illegible. Turbidity at the end point is caused by precipitation of the kauri resin at incipient incompatibility.

This test is not applicable to oxygenated solvents.

ANILINE POINT

Aniline point (or mixed aniline point) is another measure of solvency of hydrocarbon solvents. In addition, it is often used to provide an estimate of the aromatics content of hydrocarbon mixtures. Aromatic hydrocarbons (strong solvents) exhibit the lowest aniline points and aliphatics (weak solvents) the highest. Naphthenes have values between those for aromatics and aliphatics. In homologous series, the aniline point increases with increasing molecular weight, i.e., decreasing solvency.

Aniline point is defined in ASTM Method D611, Aniline Point and Mixed Aniline Point of Petroleum Products and Hydrocarbon Solvents [11], as the minimum equilibrium solution temperature for equal volumes of aniline and solvent. The reagent for this test is aniline, a clear liquid at room temperature. The procedure requires that equal volumes of aniline and hydrocarbon solvent be placed in a jacketed tube and mechanically mixed. The basic apparatus is shown in Fig. 2, although ASTM D611 also describes alternative variations in the manual apparatus and an automatic apparatus as well.

Hydrocarbon solvents containing less than 50 % aromatics will generally form an incompatible, turbid mixture at room temperature [12]. Therefore, the stirred mixture is heated at a controlled rate until the two phases become miscible and clear. The stirred mixture is then allowed to cool at a controlled rate until it suddenly becomes cloudy throughout. The temperature at this end point is recorded as the aniline point of the solvent.

Hydrocarbon solvents containing more than 50 % aromatics will generally form clear, miscible solutions with aniline at room temperature [12]. When this occurs, the stirred mixture must be cooled below room temperature at a controlled rate until the cloudy transition point suddenly appears. The temperature at this cloud point is the aniline point.

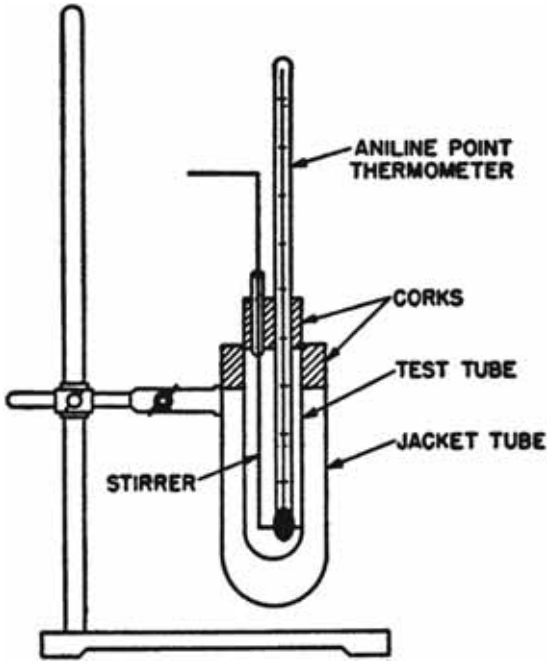


Fig. 2—Basic aniline point apparatus.

With hydrocarbons having high aromatics content, the aniline point may be far below room temperature and below the temperature at which aniline will crystallize from the aniline-sample mixture. To treat this circumstance, it becomes necessary to perform a "mixed aniline point" test. Instead of using equal volumes of aniline and sample, a mixture containing two volumes of aniline, one volume of sample, and one volume of n-heptane of specified purity is made. The test is then performed as described above, and the result is reported as the mixed aniline point. Again, low values indicate strong solvency (the opposite of kauri-butanol values).

Unlike the continuous KBV scale, a disadvantage of the aniline point and mixed aniline point is that the two scales are not continuous. Therefore, it is difficult to directly compare high- and low-aromatic content solvents [12].

This test is not applicable to oxygenated solvents.

DILUENT RATIO

The diluent ratio test measures the solvency of oxygenated (active) solvents by determining their ability to hold in solution a difficult-to-dissolve resin, nitrocellulose, in the presence of hydrocarbon diluent. The test measures the maximum ratio of hydrocarbon diluent to oxygenated solvent that can be tolerated by the nitrocellulose solution. Strong oxygenated solvents provide a high tolerance for diluent and have high diluent dilution ratios. Typical values may be compared in Tables 5–7.

ASTM D1720 defines diluent ratio as the maximum number of unit volumes of a diluent that can be added to a unit volume of solvent to cause the first persistent heterogeneity (precipitation) in the solution at a concentration of 8 g of cellulose nitrate per 100 mL of combined solvent plus diluent at 25°C.

The procedure is to dissolve dried nitrocellulose in the oxygenated (active) solvent, and with stirring, add hydrocarbon diluent by titration. The end point occurs at the first persistent appearance of resin precipitation or gelation. Additional active solvent is then added to redissolve the resin, and titration is continued to a second end point. The data are plotted to determine the ratio of diluent to active solvent at exactly 8 g of cellulose nitrate per 100 mL of total solvent.

Most often, toluene is used as the diluent in the test, and the result is expressed as the "toluene dilution ratio." However, other hydrocarbons, e.g., VM&P naphtha, may also be used, thereby producing different (lower) values expressed as "naphtha dilution ratios." Although cellulose nitrate is used as the "reagent" in this test, and the results are most meaningful for formulating nitrocellulose lacquers, it has been found from experience that the solvency ranking of oxygenated solvents according to their diluent dilution ratios applies to other coating resins as well.

As described in the section entitled "Diluents," ASTM D1720 may also be applied to compare and measure the suitability of specific diluents for use in lacquer solvent and thinner formulations by using *n*-butyl acetate as the reference active solvent in the test.

DILUTION LIMIT

Some resins are soluble at high concentrations in a solvent but become incompatible and precipitate when diluted below a critical concentration, which is termed the dilution

limit. Sometimes, this concentration is within the range of practical formulations. Therefore, it is important to know whether a dilution limit exists for a particular resin. To determine the dilution limit, a known weight of resin is dissolved in the solvent. Solvent is then added until precipitation, the first persistent cloudiness, appears. Dilution limit is expressed as the percent by weight of resin at the end point [12].

VISCOSITY REDUCTION

The relative solvency of different solvents for a given resin may be compared with each other or with a reference solvent by measuring the viscosities of different concentrations of the given resin in each of the solvents. The viscosities are then plotted as a function of resin concentration. An example is shown in Fig. 3 [1].

Viscosities of resin solutions can be measured precisely by ASTM D445, Method for Kinematic Viscosity of Transparent and Opaque Liquids [11], or by ASTM D1725, Method for Viscosity of Resin Solutions [5]. A simpler, more widely used, but less precise, method for determining resin solution viscosities is ASTM D1545, Method for Viscosity of Transparent Liquids by Bubble Time Method (Gardner-Holdt Viscosity) [5].

At high resin concentrations, solution viscosity will depend on solvency of the solvent and solubility of the resin. However, at low resin concentrations, the solution viscosity becomes more influenced by viscosity of the pure (neat) solvent. Viscosities of selected solvents are listed in Table 10 [13].

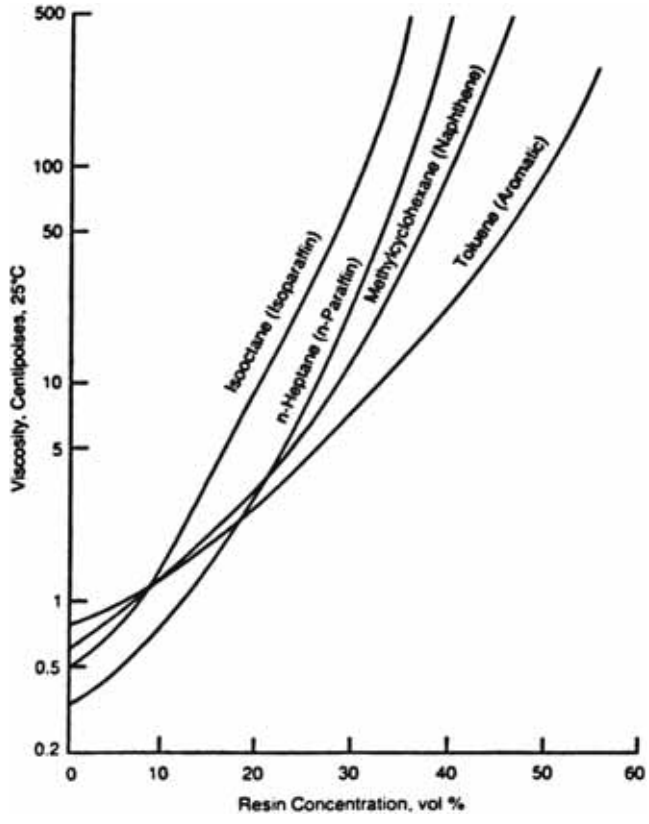


Fig. 3—Effect of solvent type on solution viscosity (medium oil alkyd in four hydrocarbon types) [1].

TABLE 10—Viscosities of typical commercial solvent

Solvent	Viscosity cp at 25°C
Hydrocarbons	
VM&P naphtha	0.68
Mineral spirits	1.10
Toluene	0.62
Xylene	0.67
High–flash aromatic naphtha	1.08
Ketones	
Acetone	0.31
Methyl ethyl ketone	0.41
Methyl isobutyl ketone	0.56
Methyl isoamyl ketone	0.73
Methyl n-amyl ketone	0.77
Isophorone	2.3
Esters	
Ethyl acetate	0.45
Isopropyl acetate	0.52
Isobutyl acetate	0.68
n-Butyl acetate	0.68
n-Amyl acetate	0.83
Propylene glycol monomethyl ether acetate	1.1
Ethylene glycol monoethyl ether acetate	1.2
Ethylene glycol monobutyl ether acetate	1.7
Alcohols	
Ethanol	1.1
n-Propanol	2.0
i-Propanol	2.4
n-Butanol	2.6
s-Butanol	2.9
n-Amyl alcohol	3.7
Glycol ethers	
Propylene glycol monomethyl ether	1.7
Ethylene glycol monoethyl ether	1.9
Ethylene glycol monobutyl ether	2.9

SOLUBILITY PARAMETERS

Great strides have been made in developing theoretical models to describe solvency and to predict the capacity of a pure solvent or solvent blend to dissolve a given resin. The concept of solubility parameters was first proposed by Hildebrand [14,15], and it was applied to practical

applications in the coatings industry by Burrell [16]. Further refinements and enhancements to the solvency model made by Burrell [17], Crowley [18], Hansen [19,20], and others have resulted in the evolution of a model that is workable, reasonably accurate in its predictions, and useful as a formulating tool.

The three-dimensional solubility parameter is the most widely used method for predicting miscibility/solvency between solvents and polymers. In this method, each polymer and each solvent is characterized by three solubility parameters: δ_d representing dispersion forces, δ_p representing polar forces, and δ_h representing hydrogen bonding forces. Therefore, polymers and solvents can be represented by points in a three-dimensional plot using the three solubility parameters.

Each polymer point may constitute the center of a sphere, the so-called "sphere of solubility," of radius *R*, known as the radius of interaction. Solvents whose points lie at a distance less than *R* from the center of the polymer's sphere, i.e., within the sphere, should dissolve the polymer. Conversely, solvents whose point coordinates lie outside of the sphere are not expected to dissolve the polymer [21]. A more thorough discussion of solubility parameters can be found in Chapter 35 of this manual.

A very comprehensive source of solubility parameter information and data is the "CRC Handbook of Solubility Parameters and Other Cohesive Parameters" by A. F. M. Burton [22]. A simpler, two-dimensional approach to solubility parameters, employing only the dispersion and hydrogen bonding parameters, is described in ASTM D3132, Test for Solubility Range of Resins and Polymers [5]. Most major solvent suppliers have developed computer programs, based on the solubility parameter concept, to aid in formulating solvent blends to optimize solvency, obtain desired performance requirements, and minimize cost.

Volatility

Volatility of a solvent describes its inherent tendency to transform from a liquid to a vapor. The fundamental controlling property is vapor pressure. Volatility is manifested by such properties as evaporation rate, boiling point, and flash point.

VAPOR PRESSURE

All liquids have a tendency to vaporize and become gases, depending upon their relative vapor pressures. A solvent's liquid vapor pressure is the pressure exerted by molecules at the liquid surface in their attempt to escape the liquid phase and penetrate their gaseous environment. In a physical sense, vapor pressure is the force exerted on the walls of a closed container by the vaporized portion of the liquid. Conversely, it is the force that must be exerted on the liquid to prevent it from vaporizing further. For a given liquid solvent, vapor pressure is a function purely of temperature. The more volatile a solvent, the higher the liquid vapor pressure at a specified temperature and the faster the vaporization, i.e., evaporation rate. A knowledge of the vapor pressure/temperature relationship is important in the safe design of solvent storage and distribution equipment to minimize solvent losses by vaporization.

Relative vapor pressures of pure solvents and blends are measured at 100°F (38°C) by ASTM D323, Method for Reid Vapor Pressure (RVP) [11]. The RVP apparatus consists of a double-chamber bomb fitted with a pressure gage. The lower chamber, which has one quarter the capacity of the upper chamber, is filled with the liquid solvent sample. The sample and its chamber are chilled to 0°C (32°F) to reduce premature evaporation, the bomb is sealed, and it is immersed in a 100°F (38°C) water bath. To assure full opportunity for vaporization, the bomb is removed from the bath periodically for a brief vigorous shaking. When an equilibrium temperature is reached and when the bomb pressure gage (which initially registered zero) has stabilized at maximum value, the pressure is recorded. After applying appropriate correction factors, the pressure is reported as the Reid vapor pressure at 100°F (38°C).

Alternatively, vapor pressure of a solvent can be measured over a wide range of temperatures by ASTM Method D2879, Method for Vapor Pressure by Isoteniscope [23]. This procedure utilizes a differential manometer, one leg of which is exposed to saturated vapor while the other is evacuated. Measurements are reported in absolute units. Absolute vapor pressures of selected solvents at 20°C are listed in Table 11 [8,13].

In the last 15 years, the use of automatic instruments for measuring vapor pressure have grown. ASTM D5190, Method for Vapor Pressure of Petroleum Products (Automatic Method) [49]; ASTM D5191, Method for Vapor Pressure of Petroleum Products (Mini Method) [49]; and ASTM D5482, Method for Vapor Pressure of Petroleum Products (Mini-Method-Atmospheric) [49] are all automatic vapor pressure test methods. Although primarily used for gasoline and reformulated gasoline, the performance of the various automatic vapor pressure instruments are checked using pure hydrocarbon liquid materials.

EVAPORATION RATE

Evaporation rate of a solvent is second only to solvency in its importance to the coatings industry. Although solvents are transient ingredients of a coating, they perform vital functions but must ultimately leave the coating film by evaporation. During application of a coating, solvents play a role in controlling flow characteristics as the film forms. If solvent evaporation is too fast, the coating film will not level and flow out to form a smooth surface, the result being a rough, "orange peel" effect in spray-applied coatings, or brush marks if brush applied. Conversely, if solvent evaporation is too slow, the coating may run and sag on vertical surfaces, or solvents may become trapped in the film as it cures, thus impairing performance properties of the coating.

For proper solvent balance, the ratio of active solvent to diluent is important. If this balance becomes upset as a result of composition changes during evaporation, resin precipitation can occur, thereby causing a loss of film integrity. Therefore, solvent evaporation rate is a key factor in the formulation of coatings. Relative evaporation rates of selected solvents of various types may be compared in Fig. 4 and in Tables 1–9.

Evaporation rates of solvents are always expressed on a relative basis. They are not absolute values in practical situations because evaporation rates are dependent upon numerous environmental factors including temperature, airflow, humidity, exposed surface area, and the presence of resin and pigment. Humidity has no effect on the evaporation of hydrocarbon solvents, but it can significantly retard

TABLE 11—Vapor pressures of typical commercial solvents

Solvent	Vapor Pressure at 20°C, 760 mm Hg
Hydrocarbons	
VM&P naphtha	5.2
Mineral spirits	3.4
Toluene	38
Xylene	9.5
High–flash aromatic naphtha	<1
Ketones	
Acetone	185
Methyl ethyl ketone	85
Methyl isobutyl ketone	16
Methyl isoamyl ketone	4.0
Methyl n-amyl ketone	1.0
Isophorone	0.3
Esters	
Ethyl acetate	76
Isopropyl acetate	48
Isobutyl acetate	12.5
n-Butyl acetate	7.8
n-Amyl acetate	4.0
Propylene glycol monomethyl ether acetate	3.7
Ethylene glycol monoethyl ether acetate	1.7
Ethylene glycol monobutyl ether acetate	0.29
Alcohols	
Ethanol	44
n-Propanol	31
i–Propanol	15
n-Butanol	12
s–Butanol	4.4
n-Amyl alcohol	2.0
Glycol ethers	
Propylene glycol monomethyl ether	11
Ethylene glycol monoethyl ether	4.1
Ethylene glycol monobutyl ether	0.9

evaporation of oxygenated solvents, which are completely or partially water miscible.

It is common practice to express evaporation rates relative to *n*-butyl acetate, a widely used, medium-evaporating solvent as a reference. The evaporation rate of *n*-butyl acetate is arbitrarily assigned a value of 100 (or sometimes 1.0 depending on the scale used). Solvents evaporating faster than *n*-butyl acetate have higher values for evaporation rate; while those solvents evaporating slower have lower numerical values. Use of a reference standard compensates for differences in test procedure and environmental factors.

Numerous techniques have been used for measuring relative evaporation rates, some of them gravimetric, some volumetric. The ones currently most widely used are based on a gravimetric procedure and instrumentation (or some variation thereof) described in ASTM D3539, Method for Evaporation Rates of Volatile Liquids by Shell Thin-Film Evaporometer [24]. In this method, a measured volume of liquid solvent is spread on a known area of filter paper that is suspended from a sensitive balance in a controlled environment cabinet. Weight loss of the filter paper/solvent liquid is measured as a function of time as the solvent evaporates.

Early models of the apparatus use a Jolly spring as the gravimetric measuring device and require manual measurement of weight and time (Fig. 5). More recent models employ an electrobalance and automatically record weight loss versus time (Fig. 6). The Shell Thin-Film Evaporometer and the Chevron Research Evapograph operate under similar principles.

The basic procedure with both the manual and automatic instruments is similar. The evaporation chamber and sample are conditioned to 25°C (77°F). Airflow rate (21 L/min) and relative humidity (less than 5 %) in the chamber are set. A filter paper, 90 mm in diameter, is horizontally suspended in the evaporation chamber from the weight-sensing device. The solvent sample (0.7 mL) is added from a hypodermic syringe and distributed over the entire area of the filter paper within a period of 10 s. Data are reported as time in seconds for 10 % solvent weight increments through the evaporation cycle, and they are plotted as percent solvent evaporated versus elapsed time (for example, see Fig. 7)[12,25].

The procedure is repeated using n-butyl acetate as the reference standard. Elapsed time for 90 % evaporation of specimen and standard are determined. Evaporation *rate* of the solvent specimen is calculated as the ratio of 90 % evaporation time for *n*-butyl acetate standard divided by the 90 % evaporation time for the solvent specimen and normalized so that the evaporation rate of *n*-butyl acetate is 100 (or 1.0). The 90 % evaporation time is generally used since some curvature of the plot usually occurs above that data point. Evaporation plots for pure solvents are nearly straight lines. Solvent mixtures or blends produce curved plots, the curvature becoming more extreme as differences in the evaporation rates of individual blend components become greater. Several solvent suppliers have developed computer programs to model and predict evaporation rates of solvent blends [26–30].

The information presented so far has dealt with the evaporation of neat (pure) solvents. The presence of resin solute, e.g., in a lacquer or paint, retards solvent evaporation, as illustrated in Fig. 8. In addition, some solvents are preferentially retained more than others by certain polymers due to solvent/polymer interactions arising from factors such as polarity and hydrogen bonding.

As solvent evaporation from a coating film progresses, it slows down markedly. The evaporation rate-limiting factor changes from neat solvent volatility to diffusion through

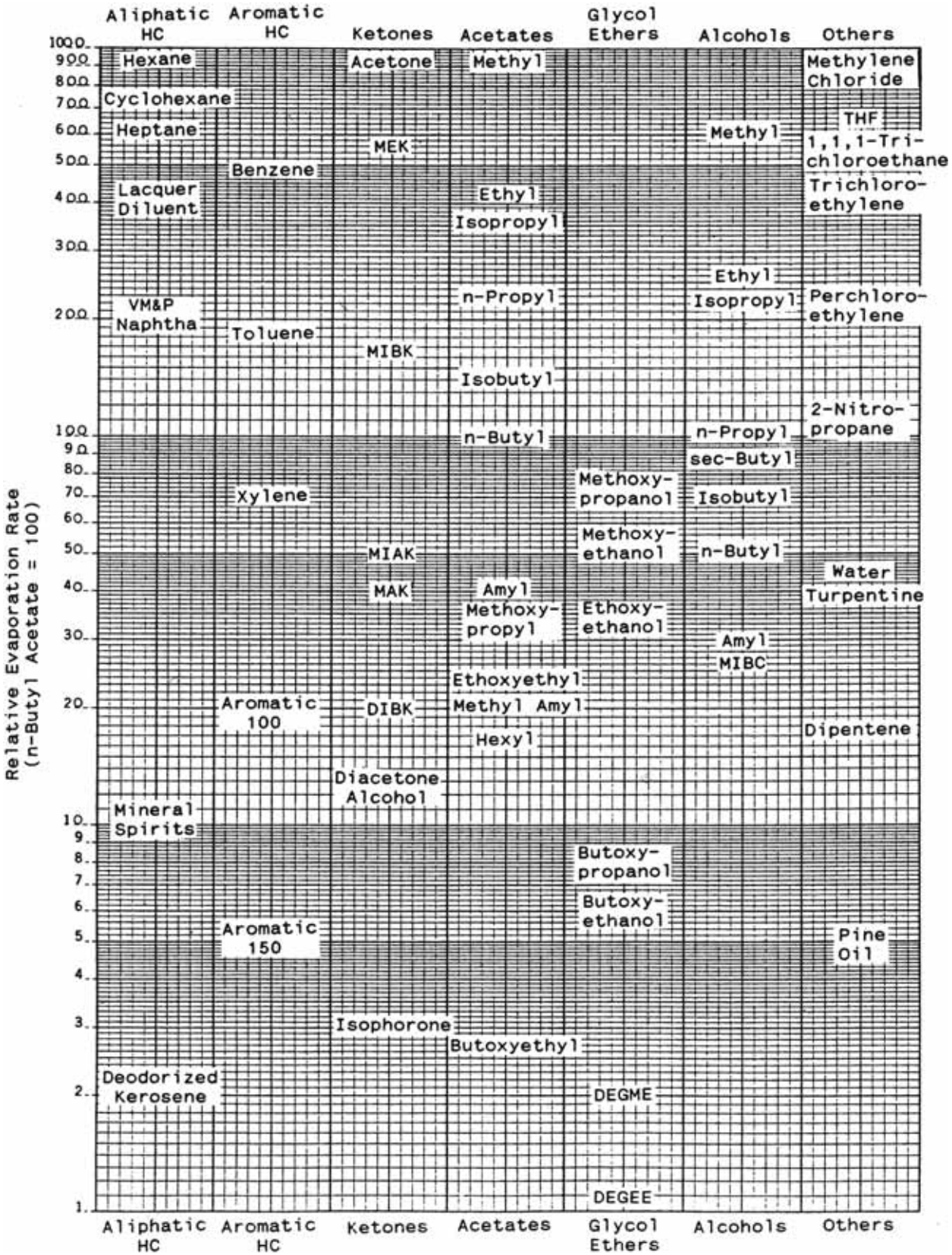


Fig. 4—Relative solvent evaporation rates.

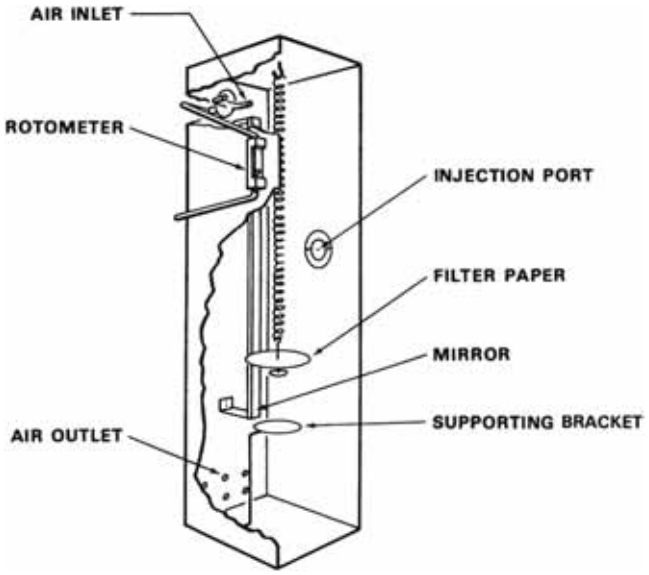


Fig. 5—Thin-film evaporometer.

Fig. 6—Automatic thin-film evaporometer.

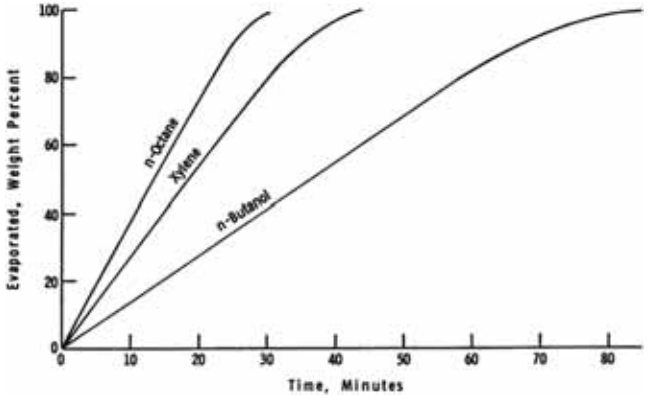


Fig. 7—Evaporation rates of typical solvents (Chevron Research Evapograph at 80°F).

the coating film. Diffusion-limited evaporation is much slower [31].

Actual evaporation of solvents from polymer films must be determined empirically. Although there are no standard test methods for doing so, various experimental procedures are reported in the literature [12]. Murdock

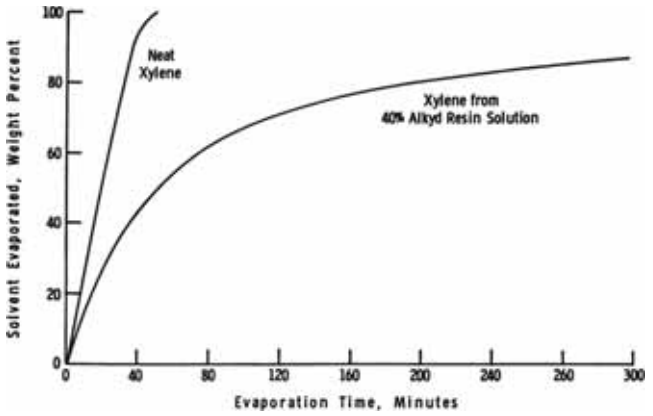


Fig. 8—Evaporation rate of xylene Neat, and from a 40 % solution of medium oil alkyd (Chevron Research Evapograph at 80°F).

and Wirkus [32], as well as Hays [33], tagged solvents with carbon-14 and measured residual radioactivity after the bulk of the solvent had evaporated. More recently, gas chromatography has been used effectively. Sletmoe modified a Shell thin-film evaporometer to permit sampling and subsequent analysis of evaporating vapor [34]. Lesnini evaporated the solvent from a series of solution aliquots and used a gas chromatograph to determine the type and amount of solvent remaining [35]. He dissolved the resin solution in a carrier solvent to ensure that a representative sample of the retained solvent was recovered for analysis.

A similar empirical procedure was used by a major solvent supplier to develop a database and appropriate algorithms for a solvency/evaporation rate computer program [36,26]. The program models solvency and evaporation rates of solvent blends from coating films, taking into account specific resin/solvent interactions. It calculates evaporation data for solvent blends evaporating from coating films and the compositions and solvency interaction radii of the solvent blends remaining in the film at any time.

BOILING POINT/DISTILLATION RANGE

Vapor pressure of a solvent increases as its temperature increases, as illustrated in the generalized graph in Fig. 9. If a solvent is heated to a high enough temperature, its vapor pressure will eventually rise to a value equal to 1 atm (e.g., 760 mm mercury pressure at sea level). At that point, the solvent will vaporize not only from the surface of the liquid, but vapor bubbles will form within the body of the liquid. This phenomenon is called "boiling," and the corresponding temperature at which it initially occurs is the "boiling point" [37]. When a solvent consists of a mixture of chemical components, as is the case with most hydrocarbon solvents, boiling occurs over a range of temperatures referred to as the "boiling range" or "distillation range." Single-component, pure solvents have single, unique boiling points or very narrow distillation ranges.

Distillation temperature or range is an important physical property, which is listed in all solvent specifications. It is useful as an identification test (in combination with other tests, such as specific gravity), but will not differentiate between solvents of similar boiling point or range. Distillation range also gives an indication of solvent purity. This is particularly true for oxygenated solvents,

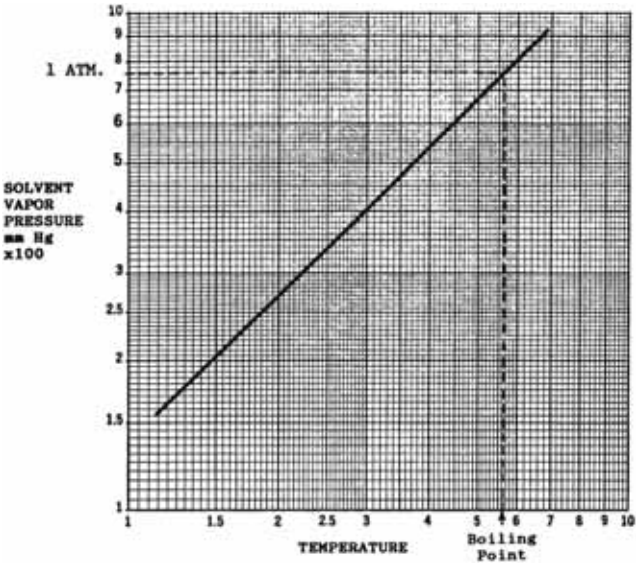


Fig. 9—Solvent vapor pressure versus temperature (idealized representation) [37].

which are relatively pure compounds. The more narrow the distillation range, the more pure is the solvent. Therefore, it is a useful test for detecting the presence of impurities or contaminants.

In addition, distillation temperature may be used to approximate the relative evaporation properties of one solvent versus another, although it does not provide precise information about evaporation rate. Evaporation/distillation temperature comparisons should not be made between dissimilar types of solvents since such predictions would be erroneous. However, for similar types of solvents, distillation data can be used effectively as a first approximation or gross measure of relative evaporation rate. For hydrocarbon solvents, the 50 % distillation point (i.e., the temperature at which 50 % of the solvent has distilled) has been found to have a good correlation with evaporation rate [12].

The McArdle-Robertson evaporation index is based on the 50 % distillation temperature [38]. It is intended primarily to apply to straight-run paraffinic naphthas having distillation ranges of not more than 40°C and to compare their relative evaporation times.

There are three ASTM distillation test methods, which are used for different kinds of solvents:

1. ASTM D86, Method for Distillation of Petroleum Products [11], is intended to be used for wide-boiling hydrocarbon solvents such as VM&P naphthas and mineral spirits.
2. ASTM D850, Method for Distillation of Industrial Aromatic Hydrocarbons and Related Materials [2], is in tended for narrow-boiling aromatic solvents such as toluene, ethylbenzene, and xylenes.
3. ASTM D1078, Method for Distillation Range of Volatile Organic Liquids [2], is intended for narrow-boiling solvents, oxygenated solvents in particular, and also for certain hydrocarbon solvents, chlorinated solvents, and others.

The same solvent sample, tested by each of the three ASTM methods, may produce different distillation data due to variations in the equipment and procedures. It is important, therefore, when presenting distillation data or solvent specifications, to indicate the test method used.

The basic test procedure described in all three test methods is similar, although there are differences as noted in Table 12. The sample is heated in a glass distillation flask until it boils. Solvent vapors are cooled and condensed by passing them through a jacketed, water-cooled tube. Condensate is collected in a calibrated receiver. Distillation temperatures are read from a thermometer immersed in the vapor in the neck of the distillation flask. Distillation temperatures are usually recorded at the initial boiling point, and when 5, 10, and each additional 10 % up to 90 %, and 95 % of the sample have distilled over, and at the dry point. Observed distillation temperatures are corrected to standard barometric pressure. Typical distillation temperatures of selected commercial solvents are listed in Tables 1–9.

The basic assembly of the manual distillation apparatus is illustrated in Fig. 10. Automatic distillation equipment (Fig. 11) employing the same basic principles is available. The automatic equipment uses a thermocouple or RTD probe for temperature measurement, and an automatic moving photocell sensing device to measure liquid level in the receiver. Required distillation rate is also accurately controlled in automatic apparatus compared to manual units. In older versions of automatic distillation apparatus,

TABLE 12—Comparison of ASTM distillation test methods for solvents

Sample Type	ASTM D86, Wide-Boiling Hydrocarbons	ASTM D850, Narrow-Boiling Aromatics	ASTM D1078, Narrow-Boiling Oxygenated (and others)
Sample size, mL	100	100	100
Distillation flask size, mL	125	200	200
Number of specified thermometers	2	8	14
Insulating shield hole size, mm	50	25–50[a]	38
Condenser temperature, °C	0–60[a]	10–20	0–50[a]
Rate of heat up to IBP, time, min	5–15[a]	5–10	5–15[a]
Rate of distillation, mL/min	4–5	5–7	4–5
95 % point to EP, time, min	5	. . .	5
[a] Varies depending on boiling point and range of sample.			

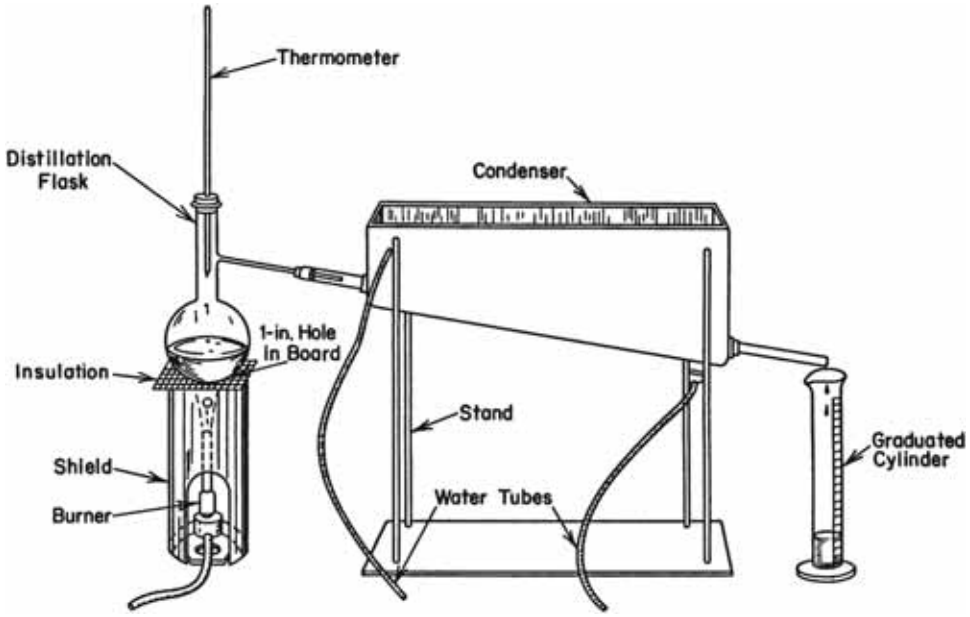


Fig. 10—Manual apparatus assembly for distillation test.

a recorder charts the volume of distillate recovered versus temperature. However, in current models of automatic units, distillation results are reported automatically by data processors. The distillation curve can be reported if desired. Automatic barometric pressure correction is available in most models of automatic distillation apparatus.

There are specific terms to describe key temperatures in all ASTM distillations:

1. *Initial boiling point*—The temperature indicated by the distillation thermometer at the instant that the first drop of condensate falls from the condenser tube into the receiver.
2. *Dry point*—The temperature indicated at the instant that the last drop of liquid evaporates from the lowest point in the distillation flask.
3. *End point, final boiling point,* or *maximum temperature*—The maximum thermometer reading obtained during the test. This usually occurs after the evaporation of all liquid from the bottom of the distillation flask. If there are "heavies" in the sample, and there is no clean dry point, the end point is taken as the thermometer reading 5 min after the 95 % distillation point.
4. *Decomposition Point*—The temperature reading that coincides with the first indication of decomposition of the liquid in the flask. Decomposition, if it occurs, is evidenced by smoke and fumes in the flask; the temperature ceases to rise and begins to fall.

Two common sources of error or bias in distillation data are (a) improper placement of the thermometer in the distillation flask and (b) failure to make appropriate corrections for barometric pressure. The thermometer must be positioned exactly as shown in Fig. 12. Higher placement will result in consistently lower temperature readings; lower placement may give higher readings.

Fig. 11—Typical automatic distillation apparatus (Courtesy of Petroleum Analyzer Co.).

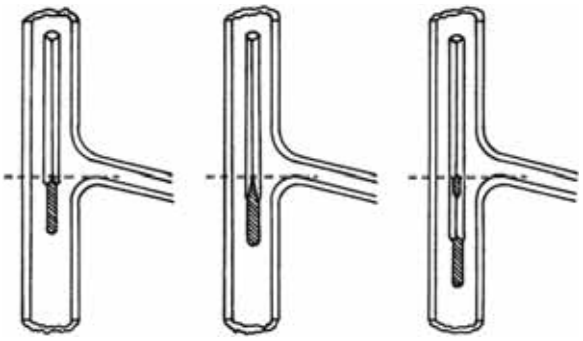


Fig. 12—Position of thermometer in distillation flask.

Distillation temperature readings must be corrected for deviations from standard sea-level barometric pressure. Otherwise, tests run at high altitude or low barometric pressure will result in inaccurate, low distillation temperatures, while high barometric pressure will cause high distillation temperatures. Correction factors appropriate for specific solvents are listed in the ASTM test methods.

FLASH POINT

Flash point is another indicator of volatility. The flash point of a liquid is defined as the lowest temperature at which the liquid gives off enough vapor to form an ignitable mixture with air to produce a flame when a source of ignition is brought close to the surface of the liquid under specified conditions of test at standard barometric pressure (760 mmHg, 101.3 kPa). Appropriate corrections must be made for barometric pressure deviations from standard pressure since flash point is dependent on vapor concentration, which is governed by vapor pressure.

Similar to the vapor pressure/temperature relationship, solvent vapor pressure *concentration* in air is also a function of temperature, as shown in the generalized illustration in Fig. 13 [37]. At low temperatures, there is insufficient vapor concentration (fuel) available to ignite and produce a flame. In this temperature region, below the flash point temperature, the solvent vapor cannot be ignited by a spark, gas flame, or other ignition source.

As the temperature of the solvent is gradually increased, there is an accompanying increase in vapor concentration above the surface of the liquid. At a certain temperature, there will be sufficient vapor (fuel) to form a flammable (or explosive) mixture, and a flame is observed if a spark, a gas flame, or ignition source is introduced. The temperature of the liquid at this point is called the "flash point," and the concentration of vapor at this temperature is called the "lower flammable limit" or "lower explosive limit" (LEL). Typical flash points of selected commercial solvents are listed in Tables 1–8.

At temperatures above the flash point, a flammable mixture of solvent vapor and air is present above the surface of the solvent. While the flash point represents the lower temperature limit for ignition, there is also an upper limit beyond which the vapor/air mixture is too rich to ignite and burn. The vapor concentration at the upper temperature limit is called the "upper flammable limit" or "upper explosive limit" (UEL). *It must be emphasized that these phenomena apply only to equilibrium, closed systems.* For hydrocarbon solvents, the LEL is usually about 1 vol % solvent vapor in air, and the UEL is about 7 vol %, but for oxygenated solvents, these values can vary over a wide range.

Flash point is one indicator of the relative flammability hazard of solvents and solvent-containing products. Within the United States, the U.S. Department of Transportation (DOT) and the U.S. Department of Labor (OSHA) designate "flammable liquids" as those having flash points below 100°F (38°C) [39]. These require special packaging and handling. International cargo regulations specify a 140°F (60°C) flash point as the upper limit for flammable liquids. In addition to being used to classify materials in government regulations, flash point limits are often listed as one of the requirements in solvent specifications and for hydrocarbon solvents in particular. Flash point may also be used to indicate the presence of impurities or contaminants in a

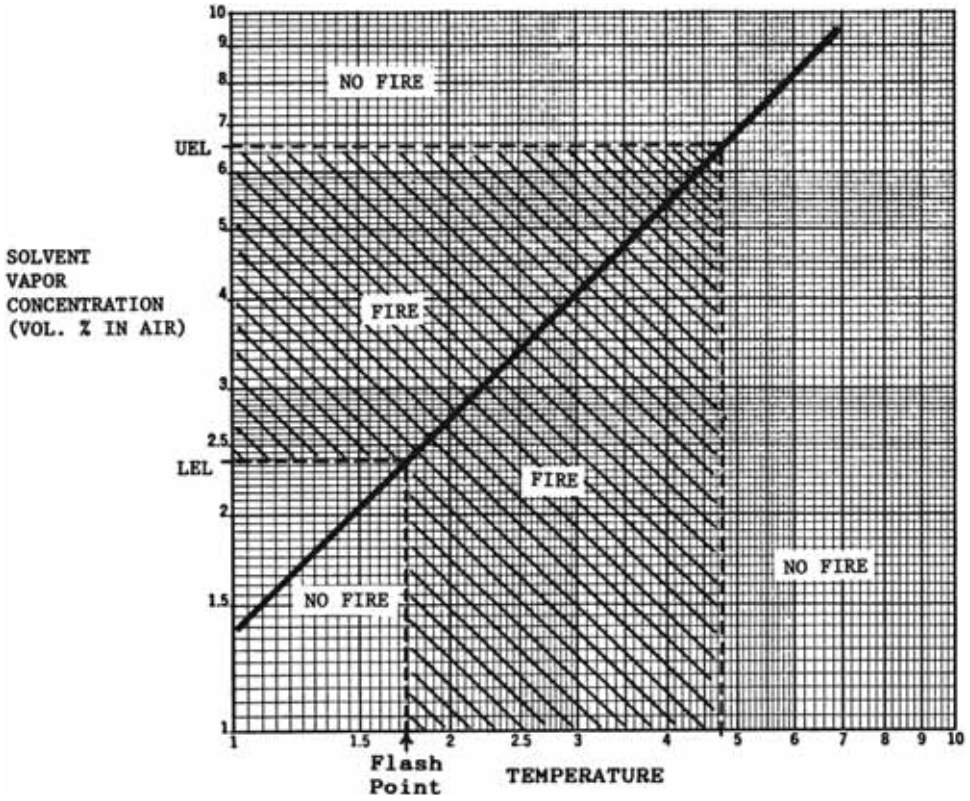


Fig. 13—Solvent vapor concentration versus temperature (idealized representation) [37].

given liquid, such as the presence of residual solvents in solvent-refined drying oils.

Flash point is roughly inversely proportional to volatility. The most volatile solvents tend to have the lowest flash points, which are indicative of the greatest fire hazard. With mixtures of miscible solvents, the component having the lowest flash point largely determines the flash point of the mixture when that component is present in substantial proportion, e.g., 5 % or more. Mutually miscible mixtures of flammable/nonflammable liquids exhibit a direct, though often complex, relationship between flash point and the concentration of the flammable component, e.g., alcohols and water.

Chlorinated solvents, most of which are nonflammable, will have various effects in mixtures with flammable solvents. Some will suppress (i.e., raise or prevent) the flash point of flammable liquids because of the high vapor pressure of the nonflammable chlorinated solvent. Some mixtures of chlorinated solvents and flammable liquids will lower the flash point below that of the flammable liquid, e.g., mineral spirits and methylene chloride [40].

It is good practice to actually measure the flash point of solvent blends because of the uncertainty of making predictions. There are several test methods commonly used.

Tag Open Cup—ASTM D1310, Method for Flash Point and Fire Points of Liquids by Tag Open-Cup Apparatus [24], may be used for determining the *open cup* flash points of liquids having flash points between zero and 325°F (–18 and 165°C). The sample is cooled to at least 20°F (11°C) below the expected flash point, and it is placed in an uncovered cup jacketed by a heat transfer fluid. The sample cup is filled to a depth of approximately 1/8 in. below the rim of the sample cup, and it is heated at a slow, constant rate. Temperature is measured by a thermometer immersed in the sample. A small test flame is passed at a uniform rate across the surface of the cup at 2°F (1°C) intervals of temperature rise until a flash of flame is observed. The sample temperature corresponding to the instantaneous propagation of a flame across the surface of the sample is the flash point. Fig. 14 shows a graphical sketch of a Tag open-cup flash point tester.

"Fire point" can be determined with the same apparatus by continuing the test. Fire point is defined as the lowest temperature at which sustained burning of the sample takes place for at least 5 s.

Although the Tag Open-Cup Flash Point test may appear to represent real-life situations of open containers or accidental solvent spills, the test results could be misleading, especially for solvent blends. As the sample is slowly heated, the lightest, most volatile component in the blend may escape without being ignited. Therefore, *closed-cup* test methods are now preferred by most regulatory agencies.

Tag Closed Cup—ASTM D56, Method for Flash Point by Tag Closed-Cup Tester, uses an apparatus that confines solvent vapors in a closed-cup apparatus (manual unit is shown in Fig. 15). It is intended for testing liquids (a) which contain no suspended solids, (b) which do not form a surface film under test conditions, (c) with viscosities below 9.5 mm^2/s (cSt) at 77°F (25°C) or below 5.5 mm^2/s (cSt) at 104°F (40°C), and (d) with flash points below 200°F (93°C).

The 50 mL sample, cup, and heat transfer fluid in the cup jacket are cooled to 20°F (11°C) below the expected

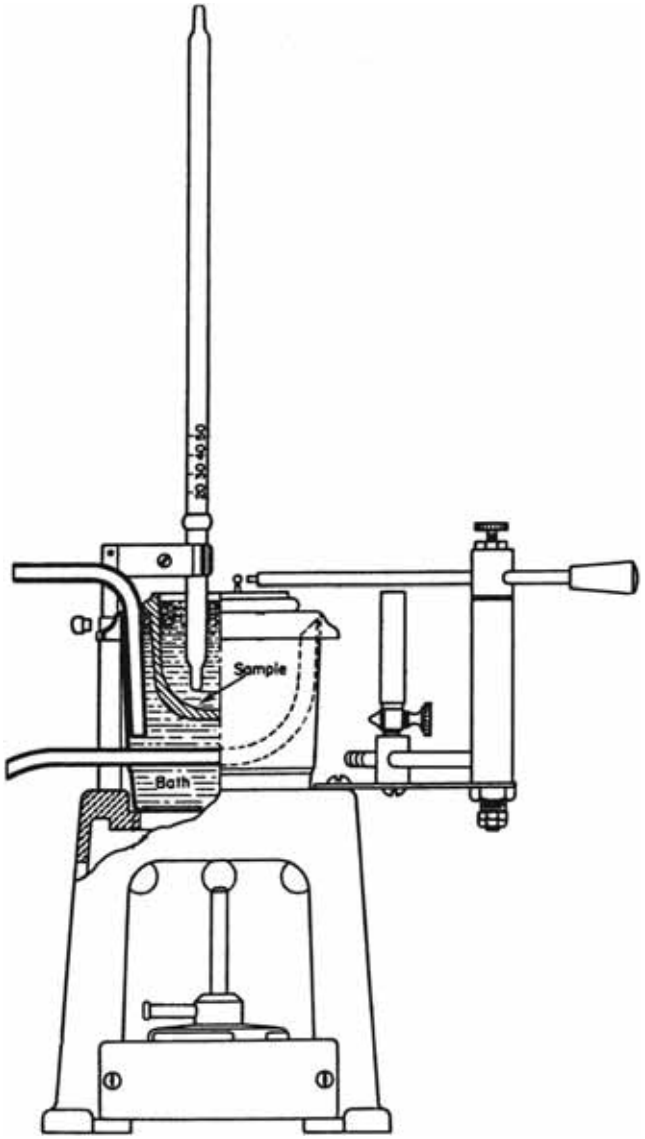


Fig. 14—Tag open-cup flash point tester.

flash point. With the cup lid closed, the sample is heated at a specified slow, constant rate, as measured by a thermometer immersed in the sample. A small test flame of specified size is momentarily directed into the cup through an opening in the lid that is simultaneously opened at regular intervals of temperature rise; after each 1°F (0.5°C) for samples with flash points below 140°F (60°C) or 2°F (1°C) for samples with flash points above 140°F. The flash point is taken as the lowest temperature at which application of the test flame causes the vapor in the cup to ignite.

The advent of automatic Tag closed-cup flash point testers, which can provide more accurate heating rate control and automatic detection of flash points, has led to a movement away from the manual apparatus. Flash point detection mechanisms other than visual observation, such as flame ionization and temperature differential, provide more efficient measurement of flash points. Some automatic instruments also correct for barometric pressure automatically. An example of a typical automatic Tag closed-cup flash point tester is shown in Fig. 16. There are newer models of Tag closed-cup flash point tester utilizing

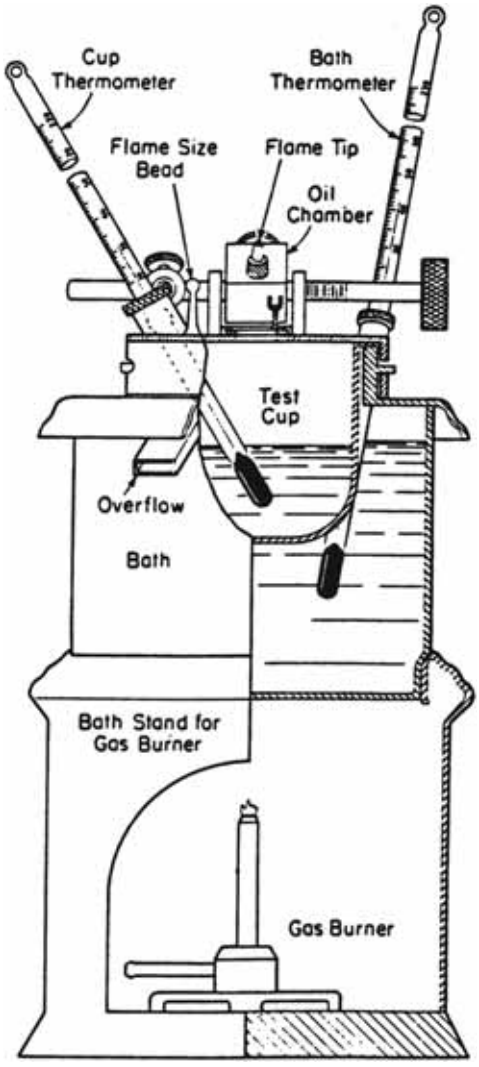


Fig. 15—Manual Tag closed-cup flash point tester.

Peltier technology for cooling samples and can determine flash points to lower temperatures.

Pensky-Martens—ASTM D93, Method for Flash Point by Pensky-Martens Closed-Cup Tester [11], is used for the measurement of flash points of homogeneous liquids as well as for viscous liquids, suspensions of solids, and liquids that tend to form a surface film under test conditions.

Fig. 16—Typical automatic Tag closed-cup flash point tester (Courtesy of Petroleum Analyzer Co.).

It differs from the Tag Closed-Cup Test in that (a) it employs an air bath device instead of a liquid jacket around the test cup, and (b) the sample is mechanically stirred during the test (Figs. 17 and 19). This test method is particularly suited for samples such as resin solutions, paints, varnishes, lacquers, printing inks, and certain adhesives. Materials with flash points as high as 698°F (370°C) can be tested.

The sample and test cup are first brought to a temperature of 60°F (15°C) or 32°F (18°C) below the expected flash point, whichever is lower (see test method for exact details). The sample is then heated at a slow, constant rate with continual stirring to provide uniform temperature throughout and to prevent formation of a surface film, which would otherwise retard solvent vaporization. A small test flame is momentarily directed into the cup through a shuttered opening in the lid at regular temperature intervals with simultaneous interruption of stirring. The flash point is the lowest temperature at which application of the test flame causes vapor in the cup to ignite.

Automatic Pensky-Martens closed-cup testers have gained popularity over the manual equipment. A typical example of an automatic Pensky-Martens flash point tester is shown in Fig. 18. More accurate heating rate control, and unattended flash point detection are advantages of the automatic apparatus. Some automatic apparatus correct for barometric pressure automatically (Fig. 19).

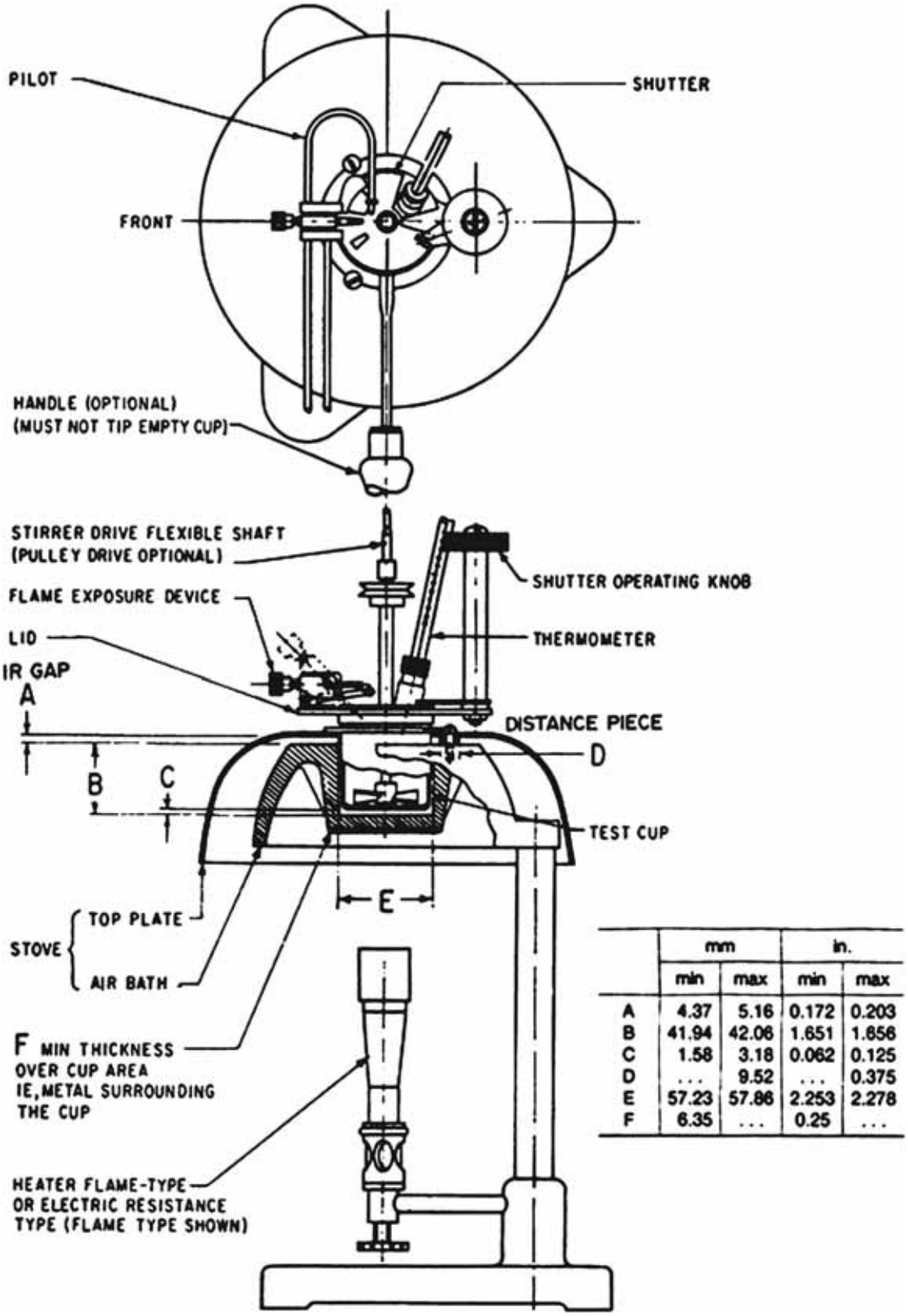
Small-Scale—ASTM D3278, Method for Flash Point of Liquids by Small-Scale Closed-Cup Apparatus [24] (formerly known as Setaflash), describes procedures for (a) determining whether a material does or does not flash at a specified temperature, or (b) determining the lowest finite temperature at which a material does flash. The procedures are applicable to paints, enamels, lacquers, varnishes, and related products having a flash point between 32 and 230°F (0 and 110°C) and viscosity lower than 150 St at 77°F (25°C). These test methods are similar to international standards ISO 3679 and ISO 3680. The Small-Scale apparatus requires only a 2 to 4 mL sample instead of 50 to 70 mL (Figs. 20 and 21).

To perform a "flash/no flash" test, 2 mL of sample is introduced by means of a syringe through a leakproof entry port into the tightly closed Small Scale tester or, with very viscous materials, directly into the cup that has been brought to the required test temperature. As a flash/no flash test, the expected flash point temperature may be a specification or other operating requirement. After 1 min, a test flame is applied inside the cup and note is taken whether or not the specimen flashes. A fresh specimen must be used if a repeat test is necessary.

For a finite flash point measurement, the temperature is sequentially increased through the anticipated range, the test flame being applied at 9°F (5°C) intervals until a flash is observed. A true determination is then made using a fresh specimen, starting the test at the temperature of the last interval before the flash point of the material and making tests at increasing 1°F (0.5°C) intervals.

Semi-automatic Small-Scale testers are now available (Fig. 21).

Equilibrium Flash Point—The Tag Closed-Cup and Pensky-Martens flash point test methods depend on a definite rate of temperature increase to control the precision of the test method. However, the rate of heating may not in all cases give the accuracy expected because of the low thermal conductivity of some liquids such as paints, resin solutions,



	mm		in.	
	min	max	min	max
A	4.37	5.16	0.172	0.203
B	41.94	42.06	1.651	1.656
C	1.58	3.18	0.062	0.125
D	...	9.52	...	0.375
E	57.23	57.86	2.253	2.278
F	6.35	...	0.25	...

Fig. 17—Manual Pensky-Martens closed-cup flash point tester.

and related viscous materials. To reduce this effect, ASTM D3941, Method for Flash Point by the Equilibrium Method with a Closed-Cup Apparatus [24], uses a slow rate of heating to allow temperature equilibrium between the vapor and the sample specimen.

The specimen is heated in a closed cup of standard design in a suitable water bath at a rate of 1.0°F (0.5°C) in not less than 1.5 min so that the difference in temperature between the specimen in the cup and the bath never exceeds 3.5°F (2.0°C). Flash determinations are made at

Fig. 18—Typical automatic Pensky-Martens closed-cup flash point tester (courtesy of Petroleum Analyzer Co.).

intervals of not less than 1.5 min. Since the specimen is heated at a reduced rate, a longer time interval between each determination is necessary to re-establish the temperature equilibrium of vapor in the air space above the specimen after each flash test.

Equilibrium Flash/No Flash—ASTM D3934, Method for Flash/No Flash Test—Equilibrium Method by Closed-Cup Apparatus [24], does not determine a finite flash point, but it verifies whether or not flashing occurs at a single

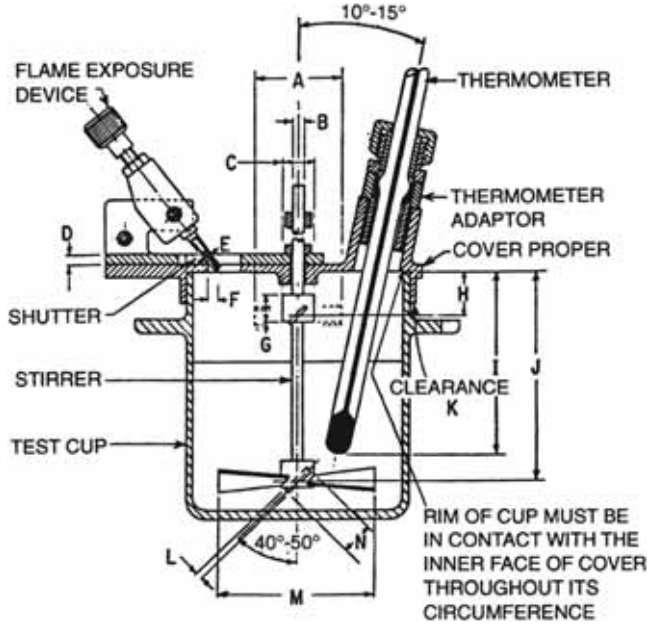


Fig. 19—Pensky-Martens flash point test cup and cover assembly.

Fig. 20—Manual small-scale (Setaflash) flash point tester.

specified temperature, which may be a product specification or agency requirement. The determination is made more accurate by ensuring that the flash test is carried out only when the material under test and the air/vapor mixture above it are in approximate equilibrium at the specified temperature.

Standard closed cups are used, i.e., Tag, Pensky-Martens, or Setaflash, and this test is run such that the air/vapor space above the specimen to be thermally equilibrated with the specimen before the test flame is applied. The specimen is held at the specified temperature for at least a 10 min period before the test flame is applied. This test method does not provide for the determination of the actual flash point, but only whether a specimen does or does not flash at a specified temperature.

Continuously Closed-Cup Flash Point—a new automatic flash point measurement method using pressure differential detection mechanism is described in ASTM D6450, Method for Flash Point by Continuously Closed-Cup (CCCFP) Tester [50]. Only 1 mL sample is required for the test, and an arc of defined energy is used as the ignition source. The specimen and the cell temperatures are brought to 18°C below the expected flash point. The temperature is increased at a prescribed rate and the ignition source is introduced at 1°C interval. The sudden change in pressure within the specimen cell when the flash point is reached is used as the mechanism for flash point detection. Not much data is known in the use of this test method for paints and coatings, but it should be applicable to resin solutions, paints, solvents, varnishes, and similar materials.

Fig. 21—Semiautomatic small-scale (Setaflash) flash point tester (courtesy of Stanhope-Seta).

PHYSICAL PROPERTIES

Density and Specific Gravity

SIGNIFICANCE

Specific gravity is an inherent property that is listed as a requirement in most solvent specifications and is often used to set specifications. It is a good, simple, qualitative test when used with other tests can establish or confirm the identity of a solvent. In addition, it is useful for quality control, to provide a check on product uniformity, and to detect gross contamination.

Accurate specific gravity values are essential for the calculation of the volume occupied by a product whose weight is known or of the weight of a product when the volume is known. This information is necessary for accurately surveying large shipments of materials by vessels, barges, railroad tank cars, or tank trucks to calculate costs and freight rates, and for inventory measurement and control.

It is customary to buy and sell hydrocarbon solvents on a volumetric basis (e.g., gallons, liters), converting measured values to volume at a standard temperature of 60°F (15.56°C). International transactions, however, are made on a gravimetric basis (e.g., metric tons) calculated at a standard 15°C temperature.

For oxygenated and other solvents, commercial transactions are customarily made on a gravimetric basis (e.g., pounds, kilograms, tons) converting measured values to weight at a standard temperature of 20°C (68°F). However, there is a trend toward changing the standard temperature to 25°C (77°F).

Finally, a knowledge of specific gravities of solvents and other paint components is important for the formulation of paints, varnishes, and lacquers. It is often necessary to make conversions between weight and volume bases and to calculate parameters such as pounds per gallon or kilograms per liter.

Typical specific gravities of selected commercial solvents are listed in Tables 1–9.

DEFINITIONS

The terminology relating to density and specific gravity is often confusing: Density and apparent density, specific gravity and apparent specific gravity, and mass and apparent mass versus weight. Definitions for these terms as they are applied in ASTM standards are contained in ASTM E1547, Terminology Relating to Density and Specific Gravity of Solids, Liquids, and Gases [41]. Key definitions pertaining to liquid solvents are as follows.

density—the mass of a unit volume of a material at a specified temperature. The units shall be stated, such as grams per milliliter, grams per cubic centimeter, pounds per cubic foot, or other. The form of expression shall be

"density at *x*"

where *x* is the temperature of the material.

density, apparent—the weight in air of a unit volume of a material at a specified temperature. The units shall be stated. The form of expression shall be

"apparent density at *x*"

where *x* is the temperature of the material.

specific gravity—the ratio of the mass of a unit volume of a material at a stated temperature to the mass of the same volume of gas-free distilled water at a stated temperature. The form of the expression shall be

"specific gravity *x*/*y*°C"

where *x* is the temperature of the material and *y* is the temperature of the water. The term "relative density" with the same meaning as specific gravity is becoming more widely used than "specific gravity."

specific gravity, apparent—the ratio of the weight in air of a unit volume of a material at a stated temperature to the weight in air of equal density of an equal volume of gas-free distilled water at a stated temperature. The form of expression shall be

"apparent specific gravity *x*/*y*°C"

where *x* is the temperature of the material and *y* is the temperature of the water.

API gravity—a special function of relative density (specific gravity) 60/60°F (15.56/15.56°C) represented by

$$\text{API Gravity, deg} = \left(\frac{141.5}{Sp.Gr.60°\text{F} / 60°\text{F}} \right) - 131.5$$

No statement of reference temperature is required, since 60°F is included in the definition. API gravity applies specifically to crude petroleum and to petroleum products such as hydrocarbon solvents. Gravities are determined at 60°F (15.56°C) or are converted to values at 60°F by means of standard tables. These tables are *not applicable* to nonhydrocarbons nor to essentially pure hydrocarbons such as the aromatics.

A brief discussion of these definitions may be useful. In scientific terminology, *mass* is a measure of the quantity of material in a body, and it is constant regardless of geographical location, altitude, or atmospheric conditions as long as no material is added or taken away. *Weight* is the force with which a body is attracted to the earth, and it varies from place to place with the acceleration of gravity.

When an equal-arm balance is used to compare an object with standards of mass ("weights"), the effects of variations in the acceleration of gravity are self-eliminating and need not be taken into account, but the apparent mass of the object is slightly different from the true mass because of the buoyant effects of the surrounding air. Mass can then be computed from apparent mass by applying a correction for air buoyancy. When a spring balance is used, an additional correction accounting for the local value of the acceleration of gravity is required for the computation of mass.

For many commercial and industrial processes the scientific distinction between mass, apparent mass, and weight is of no practical consequence and is therefore ignored. The term weight in general practice has been accepted as being the value secured when an object is weighed in air. This weight or "weight in air" is often converted to "weight in vacuo" by the application of an air buoyancy correction, and it is then considered synonymous with mass.

All of the definitions listed above are based on either "mass" or "weight in air," with the distinction being that air buoyancy corrections have been applied in the former case and not in the latter. Density and specific gravity are

based on mass and should be similarly constant. Apparent density and apparent specific gravity are based on weight in air, and therefore they are subject to change with atmospheric conditions, locality, and altitude. These changes may be negligible, depending on the accuracy required for the particular application.

HYDROMETER METHODS

Hydrometer methods are the quickest, simplest means for measuring density, specific gravity (relative density), and API gravity, especially in the field. These methods are based on the principle that the specific gravity of a liquid varies directly with the depth of immersion of a body floating in it. The floating body, called a hydrometer, is graduated in units of density, specific gravity, or API gravity units. Hydrometers are useful when accuracy to three decimal places is adequate.

The sample is brought to the prescribed temperature, and it is transferred to a clear glass or plastic cylinder, which is at approximately the same temperature. The appropriate hydrometer, having the scale of interest, is lowered into the sample and is allowed to float freely and settle. After temperature equilibrium has been reached, the hydrometer scale is read. Note is made of the hydrometer scale graduation nearest to the apparent intersection of the horizontal plane surface of the liquid (Fig. 22). Temperature of the sample is read from a separate thermometer or from a thermometer integrated into the design of the hydrometer.

Detailed descriptions of test methods for the proper use of hydrometers can be found in ASTM D891, (Method A), Specific Gravity, Apparent, of Liquid Industrial Chemicals [9]; ASTM D287, Method for API Gravity of Crude Petroleum and Petroleum Products (Hydrometer Method) [11]; and ASTM D1298, Method for Density, Relative Density (Specific Gravity), or API Gravity of Crude Petroleum and Liquid Petroleum Products by Hydrometer Method [11].

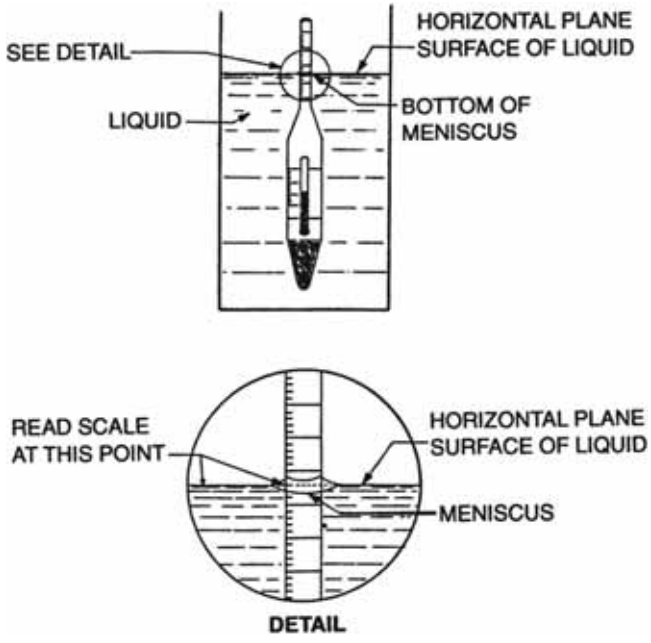


Fig. 22—Hydrometer and meniscus detail.

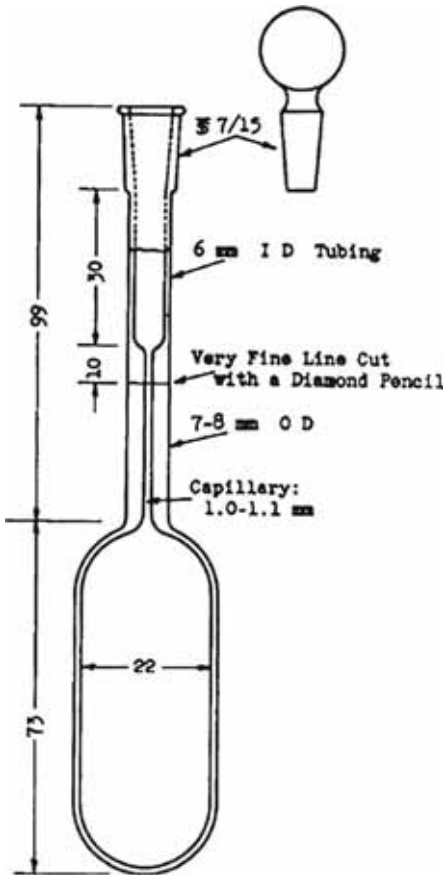


Fig. 23—Bingham-type pycnometer.

For hydrocarbon solvent naphthas, values can be measured on a hydrometer at convenient temperatures, the readings of density may then be reduced to 15°C, and readings of relative density (specific gravity) and API gravity at 60°F are obtained by means of international standard tables. By means of these tables, values determined in any one of the three systems of measurement are convertible to equivalent values in either of the other two systems so that measurements may be made in the units of local convenience.

PYCNOMETER METHODS

Pycnometer methods for measuring specific gravity are more accurate and precise than hydrometer methods. They are used when accuracy to four or more decimal places is required. ASTM D891, (Method B), Specific Gravity, Apparent, of Liquid Industrial Chemicals [9], describes the general test method for using a pycnometer.

A pycnometer is a tared vessel which is filled with water and weighed. It is then filled with the sample and weighed. Water, sample, and pycnometer are at a specified temperature. The ratio of the weight of sample to weight of water in air is the apparent specific gravity.

Bingham Pycnometer—A Bingham-type pycnometer may be used when density or specific gravity needs to be determined to five decimal places (Fig. 23). Its use is described in ASTM D1217, Method for Density and Relative Density (Specific Gravity) of Liquids by Bingham Pycnometer [11].

The pycnometer is first carefully calibrated by determining the weight of freshly boiled and cooled distilled water (distilled from alkaline permanganate through a tin condenser) held by the pycnometer when equilibrated to volume at the bath temperature to be used for the determination. The liquid sample is introduced into the tared, clean, dry pycnometer, equilibrated to the desired temperature, and weighted. The relative density (specific gravity) or density is then calculated from this weight and the previously determined weight of water required to fill the pycnometer at the same temperature, both weights being corrected for the buoyancy of air.

Lipkin Bicapillary Pycnometer—The Lipkin bicapillary pycnometer is another type that is capable of high accuracy and precision when density or specific gravity needs to be determined to five decimal places [42]. Its use was described in ASTM D941, Method for Density and Relative Density (Specific Gravity) of Liquids by Lipkin Bicapillary Pycnometer, but this test method was discontinued in 1993.

The liquid sample is drawn into the pycnometer and weighed. It is then equilibrated at the test temperature, and the positions of the liquid levels in the capillaries are observed (Fig. 24). The density or relative density of the sample is then calculated from its weight, a calibration factor proportional to an equal volume of water, and a term that corrects for the buoyancy of air. NOTE: This test method has been discontinued and is included for historical purposes.

DIGITAL DENSITY METER

A rapid, direct-reading, instrumental method for measuring density or specific gravity is by means of a digital density meter. Its use is described in ASTM D4052, Method for Density and Relative Density of Liquids by Digital Density Meter [23]. A small amount of sample (several milliliters) is introduced into a oscillating quartz tube in the instrument at a preset temperature. Operation of the instrument is based on the principle that the period of oscillation of the quartz tube is affected by the density of the sample within it. The instrument provides a digital readout of either density or specific gravity at the specified temperature.

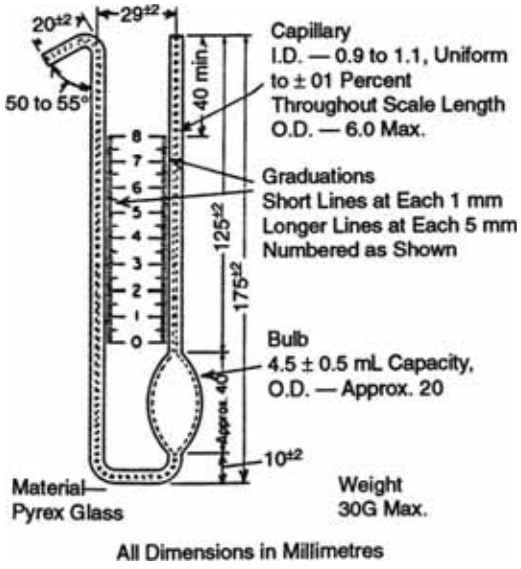


Fig. 24—Lipkin-type pycnometer.

CALCULATIONS AND CONVERSION TABLES

ASTM D1250, Guide for Petroleum Measurement Tables [11], is a description of the tables that comprise Chapter 11, Section 1, of the *API Manual of Petroleum Measurement Standards* [43]. These are distributed in three basic systems of measurement: °API, °F, 60°F; relative density, °F, 60°F; and kilograms per cubic meter, °C, 15°C. These tables apply to crude petroleum and to all normally liquid petroleum products derived therefrom, which includes hydrocarbon solvent naphthas. They do *not* apply to oxygenated and other solvents nor to pure hydrocarbon solvents such as the aromatics.

ASTM D1555, Method for Calculation of Volume and Weight of Industrial Aromatic Hydrocarbons [2], contains tables for use in calculating the weights and volumes of the following solvents: benzene, toluene, mixed xylenes, *o*-, *m*-, p-xylene, cumene, ethylbenzene, high-flash aromatic naphthas, and cyclohexane. A method is given for calculating the volume at 60°F from an observed volume at any convenient temperature.

ASTM D3505, Method for Density or Relative Density of Pure Liquid Chemicals [2], describes the measurement of density or relative density using a Lipkin-type pycnometer, and it provides methods for reporting results in the following units:

Density, g/cm^3 at 20°C
Density, g/mL at 20°C
Relative density, 20°C/4°C
Relative density, 60°F/60°F (15.56°C/15.56°C)
Commercial density, pounds (in air)/U.S. gal. at 60°F
Commercial density, pounds (in air)/U.K. gal. at 60°F

Tables of factors versus temperature are presented for benzene, toluene, mixed xylenes, *o*-, *m*-, *p*-xylene, and cyclohexane.

ASTM D2935, Method for Apparent Density of Industrial Aromatic Hydrocarbons [2], describes the measurement of apparent density in pounds (in air) per U.S. gallon at convenient temperature using a hydrometer and reporting values at any specified temperature. This method contains tables of "pounds in air per U.S. gallon" versus temperature. It applies only to the following solvents: benzene, toluene, mixed xylenes, *o*-, *m*-, p-xylenes, ethylbenzene, and cyclohexane. NOTE: This test method has been discontinued and is included for historical purposes.

ASTM E201, Method for Calculation of Volume and Weight of Industrial Chemical Liquids [9], presents tables for use in calculating the volume and weight of the following solvents: acetone, ethyl acetate (85-88 wt%), ethylene dichloride, ethylene glycol monomethyl ether, isobutyl alcohol, isopropyl alcohol (anhydrous), isopropyl alcohol (91 vol %), methyl ethyl ketone, methyl isobutyl ketone, and perchloroethylene.

A method is given for calculating the volume at 60°F from a volume observed at another convenient temperature. (Tables at 20°C can be calculated from the data and information provided.)

Also, a method is given for determining the weight in pounds per U.S. gallon (in air) at 60°F from an observed specific gravity and to compute therefrom the weight in pounds of a given volume of the liquid in U. S. gallons at 60°F. NOTE: This test method has been discontinued and is included for historical proposes.

TABLE 13—Approximate comparison of platinum-cobalt and Saybolt color scales

Color Generalization	Platinum-Cobalt Color ASTM D1209	Saybolt Color ASTM D156
Lightest	0	+30
↓	10	+28
	20	+26
	30	+23
	40	+21
	50	+19
	+70	15
	100	+10
	150	+3
	180	0
	200	-3
	250	-8
To		
Dark amber	300	-23

Color

Most solvents are "water-white" or clear and essentially colorless. Color is an important specification requirement. If a solvent has color greater than the specification limit, it may be an indication of (a) inadequate processing, (b) contamination that might have occurred during storage and distribution, e.g., pickup of rust from tanks or pipes or color extracted from improper tank linings or loading hoses, or (c) oxidative degradation as a result of aging.

The property of color of a solvent varies in importance with the application for which the solvent is intended, the amount of color that can be tolerated being dependent on the color characteristics of the material in which it is used. For example, solvent color may undesirably contribute color to white paints or to fabrics if it is used for dry cleaning. Solvents that are off-specification in color are often found to be off-specification in other properties as well.

There are two visual test methods used for measuring the color of solvents; platinum-cobalt color and Saybolt Color. Table 13 compares the approximate color values of the two scales.

PLATINUM-COBALT COLOR

ASTM D1209, Method for Color of Clear Liquids (Platinum-Cobalt Scale) [2], describes a procedure for the visual measurement of the color of nearly colorless liquids. It is used for oxygenated solvents and is gradually being used also for hydrocarbon solvents, where Saybolt Color still predominates.

For a number of years the term water-white was considered sufficient as a measurement of solvent color. Several expressions for defining water-white gradually appeared, and it became evident that a more precise color standard was needed. This was accomplished in 1952 with the adoption of ASTM Test Method D1209 using the platinum-cobalt (Pt-Co) scale.

This test method is similar to the description given in "Standard Methods for the Examination of Water and Waste Water" [44] and is sometimes referred to as "APHA Color." The properties of these platinum-cobalt color standards were originally described by A. Hazen in 1892 in a paper entitled, "New Color Standard for Natural Waters" [45]. He assigned the number 5 (parts per ten thousand) to his platinum-cobalt stock solution.

Subsequently the American Public Health Association (APHA) in their first edition (1905) of "Standard Methods for the Examination of Water" used exactly the same concentration of reagents as did Hazen, and they assigned the color designation 500 (parts per million) to the same stock solution. (The parts per million nomenclature is not used since color is not referred directly to a weight relationship.)

The terms "Hazen Color" and "APHA Color" should not be used for solvents because they refer primarily to water. The recommended nomenclature for referring to the color of organic liquids is "Platinum-Cobalt Color, Test Method D1209."

The method involves comparing visually the color of the solvent sample with colors of standard dilutions of the Pt-Co stock reference solution in Nessler tubes. The tubes are viewed vertically. The color standards are aqueous solutions of mixtures of cobalt chloride, potassium chloroplatinate, and hydrochloric acid. The scale runs from zero for pure water to 500 for the stock solution of 1.000 g of cobalt chloride, 1.245 g of potassium chloroplatinate, and 100 mL of hydrochloric acid made up to 1 L of solution. Most solvents have color values of less than 5 on the Pt-Co scale.

SAYBOLT COLOR

ASTM D156, Method for Saybolt Color of Petroleum Products [11], is used most often to measure the color of hydrocarbon solvents. This system of color measurement is not commonly employed outside of the petroleum industry.

In this method, a column of sample is viewed vertically, and its color is compared with that of a reference glass disk in the Saybolt chromometer. The height of the column of liquid is adjusted until the observed color intensity is equal to that of the colored glass disk. The depth of the liquid column is a measure of the Saybolt color, which is read directly from a scale on the instrument. The scale runs from +30 for colorless liquids to -30 for dark liquids.

TRISTIMULUS COLORIMETRY

More recently, automatic instrumental color measurements using tristimulus colorimetry has gained acceptance. ASTM D6045, Method for Color of Petroleum Products by the Automatic Tristimulus Method [50], and ASTM D5386, Method for Color of Liquids Using Tristimulus Colorimetry [2], are two test methods that describe automatic color measurements. ASTM D6045 has been used mainly for petroleum products, while ASTM D5386 is used primarily for near-clear aromatic hydrocarbons. Both test methods specify the use of spectro-photometers capable of converting light measured in total transmission through the sample into CIE XYZ tristimulus values using the CIE Illuminant C and the 1931 CIE Standard Observer as per ASTM E308, Practice for Computing Colors of Objects by Using the CIE Systems [23]. D5386 is capable

of reporting equivalent D1209 Platinum-Cobalt color values, while D6045 can report equivalent D156 Saybolt color values.

Odor

Odor is an inherent, characteristic property of most solvents. Evaluation of the *characteristic odor* by a trained person is a quick and simple means of identifying a solvent (when combined with other tests) as well as for determining its suitability for an application from an odor point of view. *Residual odor* can be used to detect the presence of low-volatility materials that may be associated with manufacture, product degradation, or contamination during distribution.

ASTM D1296, Method for Odor of Volatile Solvents and Diluents [2], describes procedures for testing both the characteristic and residual odors of solvents. It involves dipping strips of filter paper into the sample and into a reference standard. To judge characteristic odor, an immediate comparison is made between the odor of the sample and reference standard on the filter paper. Residual odor is judged by permitting the papers to dry in air at room temperature and examining them at suitable time intervals for differences in odor. Because of safety and health concerns, many solvent specifications have made odor an optional specification requirement and subject to the mutual consent between the solvent manufacturer and user.

Electrical Resistivity

Control of electrical resistivity is critical to the application of electrostatically sprayed coatings. It impacts the transfer efficiency (efficiency of paint application), coating appearance, and economics. Electrical resistivity of the paint must be properly adjusted to obtain optimum atomization characteristics and deposition. The adjustment is mainly accomplished through appropriate selection of solvents [46]. Non-polar solvents, such as hydrocarbon solvents, have high electrical resistivity (low conductivity). Polar solvents such as ketones, alcohols, glycol ethers, and esters generally have low electrical resistivity (high conductivity), although some (e.g., higher molecular weight esters) have high resistivity. Typical values for commercial solvents are shown in Table 14.

ASTM D5682, Method for Electrical Resistivity of Liquid Paint and Related Materials [24], describes the use of two different test meters and probes, Ransburg and BYK-Gardner. Electrical resistivity values are often expressed in terms of "Ransburg megohms," which are read from the meter scale. Multiplication of these values by an appropriate cell constant, which is typically about 132, converts Ransburg megohms to specific resistivity in megohm-cm units.

Refractive Index

Refractive index is defined as the ratio of the speed of light through a vacuum to the speed of light through the sample. Although this property may have no fundamental significance to the practical solvent user and is generally not a specification requirement, the test is useful because measurements can be made quickly and precisely. As with specific gravity, refractive index is characteristic (although not uniquely so) of different solvents, and it is very sensitive to differences in composition of solvent blends. Therefore, it is useful for distinguishing between aromatic and saturated hydrocarbon solvents and for checking purity and uniformity of batches.

TABLE 14—Electrical resistance of typical commercial solvents

Solvent or Solvent Class	Ransburg Megohms
Hydrocarbon solvents	>20
Ketones	<1
Alcohols	<1
Glycol ethers	[1]<1
Esters	. . .
Ethyl acetate	6
n-Butyl acetate	16
Hexyl acetate	>20
Ethoxyethyl acetate	3
Methoxypropyl acetate	3

ASTM D1218, Refractive Index and Refractive Dispersion of Hydrocarbon Liquids [11], is designed to measure these properties with high precision. Manual refractometers are used less as automatic refractometers are gaining popularity. Automatic refractometers have the advantage of not requiring a constant-temperature recirculating liquid bath to control the temperature of the cell because of their use of Peltier technology. In addition, automatic refractometers provide digital readout of the refractive indices, thus eliminating the subjectivity in reading the refractive index value. The temperature at which refractive index of a material is determined must be specified since refractive index is affected by temperature.

PURITY AND COMPOSITION

Gas Chromatography

Gas chromatography (GC), also referred to in the past as gas-liquid chromatography (GLC), is commonly used for the analysis of purity and composition of solvents. GC is a powerful analytical tool, very sensitive, rapid and simple in execution. It is capable of furnishing accurate qualitative and quantitative information from extremely small amounts of sample [47].

In this analytical technique, a minute amount of solvent sample (microliters) is injected by means of a hypodermic syringe into a heated injection port in the instrument, where it is instantly vaporized. The solvent vapors are carried into a GC column by means of an inert carrier gas: helium, hydrogen, or nitrogen. The carrier gas is the eluent that transports the solvent components in vapor form through the GC column, which is maintained at a certain constant or programmed temperature.

In older models of gas chromatographs, GC columns consist of a long, coiled tube, typically 1/8 to 1/4 in. inside diameter and made of stainless steel, copper, or glass. The tube is packed with a powdered, porous substrate or support, which is coated with an absorbent, stationary liquid phase. However, in GCs more commonly in use today, the

GC column consists of a long, coiled capillary tube 1/32 in. or less in diameter, which does not contain the powdered packing support. Instead, the interior walls of the capillary tube are coated with the liquid stationary phase.

The stationary liquid phase has the ability to preferentially adsorb certain components of the vaporized solvent sample. It is selected on the basis of the analysis to be performed. The stationary phase can in some cases be a nonpolar liquid, for instance a methyl silicone, but in other cases a better separation of solvent components can be obtained by employing a highly polar liquid such as polyethylene glycol.

Actual separation of solvent components is achieved by a continuously alternating process of adsorption and vaporization as the solvent vapors pass through the GC column. Differences in adsorption characteristics and volatilities cause the individual sample components to pass through the column at different rates. The components are eluted from the column as individual bands or peaks separated by zones of inert carrier gas.

At the end of the GC column, the carrier gas and sample components flow through a sensitive detector, which is capable of indicating the presence of the components qualitatively and quantitatively. The detector may be a thermal conductivity cell, a flame ionization detector, or an electron capture detector. There are also other less-common types of detectors, and element specific detectors like nitrogen or sulfur specific detectors. Any material other than the carrier gas going through the detector will cause a peak to be plotted on a recorder chart or a data processor.

The time required for a component to flow through the column, under a given set of operating conditions, when compared to the time for known compounds, helps to identify the component. The amount of that component is proportional to the area under the recorder chart peak. Modern gas chromatographs often have a digital integrator, which prints out the elution time and the area under the peak. Temperature, column length and size, type and amount of stationary liquid phase, carrier gas pressure and flow rate, and sample size are some of the variables that can be changed to effect desired separations.

Versatility of gas chromatography in solvent analysis is very great. Good ASTM references on gas chromatography include "ASTM Standards on Chromatography," second edition [48]; ASTM E260, Practice for Packed Column Gas Chromatography [41]; and ASTM E355, Practice for Gas Chromatography Terms and Relationships [41]. Specific ASTM GC methods for analyzing the purity and composition of solvents are listed in Table 15.

Liquid Chromatography

There are two test methods that utilize a liquid chromatography procedure for measuring the volume percentages of aromatics, olefins, and saturated aliphatics (paraffins and naphthenes), which comprise a hydrocarbon solvent naphtha. Both methods involve the physical separation of these hydrocarbon types by passing the hydrocarbon sample through a tube packed with silica gel. The technique is based on the principle that polar compounds are adsorbed more strongly by silica gel than are nonpolar saturated compounds.

In a discontinued ASTM method, D936, Method for Aromatic Hydrocarbons in Olefin-Free Gasolines by Silica Gel Adsorption, a hydrocarbon solvent sample is passed through a glass column packed with silica gel. Then, alcohol, which is more strongly adsorbed than any hydrocarbon, follows the sample through the column, desorbing and forcing the hydrocarbons out. Saturated compounds are

TABLE 15—ASTM gas chromatography methods for analyzing purity and composition of solvents

Compound	ASTM Method	Compound	ASTM Method
Benzene	D4492	Mineral spirits (aromatics content)	D3257
n-Butyl acetate	D3545	i-Octane	D2268
i-Butyl acetate	D3545	n-Propyl acetate	D3545
Cyclohexane	D3054	i-Propyl acetate	D3545
Dipropylene glycol monomethyl ether	D4773	i-Propyl benzene	D3760
Ethanol (SD-3A)	E1100	Propylene glycol	E202
2-Ethoxyethyl acetate	D3545	Propylene glycol monomethyl ether	D4773
Ethyl acetate	D3545	Propylene glycol monomethyl ether acetate	D4773
Ethylene glycol	E202	1,1,1-Trichloroethane	D3742
n-Heptane	D2268	Trichlorotrifluoroethane	D3447
Methanol	E446	Turpentine	D3009
Methyl amyl ketone	D3893	Xylenes (mixed)	D2306
Methyl ethyl ketone	D2804	o-Xylene	D3797
Methyl isoamyl ketone	D3893	p-Xylene	D3798
Methyl isobutyl ketone	D3329	Hydrocarbon solvents	D6229

eluted first, unsaturated compounds next, and then aromatics. Small samples of the emerging sample are periodically collected. The refractive index of each fraction is measured. From this information, the relative percentages of aliphatics and aromatics can be determined. The precision is good, but the procedure is slow. A more modern version of the test method is ASTM D6379, Method for Aromatic Hydrocarbon Types in Aviation Fuels and Petroleum Distillates—High Performance Liquid Chromatography with Refractive Index Detector [50]. In this test method, the peaks due to the eluting components are detected by a differential refractive index detector. A nonpolar mobile phase such as hexane or heptane is used.

ASTM D1319, Method for Hydrocarbon Types in Liquid Petroleum Products by Fluorescent Indicator Adsorption (FIA) [11], is a refinement of the earlier silica gel adsorption procedure. A mixture of fluorescent dyes is added to the hydrocarbon solvent sample before it is put into the silica gel column. When all of the sample has been adsorbed on the silica gel, alcohol is added under pressure to desorb and force the sample down the column. The fluorescent dyes are also selectively separated with the sample fractions, and they make the boundaries of the aromatics, olefins, and saturates clearly visible under ultraviolet light. The zone of aromatics fluoresces violet, and the zone of olefins fluoresces a chartreuse color. The zone of paraffins plus naphthenes remains colorless. Volume percentage of each hydrocarbon type is determined by measuring the length of each zone in a long, narrow extension of the silica gel column.

Purity of Ketones

ASTM D2192, Method for Purity of Aldehydes and Ketones [2], is an alternative to gas chromatography for measurement of the purity of ketone solvents. This is a wet chemical procedure and is applicable for testing ketones having greater than 98 % purity.

The test is based on the reaction of ketones with hydroxylamine to form an oxime. Hydroxylamine hydrochloride is first converted in part to free hydroxylamine by reaction with a known amount of aqueous triethanolamine.

$$H_2NOH \bullet HCI + (HOCH_2CH_2)_3N \rightarrow H_2NOH + (HOCH_2CH_2)_3N \cdot HCI$$

The free hydroxylamine then reacts with the ketone to form an oxime.

$$R_1R_2C = 0 + H_2NOH \rightarrow R_2C = NOH + H_2O$$

where R_1 and R_2 arealkyl groups.

The amount of hydroxylamine consumed, which is determined by titration of the excess base with standard sulfuric acid, using bromophenol blue indicator, is a measure of the ketone originally present. Water, alcohols, saturated esters, and hydrocarbons do not react with the reagent, but large amounts of inert organic solvents are undesirable because of the possible effect on the indicator.

Purity of Esters

ASTM D1617, Method for Ester Value of Solvents and Thinners [2], is an alternative to gas chromatography for the measurement of purity of ester solvents. It may also be used for determining the ester content of lacquer thinners.

This is a wet chemical test and involves the reaction of the solvent sample with a measured excess of aqueous potassium hydroxide, using isopropanol as a mutual solvent if necessary

$$R_1COOR_2 + KOH \rightarrow [R_1COO]^- K^+ + R_2OH$$

where R_1 and R_2 are alkyl groups. The amount of potassium hydroxide consumed, which is determined by titrating the excess with standard mineral acid, is a measure of the amount of ester originally present.

This test method has its greatest application where the solvent or thinner is not a pure ester. The type of ester present must be known to perform the calculations. The test may also be used for assessing compliance with ester specifications.

IMPURITIES

Acidity

Solvents may have residual acidity from manufacturing processes, or acidity may be present as a result of contamination or decomposition during storage or distribution. Acidity is undesirable since it may cause corrosion of storage tanks and lines. Also, it may cause reactions with basic pigments resulting in color changes.

ASTM D847, Method for Acidity of Benzene, Toluene, Xylenes, Solvent Naphthas, and Similar Industrial Aromatic Hydrocarbons [2], expresses acidity in terms of milligrams of sodium hydroxide consumed when 100 mL of sample are titrated using phenolphthalein indicator. If two drops or less of standard 0.1N sodium hydroxide solution produce a persistent pink end point, the sample is reported to contain no free acid.

ASTM D1613, Method for Acidity in Volatile Solvents and Chemical Intermediates Used in Paint, Varnish, Lacquer, and Related Products [2], expresses total acidity in terms of weight percent acetic acid or as milligrams of sodium hydroxide required to neutralize one gram of sample.

The test is performed by mixing 50 mL of sample with an equal volume of water (or with an equal volume of alcohol if the sample is not water soluble) and titrating with aqueous 0.05N sodium hydroxide solution to the phenolphthalein end point.

Acid Wash Color

ASTM D848, Method for Acid Wash Color of Industrial Aromatic Hydrocarbons [2], is a test used for benzene, toluene, xylenes, refined solvent naphthas, and similar aromatic hydrocarbons. Acid wash color is a measure of chemical reactivity reactivity of trace impurities rather than a measure of the color of the sample itself.

The test is performed by agitating a sample with sulfuric acid under prescribed conditions. The color of the acid layer is compared with colors of aqueous reference solutions containing various concentrations of cobalt chloride, ferric chloride, potassium chromate, and potassium dichromate. The color scale ranges from zero for distilled water to 14 for the darkest reference color standard. The color developed in the acid layer gives an indication of impurities in the aromatic hydrocarbon, which when sulfonated, would cause the material to be discolored.

Alkalinity

ASTM D1614, Method for Alkalinity in Acetone [2], specifically covers the determination of alkalinity in acetone

calculated as ammonia (NH_3). The sample is added to an equal volume of water previously neutralized to the methyl red indicator end point. If alkalinity is detected, it is titrated with 0.05N sulfuric acid and is reported as weight percent ammonia.

Benzene Content

Benzene is classed as a toxic and carcinogenic compound. A knowledge of the concentration of benzene may be an aid in evaluating the possible health hazards to persons handling and using solvents, but the ASTM test methods are not intended to evaluate such hazards. In addition, benzene content is an important specification requirement for aromatic hydrocarbons used as chemical intermediates.

ASTM D4367, Method for Benzene in Hydrocarbon Solvents by Gas Chromatography [2], may be used to determine benzene content of hydrocarbon solvents at levels from 0.01 to 1 vol %. An internal standard, MEK, is added to the solvent sample, which is then introduced into a gas chromatograph equipped with two columns connected in series. The specimen passes first through a column packed with a nonpolar stationary liquid phase, methyl silicone, which separates components by boiling point. After octane has eluted, the flow through the nonpolar column is reversed, flushing out components higher boiling than octane. The octane and lighter components then pass through a column with a highly polar phase, 1,2,3-tris(2-cyanoethoxy)propane, which separates the aromatic and nonaromatic compounds. The eluted components are detected by a conventional detector and are recorded on a strip chart. Peak areas are measured, and the concentration of benzene is calculated by reference to the internal standard. A more recent test method for determining benzene down to 1 vppm level in hydrocarbon solvents is ASTM D6229, Method for Trace Benzene in Hydrocarbon Solvents by Capillary Gas Chromatography [2]. It is similar to D4367 but uses capillary columns in series instead of packed columns. The first column is a methyl silicone capillary column, and the second column is a polyethylene glycol capillary column. This test method is an external standard GC method using an automatic injector. This trace level GC method for benzene becomes increasingly important as the maximum benzene content hydrocarbon solvent gets to be more stringent.

ASTM D4534, Method for Benzene Content of Cyclic Products by Gas Chromatography [2], applies to cyclohexane, toluene, individual C_8 aromatics, cumene, and styrene. Benzene may be determined over a range from 5 to 300 mg/kg (5–300 ppm). The test is performed with a gas chromatograph equipped with a flame ionization or other detector and a column containing a polar stationary liquid phase such as tetracyanoethylated pentaerythritol. A reproducible volume of sample is injected. Quantitative results are obtained from the measured area of the recorded benzene peak by using a factor obtained from the analysis of a blend of known benzene content.

Nonaromatic Hydrocarbons in Aromatics

ASTM D2360, Method for Trace Impurities in Monocyclic Aromatic Hydrocarbons by Gas Chromatography [2], covers the determination of total nonaromatic hydrocarbons and trace monocyclic aromatic hydrocarbons at levels of 0.0005 to 1 % by weight in high-purity benzene, toluene, and mixed xylenes by gas chromatography. This inspection is of particular importance when these high-purity aromatics are used as chemical intermediates.

This test method is performed using an internal standard, *n*-butylbenzene, added to the specimen which is then introduced into a gas chromatographic column. The sample passes through the column, which contains a polyethylene glycol stationary liquid phase, and it is separated into nonaromatic and aromatic components. The components are detected by a flame ionization detector as they elute from the column and appear as peaks on the chromatogram. Peak areas are measured, and the concentration of the composite nonaromatics and each trace aromatic component is calculated with reference to the internal standard.

A more recent but similar test method for determining the nonaromatic contents of aromatic solvents is ASTM D5917, Method for Trace Impurities in Monocyclic Aromatic Hydrocarbons by Gas Chromatography and External Calibration [2]. It uses the same column and GC parameters as in D2360, and has the similar applicable range, but uses external standard calibration. Both test methods have comparable precision.

Nonvolatile Residue

ASTM D1353, Method for Nonvolatile Matter in Volatile Solvents for Use in Paint, Varnish, Lacquer, and Related Products [2], describes the analytical measurement of residual matter in solvents that are intended to be 100 % volatile at 105 ± 5°C. Volatile solvents are used in the manufacture and application of paint, varnish, lacquer, and other related products, and the presence of any residue may affect the product quality or efficiency of the process.

Nonvolatile residues may consist of oil contamination, dissolved solids, rust, sand, or dirt. Trace oil contamination, which could cause cleaning solvents to leave an objectionable deposit of oily residue, often will not be detected by any other specification test.

This test is performed by evaporating to dryness 100 mL of solvent in a carefully cleaned, dried, and tared evaporating dish of platinum, aluminum, ceramic, or glass, first on a stream bath and then in an oven at 105±5°C. The weight of any residue remaining in the dish is determined, and the result is reported as milligrams of nonvolatile residue per 100 mL.

Olefins Content

Olefins are undesirable impurities in hydrocarbon solvents. They are unsaturated, reactive compounds that tend to oxidize, causing solvent discoloration and objectionable non-characteristic odor. The level of olefins present can be determined by reacting them with bromine. The amount of bromine that will react is a measure of the olefin content.

ASTM D1159, Method for Bromine Number of Petroleum Distillates and Commercial Aliphatic Olefins by Electrometric Titration [11], is used for testing materials that have fairly high olefin contents. Bromine number is defined as the number of grams of bromine that will react with 100 g of sample.

The test is performed by first dissolving the hydrocarbon sample in a titration solvent composed of specified proportions of glacial acetic acid, dichloromethane,

methanol, and sulfuric acid. The use of 1,1,1 trichloroethane in the titration solvent has been superceded by dichloromethane. The dissolved sample is then titrated at 0–5°C with a bromide-bromate solution. (The titration is run at low temperature since addition of bromine to olefinic molecules proceeds rapidly and completely at temperatures down to or below 0°C, while competing reactions with aromatics and compounds of sulfur, nitrogen, or oxygen, if present, are minimized.) The end point of the titration is indicated by a dead-stop electrometric or potentiometric titration apparatus. Bromine number is calculated from the weight of sample and from the volume of bromide-bromate reagent titrated. Values are generally in the range of 1–100.

Hydrocarbon solvents usually have a bromine number of less than one. For greater accuracy, precision, and discrimination, it is more appropriate to use ASTM D1492, Method for Bromine Index of Aromatic Hydrocarbons by Coulometric Titration [2], or ASTM D2710, Method for Bromine Index of Petroleum Hydrocarbons by Electrometric Titration [23]. A more recent test method for Bromine index of aromatic solvents is ASTM D5776, Method for Bromine Index of Aromatic Hydrocarbons by Electrometric Titration [2]. This test method is very similar to D2710 with the exception that 1-methyl-2-pyrrolidinone is used in place of dichloromethane or 1,1,1-trichloroethane in the titration solvent. Bromine index is defined as the number of *milligrams* of bromine consumed by 100 g of sample (as compared with bromine number, which is expressed as *grams* of bromine consumed by 100 g of sample). Although the test procedures differ, bromine index is the more sensitive test and may be assumed to be numerically equal to 1000 times the bromine number.

In the coulometric titration method (ASTM D1492), the specimen is added to an electrolyte solution consisting of glacial acetic acid, methanol, potassium bromide, and mercuric acetate, and it is titrated with electrolytically generated bromine at room temperature. End point is determined by a dead-stop method when excess bromine is detected. The time of titration and generation current are proportional to the bromine generated and consumed by the sample.

Sulfur Content

Crude petroleum usually contains minor amounts of sulfur compounds, the greater proportion of which are removed during refining since they might otherwise cause objectionable corrosive tendencies and foul odors in refined products such as hydrocarbon solvents. There are several test methods that directly measure sulfur content or which indicate their presence indirectly.

COPPER STRIP CORROSION

ASTM D130, Method for Detection of Copper Corrosion from Petroleum Products by the Copper Strip Tarnish Test [11], indicates the presence of corrosive compounds (such as reactive sulfur compounds) in hydrocarbon solvents and other petroleum products by their effect on a highly polished test strip of copper. The polished copper strip is immersed in the solvent sample in a test tube and heated for 3 h at 100°C. At the end of this period, the copper strip is removed, washed, and compared with ASTM Copper Strip Corrosion Standards. Rating classifications range from "1a—slight tarnish," light orange, almost the same as the freshly polished strip, to "4c—corrosion," jet black.

ASTM D849, Method for Copper Corrosion of Industrial Aromatic Hydrocarbons [2], is similar to ASTM D130 but applies specifically to aromatic hydrocarbons. The sample and polished copper strip are placed in a flask fitted with a condenser and are placed in a boiling water bath for 30 min. At the end of this period, the copper strip is removed and compared with the ASTM Copper Strip Corrosion Standards. Aromatic solvents are reported to pass the test if the copper strip ratings are "1a" or "1b," indicating only "slight tarnish." All other ratings are considered failures.

DOCTOR TEST

ASTM D4952, Method for Qualitative Analysis of Active Sulfur Species in Fuels and Solvents (Doctor Test) [49] is a very sensitive qualitative test for detecting hydrogen sulfide and mercaptan sulfur in hydrocarbon solvent naphthas. It is referenced in section 6.1.10 of ASTM D235, Specification for Mineral Spirits [2]. The test is performed by vigorously shaking together in a test tube the solvent being tested and an aqueous sodium plumbite solution. A small amount of pure, dry flowers of sulfur is added so that practically all of it floats on the interface between the solvent and the sodium plum-bite solution after shaking. If the solvent is discolored or if the yellow color of the sulfur film is noticeably masked or discolored and blackened, the test is considered positive and the solvent is reported as "sour." If the solvent remains unchanged in color and the sulfur film is bright yellow or only slightly discolored with gray or flecked with black, the test is considered negative and the solvent is reported as "sweet."

SULFUR BY LAMP METHOD

ASTM D1266, Method for Sulfur in Petroleum Products (Lamp Method) [11], is an older test method used for quantitatively measuring total sulfur content of solvents. The sample is burned in a wick lamp in an artificial atmosphere of 70 % carbon dioxide and 30 % oxygen to prevent formation of nitrogen oxides. A solution of hydrogen peroxide is used to absorb the oxides of sulfur, which are formed during combustion and to oxidize them to sulfuric acid. After flushing with air to remove dissolved carbon dioxide, the absorbent is titrated with a standard solution of sodium hydroxide. Sulfur is calculated as percent by weight from the weight of sample burned and the volume of sodium hydroxide reagent required to titrate the acid in the absorbent. Alternatively, the sample may be burned in air, in which case the sulfur as sulfate in the absorbent is reacted with barium chloride to precipitate barium sulfate, and the sulfur content is determined gravimetrically.

TRACE SULFUR BY HYDROGENOLYSIS AND COLORIMETRIC DETECTION

There are two ASTM test methods that deal with the determination of trace sulfur in aromatic compounds: ASTM D6212, Method for Trace Sulfur in Aromatic Compounds by Hydrogenolysis and Rateometric Colorimetery [2], and ASTM D6313, Method for Trace Sulfur in Aromatic Compounds by Hydrogenolysis and Sulfur Specific Difference

Photometry [2]. The corresponding test method for petroleum products is ASTM D4045. Method for Sulfur in Petroleum Products by Hydrogenolysis and Rateometric Colorimetry [23]. Both D4045 and D6212 specify a 0.02–10 mg/kg sulfur range, while D6313 claims to be applicable down to 0.005 mg/kg sulfur.

In these three test methods, the sample is injected at a constant rate into an air stream and introduced into a pyrolysis furnace. The sulfur species reacts with oxygen and is converted to SO_2 and SO_3, which in turn are converted to H_2S in a second pyrolysis furnace at 1200 to 1300°C in the presence of hydrogen. The H_2S thus formed reacts with lead acetate, and the rate of color change of the lead acetate paper is proportional to the sulfur content.

TRACE SULFUR BY OXIDATIVE COMBUSTION AND ELECTROCHEMICAL DETECTION

A very recent method for sulfur content in aromatic hydrocarbons is described in ASTM D6428, Method for Total Sulfur in Aromatic Hydrocarbons by Oxidative Combustion and Electrochemical Detection [2]. The sample is injected at a controlled rate into a stream of inert gas (helium or argon) or inert gas mixed with oxygen. The sample is vaporized and carried into a high temperature zone (>900°C) where oxygen is introduced. Sulfur compounds, present in the specimen, are converted to sulfur dioxide, which react with the sensing electrode in a three-electrode electrochemical cell. The reaction produces a measurable current that is directly proportional to the amount of sulfur in the original material.

TRACE SULFUR BY GAS CHROMATOGRAPHY AND SULFUR SPECIFIC DETECTION

ASTM D5623, Method for Sulfur Compounds in Light Hydrocarbon Liquids by Gas Chromatography and Sulfur Selective Detection [49], describes a test method for determining individual sulfur species concentration as well as total sulfur concentration. The sample is injected into a gas chromatograph equipped with a capillary column that can separate the individual sulfur species. A sulfur specific detector such as the atomic emission detector or the sulfur chemiluminescence detector gives equimolar responses to different sulfur species in the sample. The total area of all the sulfur species peaks can be summed up to give a measure of the total sulfur concentration. This is the only sulfur test method that can determine the concentration of individual sulfur species. This test method can detect below 1 wppm of total sulfur in various hydrocarbon solvents.

Water Content

Dissolved water can have adverse effects on solvent end-use applications. For example, it can reduce solvency. Water can cause reactions with isocyanates during polyurethane preparation and with moisture-cure polyurethane paints and varnishes causing polymerization and gelation during storage. Metallic pigments can react with water to generate hydrogen gas, which can expand and burst paint cans. Dissolved water can act as a catalyst poison when a solvent is used as a reaction diluent for polyolefin polymerization.

KARL FISCHER REAGENT METHOD

ASTM D1 364, Method for Water in Volatile Solvents (Fischer Reagent Titration Method) [2], is a quantitative test. It is based on reactions involving the reduction of iodine by sulfur dioxide in the presence of water. These reactions can be used quantitatively when pyridine and an alcohol are present to react with the sulfur trioxide and hydroiodic acid produced in the reagent.

$$H_2O + I_2 + SO_2 + 3C_5H_5N \rightarrow 2C_5H_5N \cdot HI + C_5H_5N \cdot SO_3$$
$$C_5H_5N \cdot SO_3 + ROH \rightarrow C_5H_5N \cdot HSO_4R$$

To determine water content, Fischer reagent (a solution of iodine, pyridine, and sulfur dioxide in the molar ratio of 1:10:3) dissolved in anhydrous 2-methoxyethanol is added to a solution of the sample in anhydrous pyridine-ethylene glycol (1:4) until all water present has been consumed. This is evidenced colorimetrically by the persistence of an orange-red end-point color or electrometrically by an indication on a galvanometer or similar current-indicating device which records the depolarization of a pair of noble-metal electrodes. The reagent is standardized by titration of measured amounts of water.

Alternatively, automatic instruments are commercially available which operate on a coulometric principle according to ASTM E1064, Method for Water Content of Liquid Organic Chemicals by Coulometric Karl Fischer Titration [9]. A measured quantity of sample is introduced into a titration cell containing reagent, which undergoes the Karl Fischer reactions. Iodine is coulometrically regenerated, the amount of current required being proportional to the water content of the sample.

HEPTANE MISCIBILITY TEST

Oxygenated solvents are capable of dissolving sizable amounts of water. They can be checked qualitatively for water content by ASTM D1476, Method for Heptane Miscibility of Lacquer Solvents [2]. Heptane is water immiscible and has a very low tolerance for water in solvent blends. The test is performed by mixing the solvent sample under test with heptane in a 1:19 proportion and agitating. A clear solution indicates miscibility and low water content (less than about 0.5 wt%) in the solvent sample. A turbid solution indicates immiscibility and the presence of high water content in the solvent sample.

Water Solubility

Certain oxygenated solvents are completely miscible, e.g., methanol, isopropanol, and acetone. This property can provide a qualitative means for indicating the presence or absence of water-insoluble contaminants, such as oils, paraffins, olefins, aromatics, high-molecular-weight alcohols, ketones, etc. Water-insoluble materials in the solvents may interfere with many of their end-uses [50].

ASTM D1722, Method for Water Miscibility of Water-Soluble Solvents [2], covers the determination of the miscibility of water-soluble solvents with water. The sample is diluted with ten volumes of water in a glass graduated cylinder. The resulting mixture is viewed through the length of the column of liquid toward a dark background while being transversely illuminated. The sample is reported to pass the test if there is no evidence of cloudiness or turbidity initially and after 30 min.

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Part 6: Pigments

19

White Pigments

Juergen H. Braun[1]

INTRODUCTION

ALMOST EVERYTHING MANMADE THAT IS WHITE or light in color contains white pigment in its surface: houses inside and outside, industrial articles, plastics, glazes, rubber, printed surfaces, many paper products, and even some foods. Only papers and textiles can be white without pigment.

Virtually all this whiteness and lightness is supplied by titanium dioxide (TiO_2) pigments. Void pigments make a minor contribution. The classic white pigments—lithopone, zinc sulfide, and the white leads—have essentially disappeared from commerce because TiO_2 pigments perform much better, are much cheaper, and are nontoxic. Zinc oxide is still added to some paints as a mildewstat, but not for use as a white pigment.

TiO_2 pigments are manufactured by a major, globally distributed industry. Its products are sold for many applications; however, more than half of all white pigment goes into paints. In many coatings, white pigment is the single most expensive ingredient. To select the right pigment grade and use it well is an important challenge to the paint manufacturer.

This chapter will familiarize coating manufacturers with white pigments and help them understand their options for selection, utilization, and testing. Toward this objective, I will first outline the commerce and manufacture of white pigments and then discuss their function, the substances that serve this function, and the commodities available. I will distinguish between product characteristics that describe the pigment itself and product performance, which are properties of paint films, that is, systems composed of pigment and binder.

Commerce

The white pigment market is served almost exclusively by titanium dioxide pigments. Globally, about twelve billion pounds are produced annually at a value of about sixteen billion dollars. The value of TiO_2 pigments exceeds by far the combined value of all color pigments.

Five manufacturers share two-thirds of the world market. Their products are of similar quality. Most of these producers operate several large plants located in industrialized countries. The largest of these plants makes about two million pounds of pigment a day. A few small plants operate in certain countries where they manufacture the pigment for regional consumption.

In the United States and most other countries, one-half of the TiO_2 pigment is used in coatings, one-fourth in paper, and 15 % in plastics. All other end uses, pigmentary (inks, floor coverings, elastomers, roofing granules, fibers, fabrics, sealants, foods, etc.) and nonpigmentary (ceramics, welding rods, etc.), account for the remaining 10 %. In less-developed countries, most of the TiO_2 pigments go into paints and plastics.

Manufacture

TiO_2 particles, the active ingredient of pigment, are made by one of two processes:

1. The old sulfate route dissolves the ore in sulfuric acid, purifies the aqueous solution of titanyl sulfate, precipitates a hydrous titania gel, and calcines the gel to crystallize it into aggregates of pigment particles, which, in turn must be ground.
2. The newer and "greener" chloride route chlorinates the ore and purifies the $TiCl_4$ intermediate by distillation and chemical treatments. $TiCl_4$ is then flame oxidized to pigmentary TiO_2 particles and chlorine. The chlorine is recycled.

Sulfate processes are low-tech, labor-intensive operations that operate in a batch mode. Chloride processes are high-tech, automated, continuous operations. Sulfate and chloride products do not differ much in performance except that chloride TiO_2 is purer and thus brighter in nature.

Waste disposal is a significant factor and constraint. The sulfate process generates vast quantities of dilute sulfuric acid and iron(II) sulfate from its ilmenite ($FeTiO_3$) ingredient.[2] The chloride process makes iron(III)chloride by-product in much lower quantities that are dependent on ore composition: rutile (TiO_2), anatase (TiO_2), leucoxene ($TiO_2/FeTiO_3$), and ilmenite ($FeTiO_3$).

After the primary step, either process manufactures pigment particles, and their surfaces are treated to adapt the pigment to a variety of end uses. These treatments are carried out in aqueous suspension followed by drying, grinding, and dry treatment operations. Pigments are also converted into slurry grades.

By either process, manufacture involves six steps:

1. Digestion of the ore.
2. Purification of the intermediate.
3. Crystallization of pigment particles.
4. Treatment of the pigment surface.
5. A variety of finishing operations.
6. Grinding of pigment aggregates.

[1] *Consultant, 614 Loveville Road, Building E, Apartment I-H, Hockessin, DE 19707-1616.*

[2] The iron-free minerals, rutile and anatase, do not dissolve in sulfuric acid and cannot be used as such in sulfate processes.

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TABLE 1—Optics and appearance

If the Pigment in the Coating . . .		Then the Coating . . .	
Absorbs Light	**Scatters Light**	**Returns Light**	**And Appears**
All	None	None	Black
None	All	All	White
None	Some	None	Gray
Some in Specific Wave Bands		Colored	

Research and Development

For 50 years, the TiO_2 industry has been large, competitive, and profitable enough to dedicate sizable science and engineering resources to product improvement. These efforts have been remarkably successful. Today's TiO_2 pigments are complex structures composed of an optically active core with shells that adapt the pigment to specific end uses. Each feature is carefully designed into each pigment grade, optimizing it for its specific application. Their optical performance approaches the theoretical light-scattering effectiveness calculated from concepts of theoretical physics.

Experts in pigment technology, with the help of specialists in optics, surface chemistry, fine-particle technology, and chemistry have resolved many of the compromises between often-conflicting requirements. End users can contribute to progress by suggesting new opportunities. Solving pigment problems does, however, require expertise in pigment technology.

THE FUNCTION OF PIGMENTS

Most coatings have two functions, aesthetic and protective. More often than not, manufactured surfaces are visually unattractive and therefore coated for aesthetic appeal. The coating hides the substrates' discolors and contrasts and provides a visually pleasing appearance or identification with certain exceptions such as vinyl siding. ASTM D16, Standard Terminology for Paint, Related Coatings, Materials, and Applications, defines pigments as the fine solid particles used in the preparation of paint or printing ink and substantially insoluble in the vehicle.[3]

Pigments supply the hiding and color of a coating. They are incorporated in surfaces to make them look bright or dark, colorful or drab, white or black, either more appealing or more appropriate to whatever the intended service. Toward that end, pigments must hide the unattractiveness of a substrate. Thus, pigments serve the human eye. They interact with visible light and cause surfaces to be seen in colors:[4] chromatic colors such as red, blue, and green, or achromatic colors such as black, gray, and white.

To understand this primary aesthetic function of pigments, let us consider the interactions of visible light with matter at or near surfaces. Involved are two mechanisms of optics: light scattering and light absorption. White or bright hiding is achieved by light scattering, an optical mechanism by which a ray of light is scattered as it impinges on an interface. White pigments are substances selected to scatter light very well.

Hiding also can be achieved by the absorption of light that is involved in colored and black surfaces and pigments. Optical absorption is decisively more efficient than optical scattering. Thus, less color or black than white pigment is required for hiding. Dark and black paint films can therefore be thinner than their white and light counterparts.[5]

Table 1 relates appearance characteristics of surfaces to the optical phenomena that cause them. If all light is absorbed by a surface, none scattered, the surface is perceived as black. If all light is scattered, none absorbed, the surface is seen as white. If a portion of the light is scattered and another portion of it is absorbed, the surface is gray. If the absorption and scattering is wavelength dependent, for example, if red light is absorbed and green light is scattered, the surface is colored by the scattered green portion of the light. Even though common usage refers to objects as colored, i.e., red cars, green mountains, almost always only their surfaces matter.[6]

The return of light from a surface is caused by reflection at the surface and scattering from beneath with pigment causing the scattering. The optical action itself occurs at or in pigment particles, not on the particles but rather within the surface. Light reflected at the surface does not usually change its color.[7]

Light scattered and returned from inside the coatings makes a surface look white or, if color pigments are involved, gives color to the surface. It is the white pigment in the coatings that does most of the light scattering.

Light scattering can be explained quantitatively from optical theories. Geometric optics give a graphic but superficial picture that accounts well for effects of refractive indices of potential pigments but unreliably for effects of pigment particle size. Wave optics and electromagnetic theory provide a more accurate but quite abstract model, accounting for particle size but not for effects of particle shape, orientation, and crowding.

The optimum particle size at which a population of white pigment particles scatters a maximum amount of light is about[8] 0.2 μm for green and white light. Blue light is scattered more efficiently by smaller particles, red light by larger particles. For pigments of high refractive indices, the theoretical curve of optical effectiveness versus particle size

[3] The definition goes on to point out that asphaltic materials are not pigments except when they contain substances substantially insoluble in the vehicle in which they are used. It is worth pointing out that Webster's definition of a pigment is "a substance that imparts black or white or color to other materials."

[4] In most technical contexts of color and colorants, white, gray, and black are considered colors.

[5] The transparency of white clothes, in particular wet, white clothes, illustrates the relative hiding effectiveness of white and color.

[6] This comes about because visible light and thus human vision penetrates pure gasses to a depth of about 10^{-6} m, pure liquids to about 10^{-2} m, dielectric solids to about 10^{-3} m, and metals to about 10^{-9} m, a range of 15 orders of magnitude.

[7] Exceptions are the colored metals—gold, copper, and their alloys—and extremely strong colorants, for example, copper phthalocyanine and hematite.

[8] The uncertainty is not in the optical calculation but reflects difficulties in defining the size of particles other then spheres. What, for example, is larger, a large snake or a small monkey? It depends on the perspective of the observer.

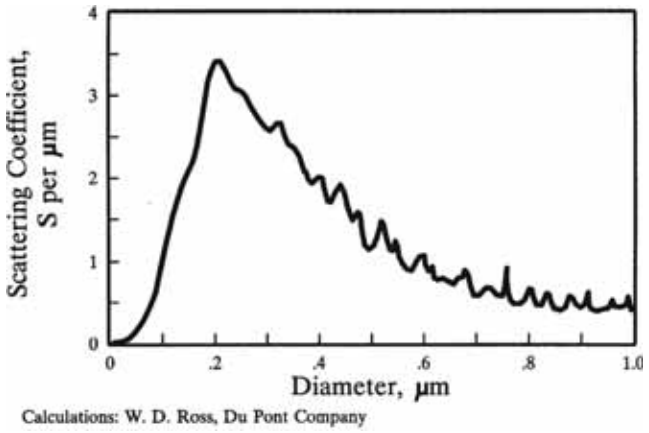

Fig. 1—Scattering by spheres of rutile in polymer. From Braun, J. H., "Introduction to Pigments," Monograph in the Federation Series on Coatings Technology, Federation of Societies for Coating Technology, United States, 1993.

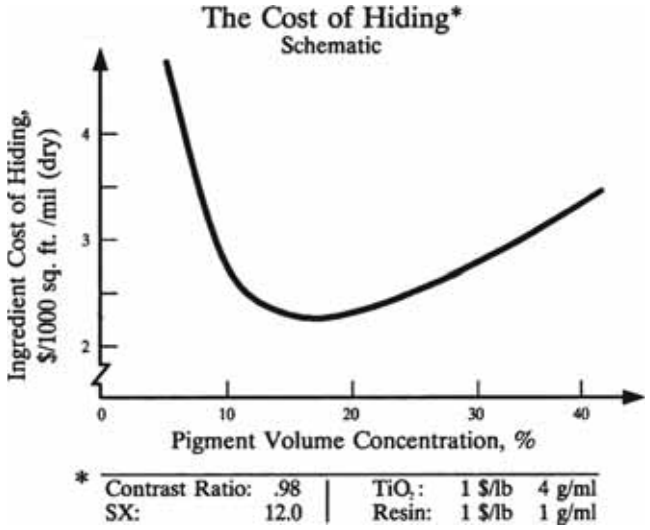

Fig. 2—The cost of hiding, from Braun, J. H., "Introduction to Pigments," Monograph in the Federation Series on Coatings Technology, Federation of Societies for Coating Technology, United States, 1993.

has a sharp peak (Fig. 1). For pigments of lower refractive indices, the peak broadens but the optimal size near 0.2 *μm* does not change much.

The pronounced wavelength dependence of optimum scattering causes a subtle color effect by white pigments in colored coatings. Their color shifts toward red if the white pigment is larger than optimal. Color shifts toward blue if the white pigment is smaller. This "undertone" is visible in colored coatings and in white coatings, at incomplete hiding. In gray coatings, the effect can be quite obvious and at times objectionable in nature.

Pigments can act by themselves, but they are usually used in combinations: White pigment with a small amount of color or black pigment, white pigment with one or more color pigments, combinations of color pigments, color pigments with some black pigment, etc. Some types of pigment particles scatter light and other types absorb it. White pigments deliver white appearance by scattering all light (see Table 1). Black pigments absorb all light. Color pigments create color by absorption of light of specific wave bands. Sometimes, though, the wavelength-specific absorption by color pigments is augmented by wavelength-specific scattering.

Pigments, because they are particulates, can affect surface texture and texture-related appearance characteristics: gloss and sheen.

Pigments do the optical, that is, the aesthetic work; they provide the color and the hiding. Binder keeps the pigment on the substrate and does the mechanical and the chemical work that protects the substrate from the environment. The less effective the pigment in its optical function, the thicker the coating must be to hide and provide the desired color. Thick coatings, however, cost more than thin ones. Since the cost of binder increases proportionally to film thickness, film costs are inversely proportional to the effectiveness of the pigment. Economics discriminate severely against pigments of low optical effectiveness.

Fig. 2 is a plot of the cost of hiding as a function of pigment volume concentration for the case of a typical white paint applied to hide color contrasts of a substrate; it illustrates the economics of hiding. The film is composed of a TiO_2 pigment at $1 per pound and a density of 4 g/mL dispersed in a polymer at $1 per pound and a density of 1 g/mL. Hiding cost has a distinct minimum. At too low a pigment volume concentration, the film must be thick to hide. The cost of hiding increases because additional polymer is required to provide the required film thickness. At too high a pigment volume concentration, the white pigment is used inefficiently, also increasing cost, albeit at a lower rate.

THE SUBSTANCE OF WHITE PIGMENT

White pigments translate light scattering into hiding power, brightness, and opacity of thin films. The films, in turn, hide the color and contrasts of the substrate. To serve as an effective white pigment, a substance must meet requirements that limit the selection to less than one dozen from among the thousands upon thousands of natural and man-made chemicals. A potential white pigment must have an extremely high refractive index.

In addition, the substance must be

- stable,
- almost colorless,
- suitable for manufacture in optimized, colloidal particle size,
- a solid,
- insoluble in water and organic solvents, and
- safe in manufacture, end use, and as a waste.

Of these criteria, the requirement of an extremely high refractive index, larger than 2.0, is essential and is most restrictive. Most materials with high refractive indices are hydrolytically unstable. A combined requirement for extreme refractive index plus stability eliminates all but a few substances.

High density is a disadvantage for a pigment. Pigments function by volume yet are sold by weight. Thus, a high-density pigment contains fewer particles per pound to do its optical work than a low-density pigment. Because of its optical performance, safety, and cost, titanium dioxide has become the only white pigment of commercial

significance. In the foreseeable future, it is quite unlikely that a better white pigment will be found to replace TiO_2 because its performance advantage results from a combination of a uniquely high refractive index with other essential characteristics.

TiO_2 has the highest refractive index of all ordinary, colorless, and stable substances, significantly higher even than diamond. Refractive indices of most compounds such as TiO_2 have been measured and can even be calculated from pure theory. No colorless substance, neither real nor hypothetical, has been found[9] that has a higher refractive index than TiO_2.

Before the commercialization of titanium dioxide, lithopone ($BaSO_4$/ZnS), zinc oxide, zinc sulfide, and white lead [lead(II)hydroxy carbonate] served as white pigments. All have lower refractive indices, scatter less effectively, and are much less cost effective than TiO_2.

Not only particulates but also air voids in coatings scatter light as if they were particles. But air voids are far less effective than TiO_2. Voids thus contribute to hiding but at direct or indirect costs. In coatings below their critical pigment volume concentration, voids scatter light and hide as such. But because they do not hide as well as TiO_2, films must be thicker, which increases binder cost. In coatings above the critical pigment volume concentration, extenders create a network of interconnected voids. These pores enhance the hiding effectiveness of the pigments. This indirect hiding contribution of voids is cheap to achieve in paint but comes at the expense of mechanical and chemical film qualities. Pores (1) concentrate mechanical stresses to where they initiate fracture and (2) conduct aggressive chemicals from the surface into the depth of the paint film. The hiding improvements and the quality detriments of coatings above their critical pigment volume concentration can be quite large.

TIO_2 PIGMENTS

Titanium dioxide has obsoleted all other white pigments because TiO_2 is cheaper to use and much safer than other pigments. TiO_2 pigments are the most effective scatterers of visible light. They hide better and provide more lightness. They are more stable and are less toxic.

Fig. 3 and Fig. 4 are descriptions of what TiO_2 pigments "look" like. Figure 3 is a transmission electron micrograph of an uncoated TiO_2 pigment grade dispersed in a dispersant by conventional techniques of grid preparation. Single crystals, twins, aggregates, and small agglomerates are visible. Weakly bonded agglomerates, though, are not distinguishable from strongly bonded aggregates because micrographs do not show strength of bonding. Fig. 4 is a description of a set of electron scanning micrographs of dry pigment in bulk and as an individual floc. Visible are masses and individual crystallites, single and twinned. At highest magnification, scanning electron microscopy shows crystals significantly more rounded in shape than they actually are.

TiO_2 pigments are made in two crystal phases, rutile and anatase, that differ in lattice structures, refractive indices, and densities. Anatase was the first commercial titanium dioxide pigment but, for the coatings industry, has now been replaced by rutile because, in organic media, rutile has an 18 % scattering advantage over anatase.

[9] Extreme pressure phases of TiO2 could be expected to have higher densities combined with higher refractive indices.

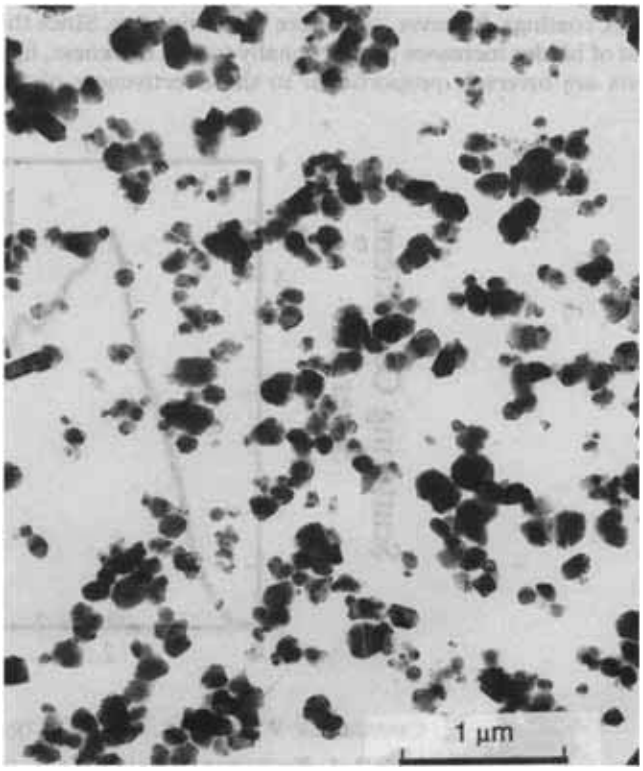

Fig. 3—Transmission electron micrograph of TiO_2 pigment.

For the sake of clarity, I will distinguish between characteristics and performance of a pigment. Composition, for example, is a characteristic of a pigment that is essentially independent of its environment. By contrast, hiding power describes the performance of a system, a pigment within a paint film. Hiding is a film characteristic that depends on pigment volume concentration and a host of formulation and application parameters of the paint in which the pigment was evaluated.

Characteristics are properties of the commodity: composition, density, particle size, etc. They can be measured on the commodity, either dry powder or slurry. Granted, some product characteristics are affected by the ambiance in which they are measured but only in secondary ways. Particle size is an example of a characteristic affected by method of measurement.

At the state of the art, it does not appear possible to establish rigid links between pigment characteristics and performance. Thus, the pigment commodity cannot be defined exclusively in terms of its characteristics. Certain characteristics can be measured reliably. Their results bear on but do not guarantee performance. Clearly, complete specifications for pigments must include both product characteristics as well as product performance measures.

A few generalizations of the connection between pigment characteristics and product performance are appropriate.

- High gloss pigments: (1) Pack densely as indicated by measures of oil absorption, liquid demand, and interstitial space; (2) contain few agglomerates larger than

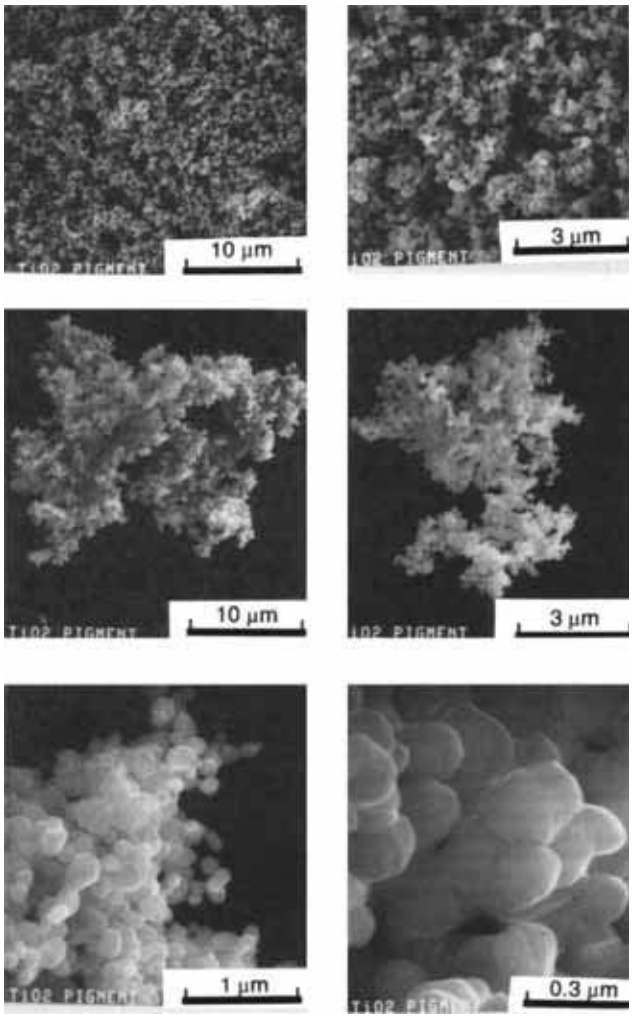

Fig. 4—Scanning electron micrographs of TiO_2 pigment.

about 0.5 μm;[10] and (3) have hydrous oxides contents that are low and TiO_2 contents that are correspondingly high [l].

- Pigments intended for high-pigment volume concentration paints contain up to 20 wt % hydrous oxides be cause fluffy oxides act as very efficient extenders. TiO_2 contents are correspondingly low.
- Satisfactory outdoor durability precludes the presence of more than about 1 wt % anatase phase with the rutile [2].
- Product fractions smaller than about 0.1/lm and larger than about 0.4/lm constitute losses to optical performance because particles that are too large or too small scatter light inefficiently.
- Impurity metal ions within the rutile crystals can de grade brightness dependent on the nature of the metal ion. Certain ions degrade color in concentrations as low as 0.00001 wt %. Effects of ion contaminants on characteristics other than brightness are generally insignificant. Hydrous oxide coatings can tolerate a much higher concentration of impurity metal ions in the coating without having much effect.
- Hydrous oxide coatings on pigment have ion-exchange characteristics. Their exchangeable ion content affects pigment performance in applications that are sensitive to *p*H (acid-catalyzed coatings) or the presence of electrolyte (electrocoatings).
- Pigment surface area affects oil absorption.

Some of these effects are sufficiently well quantified for translation into specifications.

Pigment Characteristics

TiO_2 pigment has to meet stringent specifications of crystal phase, particle size, surface characteristics, and purity. As with all chemicals, every product characteristic has some effect on every performance quality. Some specific characteristics, however, dictate equally specific performance attributes. These crucial relationships are described.

Refractive index and density are paramount to optical function, but they are not subject to manipulation. The crystal phase impacts weathering and light-scattering performance. Particle size controls light scattering and has effects on color. Surface characteristics are designed into the product through chemical treatments reflected by commodity composition. The treatments improve dispersibility, durability, and gloss performance. High purity of the pigment makes for brightness.

TIO_2 CRYSTALLITES

The active ingredients of a TiO_2 pigment commodity are its TiO_2 crystallites. Other components of the commodity affect the commodity density but do not affect the crystallite density or the refractive index of the pigment. Neither the refractive index nor the density of any chemical can be manipulated independently by conventional technology.[11] Two crystal phases of titanium dioxide serve as pigments: rutile and anatase. They differ in refractive indices, densities, and weathering performance because rutile and anatase differ by the arrangement of the titanium and oxygen ions within the crystals (Fig. 5). Rutile crystals are elongated, are denser, and have higher refractive indices.[12] Because of their higher refractive indices, rutile pigments scatter light more effectively than anatase products. They are also much less prone to cause paint films to chalk.

Rutile absorbs slightly more violet radiation than anatase and is slightly more yellow in bulk. However, little, if any, of this yellowness extends into pigment applications.

TiO_2 is an ultraviolet radiation-energized oxidation catalyst of organic polymers. Anatase surface is about ten times more reactive than rutile surface. It takes only 10 % anatase in rutile to reduce to one-half the life expectancy of a paint film. Thus, for all exterior applications, the phase purity of rutile pigments is quite important.

During paint manufacture or usage, titanium dioxide cannot undergo transitions of crystal phase, that is, it cannot change its lattice structure. This contrasts with most organic pigments, many of which phase convert readily and usually with dramatic loss of optical performance.

[10] Particle size measured as Stoke's settling diameters by sedimentation methods.

[11] Density and refractive indices of inorganic oxides can be increased together, but only at extreme pressures and astronomic cost.

[12] Actually, TiO_2 crystals have two principal refractive indices each. These two refractive indices do not differ much. They enter all relevant considerations of pigment as an appropriately weighted average.

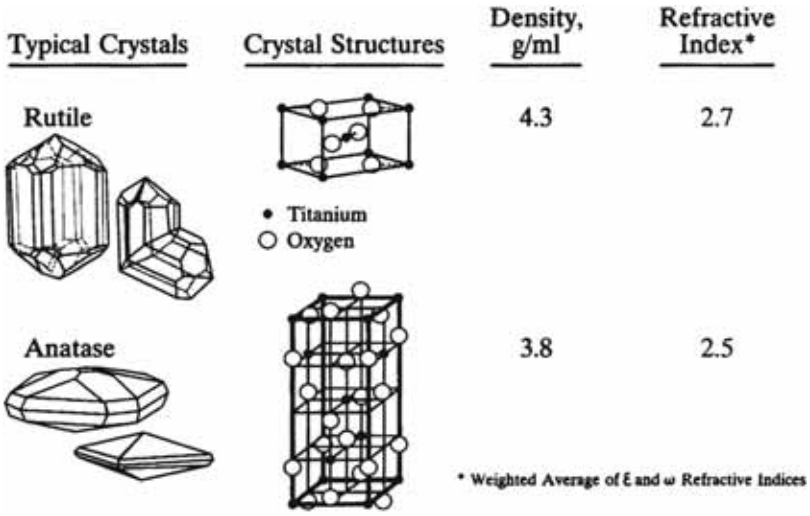

Fig. 5—Titanium dioxide crystals. From Braun, J. H., "Introduction to Pigments," Monograph in the Federation Series on Coatings Technology, Federation of Societies for Coating Technology, United States, 1993.

For example, an unstabilized a-copper phthalocyanine pigment, on exposure to an aromatic solvent, grows into long needles of β-copper phthalocyanine, losing most of its color strength in the process.

PHASE ANALYSIS

1 % or more of anatase in rutile pigment is considered undesirable because it increases the catalytic reactivity of the pigment. Fortunately, the phase analysis of TiO_2 pigment is cheap, convenient, and reliable.

Phase purity of pigment is usually measured by x-ray diffraction, for example, ASTM D3720, Standard Test Method for the Ratio of Anatase to Rutile in Titanium Dioxide Pigments by X-ray Diffraction. Conventional diffractometers can detect 1 % of pigmentary anatase in 99 % rutile by using peak intensity ratios or instrument counts. With careful attention to instrument alignment and sample preparation, a bit less anatase can be detected. Other more complex techniques are more sensitive. However, why bother since less than 1 wt % anatase does not contribute much to the catalytic activity of the pigment.

The hydrous and anhydrous oxides contributed by pigment treatment are not detectable by x-ray diffraction because they are either truly amorphous or subcrystalline in nature and that is too small and/or too disorganized to be disruptive. Their diffraction lines are diffuse and drowned in the TiO_2 signal.

PIGMENT PARTICLE SIZE

TiO_2 pigment particles are submicroscopic. They are so small that one pigment particle is to the size of a man as the size of a man is to the size of the earth. Thus, intuitive judgments based on macroscopic experiences are often misleading.

The particle size of pigment grades is tailored to the required optical performance. Pigment size depends critically on definition of "particle." For paint optics, the particle is the object that a light beam meets in the paint film. Its size is a composite of primary particles, aggregates, agglomerates, flocs, and even of casual contact of any of these assemblies. Primary particles are individual single crystals and crystallographic twins.[13] They average from 0.1 to 0.3 μm in median diameter by weight with a geometric standard deviation of about 1.4.[14] Aggregates are associations of crystallites sharing grain boundaries and are thus strongly bonded. Agglomerates are associations of crystallites and aggregates bonded by relatively weak forces. Flocs are weakly bonded associations of crystallites, aggregates, and agglomerates formed spontaneously in a liquid or even in air.

The shear forces of paint application can disperse flocs. However, they are likely to reassociate. Paint grinding breaks most agglomerates if (1) the mill base is formulated to proper viscosity and (2) the mill is well operated. Aggregates can be broken only by high-intensity mills. Crystallites cannot ordinarily be broken. Aggregates and crystals, once broken, do not reassemble because aggregate bonding and crystal growth require thermal activation to many hundred degrees centigrade. TiO_2 pigments do not degrade in conventional paint and plastics processing operations.

The inclusion of the term "casual contact" in the definition of particle is important because it links size to concentration. At low pigment concentration, the frequency of particle overlap in a beam of light is low and the casual contact contribution to effective size is small. At high concentration, casual contacts are abundant and contribute significantly to the particle size as seen by a light beam penetrating a paint film.

Optimal scattering performance calls for optimal particle size. Particles that are too small, in the extreme, are in molecular dispersions and scatter almost no light; particles too large, macroscopic crystals, are transparent. The particle size at which a population of TiO_2 particles scatters a maximum amount of light is about 0.2 μm for green[15] and white light. Blue light is scattered more effectively by

[13] Two or more single crystals intergrown according to some deducible law of symmetry.

[14] Geometric standard deviation = $\frac{1}{2}(D_{84}D_{50} + D_{50}/D_{16})$, with D = diameter, and 84, 50, and 16 signify the respective percentiles.

[15] For whiteness and brightness, green light matters most because the human eye is most sensitive in the green waveband.

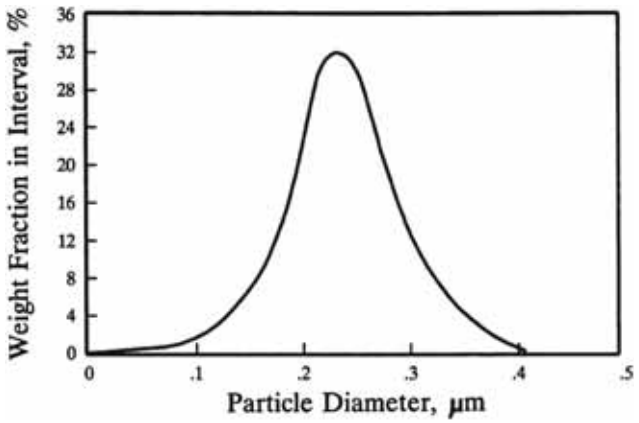

Fig. 6—Particle size distribution of TiO_2 pigment. From Braun, J. H., "Introduction to Pigments," Monograph in the Federation Series on Coatings Technology, Federation of Societies for Coating Technology, United States, 1993.

particles closer to about 0.16 μm, red light by particles of about 0.23 μm. This optically effective particle size is likely to differ from the size measured by analysis.

Particle-size distributions of commercial TiO_2 pigments are narrower than those of many so-called monodisperse particulates (Fig. 6). Population statistics approach "log-normal" character, that is, a logarithmic transform converts the size distribution curve to "normal" or Gaussian probabilities. Appropriately ground, pigment dispersions contain less than 5 wt % of particles smaller than 0.10 μm and larger than 1.0 μm. The mean particle size of pigment grades is tailored to the required light-scattering performance. Pigment grades composed of small particles are made for applications at low-pigment volume concentration.

The pronounced wavelength dependence of optimum scattering results in a subtle color effect caused by white pigments in colored coatings. Their color shifts toward red if the white pigment is larger than optimal or toward blue if the white pigment is smaller than optimal. This "undertone" is visible only in gray and colored coatings and in white at incomplete hiding. In gray coatings, the effect can be quite obvious, sometimes objectionable, sometimes desirable. Small-size TiO_2 grades with blue undertone are used to make colors look "cleaner," i.e., less yellowish.[16]

Large particles in a paint film are detrimental to gloss. Thus, the coarse tail of the size distribution of TiO_2 pigments impacts gloss performance [1]. Fig. 7 shows what particle size range impacts which performance characteristic.

Paint grind gages reveal the presence of minute quantities of grit, which are clumps composed of tens of thousands of primary particles. Grind gages do not respond to pigmentary particle sizes. For TiO_2 pigments, the presence of grit has no detectable optical effects.

Particle size control is one of the manufacturing secrets of the TiO_2 industry. Additives and process conditions during crystallization and grinding operations are crucial to particle size and product performance in both the chloride and the sulfate processes.

[16] Because dirt is colored by iron and thus reddish gray, a reddish or yellowish cast is perceived as "dirty."

PARTICLE SIZE ANALYSIS

An upfront warning: *Particle-size analysis and the interpretation of analytical data calls for specialized expertise.* Potential pitfalls are so numerous that serious misinterpretation is the rule rather than the exception, particularly in the interpretation of electron micrographs.

Problems arise in several ways. Two definitions of particle, be it clump, agglomerate, aggregate, or crystallite, are vitally important: (1) the particle of the analysis and (2) the particle that matters within the intended application. The analytical particle is almost never the same as the particle in a paint film that interacts with light.

- Dispersion is a true grinding operation that reduces particle size. In spite of this, grinding must be an integral part of the analytical procedure. Otherwise, the softest and largest clumps become valid members of population statistics.
- In the process of sample preparation, dispersive work is often expended on minute samples. Such work can add up to enormous energy concentrations that can break crystallites, which cannot be broken *en masse.*
- Sampling statistics is a frequent problem considering small quantities or low concentrations of pigment in samples.
- In microscopy, transmission images bear little resemblance to ordinary visual perceptions based on observation of surfaces. Scanning micrographs, by contrast, correspond to human vision. Differences become apparent when comparing Figs. 3 and 4.
- In light-scattering methods, the extreme refractive index of TiO_2 affects computational interpretation.
- No certified standards are available pertaining to the size range of pigments.

Numerous methods have been applied to the size analysis of pigments: Andreasan pipettes, disk centrifuges, transmission electron microscopy, light-scattering measurements, field flow fractionation, etc., have been used. They are too complex and far too costly for routine analysis.

Lately two methods have advanced TiO_2 technology because reproducible results can be obtained routinely: x-ray sedimentation and the x-ray disk centrifuge. Both methods are usually combined with ultrasonic dispersion.

X-ray sedimentation measures the Stokes' diameters of particles settling in water by gravity. Settling causes density differences in the suspension and these are detected by absorption of x-rays. Brownian motion interferes with settling and distorts the small end of the size distribution curve of the particle population. The x-ray disk centrifuge substitutes centrifugal force for gravity and this avoids misrepresentation of small particle fractions.

COMMODITY COMPOSITION

The TiO_2 in the pigment is its optically active ingredient. Other components adapt it to its end use. The commercial products have compositions that fall into one of three categories: (1) uncoated pigments, (2) coated pigments, and (3) Slurries.

Uncoated pigments contain 98 % or more titanium dioxide; some contain up to about 1 % aluminum oxide (anhydrous), and other products contain less than about 0.5 % aluminum oxide with some other inorganic, anhydrous oxides. Organic additives and their decomposition products may be present in concentrations of fractional weight percentages. Uncoated pigments are used in plastics

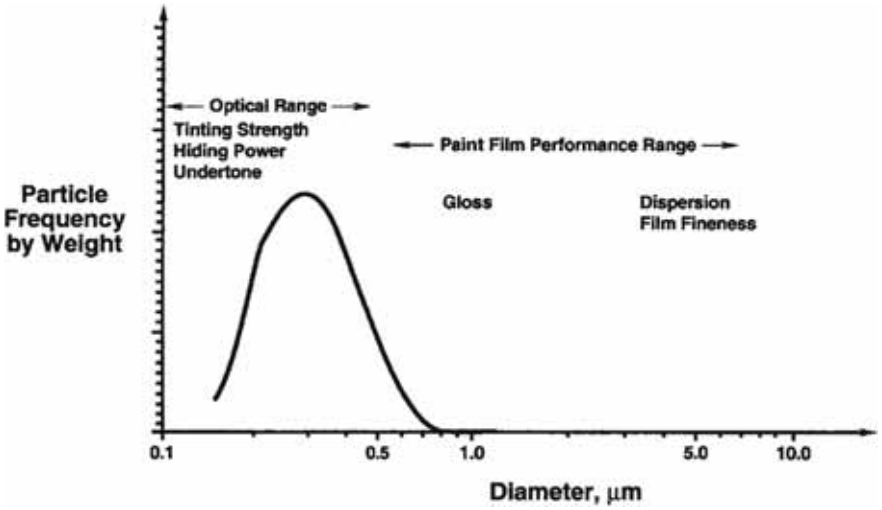

Fig. 7—TiO_2 aggregate size distribution [1].

and paper. In coatings, wet-treated pigments are preferred because they are easier to disperse into liquids of low or moderate viscosity.

Minor constituents, either carried over from the ore or added in the manufacturing process, can be important in determining pigmentary properties because they can control crystallite size. Sulfate pigments retain up to 0.3 % niobium pentoxide and 0.3 % phosphorus pentoxide from the ore. They also contain up to 0.2 % alumina, which is added to compensate for the presence of niobium. Compensation minimizes discoloration by the semiconductor imbalance that pentavalent and trivalent cations can cause in the rutile lattice.

Chloride process pigments contain practically no unwanted impurities because the titanium tetrachloride intermediate can be effectively purified. They contain about 1 % pyrogenic alumina that is added for improved process control and for photochemical stability improvement.

Trace constituents are generally unimportant except for transition metals, such as iron, chromium, vanadium, etc., which degrade color by semiconductor mechanisms.

Besides inorganic constituents, most uncoated and many coated pigments contain up to 0.5 % of an organic grinding aid to improve flow in the fluid energy mill, thereby achieving more uniform grinds. The grinding aids are usually polyhydroxyl compounds (for example, trimethylol propane, triethanolamine, etc.) that can undergo some pyrolytic degradation in the mill.

For use in coatings, i.e., to be dispersible by conventional paint-making equipment, TiO_2 pigments are "coated." In aqueous suspension, hydrous aluminum oxides are precipitated onto the surfaces of pigment particles. Interior grades contain a coating of up to 5 % hydrous alumina for ease of dispersion. Durable grades have another coating that usually consists of about 2 % silica and sometimes also oxides of zirconium, boron, zinc, cerium, and tin, usually in concentrations of less than 1 %.

Rutile pigments are made suitable for extreme exposure by encapsulating individual particles in glassy silica sheaths. Silica surface treatments on TiO_2 pigments were once considered detrimental to gloss performance. Silica on pigment, however, comes in two distinct modifications, either "fluffy" or "dense." Fluffy silica does indeed reduce gloss and is precipitated onto pigments intended for dry-hiding paints to increase oil absorption. Dense silica is used to encapsulate the TiO_2 particle in a distinct shell and thereby make the pigment durable in severe exposure.

Special high oil absorption products are made for paints formulated for dry flat hiding, that is, above the critical pigment volume concentration. They contain fluffy coatings, 5–15 % hydrous silica and 2–6 % hydrous alumina, for better spacing and improved optical efficiency in vehicle-starved formulations. The fluffy silica increases oil absorption and water demand by the pigment. Gloss is reduced.

Slurry products for coatings applications are usually based on coated pigments. In addition to the coated product, they contain organic dispersants and stabilizers. Predispersed pigments, sold as aqueous slurries, contain from 60 to almost 80 % titanium dioxide by weight. They are stabilized with low concentrations of organic chemicals.

Odorless amines are added for *pH* control. Together with preservatives, about 1 % of organic material is present. Pigment loading in slurry products is limited by the concentration at which the slurry becomes too thick to be pumped. Slurries of lightly treated grades are available at higher solids contents than slurries of heavily treated, dry flat grades. The slurries can be shear thickening. Effects can be severe.

The pigment industry describes its products and the hydrous oxides they contain in terms of their analytical equivalents, alumina ($A1_2O_3$), silica (SiO_2), and water (H_2O) or moisture content. Such description does not imply structure or chemical characteristics of the components but reflects analytical results. The actual components of pigment coatings are hydrous oxides: boehmite (γ-AlOOH), diaspor (α-AlOOH), hydrargillite γ-$Al(OH)_3$, etc.

Product descriptions in terms of analytical results are preferred because they can be verified. By contrast, the precise structural analysis of colloidal coatings on pigment surfaces is always difficult and often beyond the capability of even the most sophisticated analytical techniques. Results are usually ambiguous. But because coatings are precipitated from aqueous solution, the alumina coatings on coated TiO_2 pigments contain structural water, i.e., they are hydrous.

Wet treatments have profound effects on dispersibility and durability. In dry hiding paints, they affect hiding through oil absorption and spacing. Brightness is not usually affected. Process details of wet treatment are guarded secrets of the TiO_2 industry. The patent literature provides little guidance because the most and least effective processes can be described by equally factual performance claims.

ELEMENTAL ANALYSIS

Chemical analysis of pigments presents no particular problems. The quality of the data meets the requirements of pigment and coatings technologies. For routine analyses, conventional, wet analytical methods, for example, ASTM D1394, Standard Test Methods for Chemical Analysis of White Titanium Pigments, have been replaced by instrumental techniques for cost savings, not data quality. Aluminum and silicon contents are usually determined by x-ray fluorescence techniques. Water content is analyzed as weight loss of volatiles by thermogravimetric analysis.

PIGMENT SURFACE

Because pigment particles are so very small, their surfaces are enormously large. 1 lb of untreated TiO_2 has a surface of about 1 acre. Thus, surface characteristics have a profound impact on a pigment's interactions with all the other components of paints. Furthermore, pigment surfaces are complex composites reflecting the nature of the commodity.

The rutile component of most TiO_2 pigments contributes up to 10 m^2/g of composite surface area. Inorganic treatments with hydrous aluminas and silicas can more than double the total surface area of a pigment. Most pigment surfaces are composites of Ti—O, Ti—OH, Al—O, and Al—OH groups. Many pigment surfaces include Si—O and Si—OH units. Silica-encapsulated grades have few if any Ti—O and Ti—OH surfaces.

The surface areas themselves are not homogeneous. Usually they are composites to which TiO_2 contributes 0–10 m^2/g $TiO_2$and 5–10 m^2/g pigment, hydrous aluminas with about 200 m^2/g $Al_2O_3 \bullet xH_2O$ and 2–8 m^2/g pigment, silicic acid with about 150 m_2/g $SiO_2 \bullet xH_2O$ and up to 10 m^2/g pigment, silica glass 5–10 m^2/g SiO_2, 5–10 m^2/g pigment, etc. The chemical and physical characteristics of the surface are specific to the component. Granted, the components share important similarities. They are all hydrophilic oxides with high-energy surfaces.

Even the surfaces of titanium dioxide crystallites themselves are not just composed of titanium and oxygen ions. In the sulfate process, while the rutile crystallites grow, insoluble components accumulate on their surfaces. Those components are either impurities present in the ore and not removed in the purification process or additives designed to control crystal structure and growth and to regulate agglomeration. This fortuitous surface is not necessarily suitable for a given end-use application; thus, crystallite surfaces are modified by treatments.

The surfaces of TiO_2 pigments are readily wetted. They are usually hydrophilic and disperse spontaneously into water. The energy of wetting is high, aiding dispersion into organic liquids. The ease of wetting of TiO_2 pigments contrasts with wetting problems of organic color pigments, most of which are hydrophobic and have a low negative free energy of wetting. Water does not wet them without the help of surfactants. Suitable organic solvents may wet organic pigments but often only sluggishly.

Since unmodified pigments tend to cake and flow poorly, they are treated with up to 0.5 % of a grinding aid, usually organic polyhydroxyl compounds, to improve dry flow. These organic materials remain on the pigment surface. Silicone treatment can be used to make dry pigment flow like sand, but the pigment becomes hydrophobic and unsuitable for most coatings applications.

SURFACE ANALYSES

Surface analysis of pigments involves three interrelated subjects: surface area, surface composition, and surface chemistry. For data interpretation, sample density data are also required. Methods and results tend to be more interesting to the scientist than the practitioner.

Instrumental surface area determinations are now routine. Nitrogen adsorption is used widely. Reliability of results is satisfactory. Data are affected by the composite character of pigments and its response to sample preparation.

The modem methods of surface analysis, Microprobe, ESCA, etc., have been used to study pigment surfaces and have yielded interesting results and valuable insights. Costs and technical complexity preclude their widespread and routine use.

Surface adsorption by pigments has been explored extensively by surface calorimetry and in terms of adsorption isotherms, etc. Ambiguities introduced by the composite character of the surfaces have their impacts.

The density of a pigment can be measured precisely and quickly by a helium densitometer. However, for fine powders of known composition, calculated densities are often more reliable than measured values. Density calculation requires knowledge of the pigment composition and the density data for the pure component oxides. It is decisively important to include in the calculation the total water content: absorbed moisture plus the structural water of the hydrous oxides.

PIGMENT PACKING

Pigment particle packing density affects paint film performance. This density is an inverse measure of interstitial volume, a reflection of the way pigment particles aggregate and agglomerate into either stringy assemblies that haystack loosely or compact clumps that pack densely.

Effects of packing density on performance are profound. Packing characteristics determine the critical pigment volume concentration of a pigment. Through the critical pigment volume concentration, pigment packing affects virtually all characteristics of paint films [3]. Fluffy pigments have a low critical pigment volume concentration; particulates that pack densely have high critical pigment volume concentrations. In effect, the critical pigment volume concentration itself is a measure of the interstitial volume of wetted pigment particles. Adsorption layers are also involved, but in most instances their contribution is minor.

Practitioners of coatings technology have long been aware of the importance of packing density. They used oil absorption of a pigment as one of its most important descriptors. Oil absorption is still used today because it reveals so much about the pigment even though linseed oil has lost its importance as a binder.

Oil absorption is primarily a measure of wet packing complicated by the involvement of adsorption layers,

dispersion work, and flocculation. The measure predates the insights of Asbeck/Van Loo into structure and performance of paint films.[17] Thus, the connection between oil absorption—the practical measure—and the scientific concept—critical pigment volume concentrations—is unnecessarily convoluted. Oil absorption of different pigments cannot be compared because the measure is based on weights, not volumes. Critical pigment volume concentration, by contrast, is based on volumes and lends itself readily to comparisons of particulates that differ in densities. At its best, when oil absorptions of similar pigments of identical densities are measured by an experienced individual who uses a standardized procedure to his personal end point, oil absorption values become a reasonably precise measure of the packing of pigment particles in oil.

For wetted particles, pigment packing is not affected much by the nature of the liquid—water, oil, or solvent—provided the particles are not flocculated. In practice, surfactants must be added or be present as a natural component of the system as they are in raw linseed oil. "Liquid absorption" values agree pretty well with each other if they are based on relative volumes of a pigment in a variety of liquids. Incidentally, oil absorption values correlate inversely with the bulk density of a given pigment. The fluffier the pigment packs in air, the more loosely it packs in liquids.

PACKING MEASURES

In spite of its many shortcomings, oil absorption is the only measure of packing that is widely accepted. The test is a titration of raw linseed oil into dry pigment powder to an end point at which the mass cakes. Two procedures are in common use: ASTM D281, Standard Test Method for Oil Absorption of Pigments by Spatula Rub-out and ASTM D1483, Standard Test Method for Oil Absorption of Pigments by Gardner-Coleman Method.

Precision of oil absorption data is poor unless one experienced individual makes all measurements in the data set. For tests by different laboratories, the spatula method has a coefficient of variation of 12 %, with 5.3 % for the Gardner-Coleman method. Data obtained by two analysts tend to differ because the end point of the titration is more difficult to define than to reproduce.

CONTAMINANTS

Extraneous metal ions within rutile crystallites can degrade pigment brightness. Nickel and chromium can be detrimental in concentrations as low as a few parts per million. Semi-conductor mechanisms are involved. Substitution of extraneous ions for Ti^{4+} in the TiO_2 lattices discolors the crystals usually toward gray or yellow. Impurities and coproducts introduced by the treatment chemicals are far less detrimental to brightness. Coproducts can, however, affect specialized performance requirements. Certain ions can, for example, inhibit cure of acid or base-catalyzed coatings or cause film defects in electrocoatings.

Purity and brightness of TiO_2 crystallites are process related. TiO_2 crystallites made by the chloride process are purer and brighter than sulfate products. The coproduct content of a pigment commodity is usually not a matter of poor operating practice but set by complex compromises between conflicting performance requirements.

TRACE ANALYSES

Trace impurities in pigments are analyzed by conventional emission spectroscopic and x-ray fluorescence methods. Results are considered reliable though not particularly precise.

COLOR

Titanium dioxide is a virtually colorless dielectric with some semiconductor characteristics due to small amounts of contaminants. Rutile absorbs in the violet end of the visible spectrum. Fig. 8 is a schematic representation of the reflectances of white, gray, and black paints pigmented with only TiO_2, with TiO_2 and carbon black, and with only carbon black, respectively. Absorption of far violet radiation imparts a slight yellow hue to large crystals. The anatase absorption edge is at a shorter wavelength than rutile, shifted almost completely into ultraviolet wavelengths. Thus, anatase crystals are slightly less yellow than rutile crystals. All this does not matter much in coatings. For high-purity pigment, dry powder color does not correlate with end use color because most polymers contribute far more yellowness than the pigment.

Pigment brightness matters less in most coatings applications than one might presume. Most coatings, even white ones, are toned, that is, their brightness is reduced intentionally by addition of carbon black or color pigments. Purity, thus brightness, is important only for white coatings that are usually not toned: Coatings for light fixtures, many coil coatings, most inks, and ink-similar paints.

Chloride process pigments are intrinsically brighter and whiter than their sulfate counterparts. Typically, chloride process pigments average 99.5 % L*[18] lightness,[19] and 98.5 % sulfate pigments.[20] The difference between chloride and sulfate pigments, an L lightness difference of 1 %, is about ten times larger than the least visible difference.

TiO_2 particle size has a significant effect on the color of tinted coatings and thin white films. Smaller particles scatter blue light more efficiently. As a result, pigment of a smaller average particle size will shade bluer both tinted coatings and white coatings at incomplete hiding. Pigment of a larger average particle size will shade redder in the same systems. Most TiO_2 grades for coating applications are neutral in this particle-size-related undertone. Products intended for very low end-use concentrations are often bluish. Red undertone pigments are not in demand.

COLOR MEASUREMENT

Color measurements of pigments are performed on dry pressed pellets. Modem spectrophotometers provide data with more than sufficient precision for most purposes of pigment quality control. Most of these instruments can

[17] Asbeck and Van Loo recognized that the characteristics of paint films involve volume rather than weight consideration, no small matter when densities of paint film components can range from 0.9 to 6 g/mL.

[18] CIELAB (Commision International de l'Eclairage, 1978) metric of lightness.

[19] Brightness/lightness of a dry pressed pigment pellet.

[20] In very first approximation, a TiO_2 pigment with an L* lightness of 98.5 % contains a three times higher concentration of colorant impurities than a pigment of 99.5 % brightness: 1.5 %/0.5 % = 3.

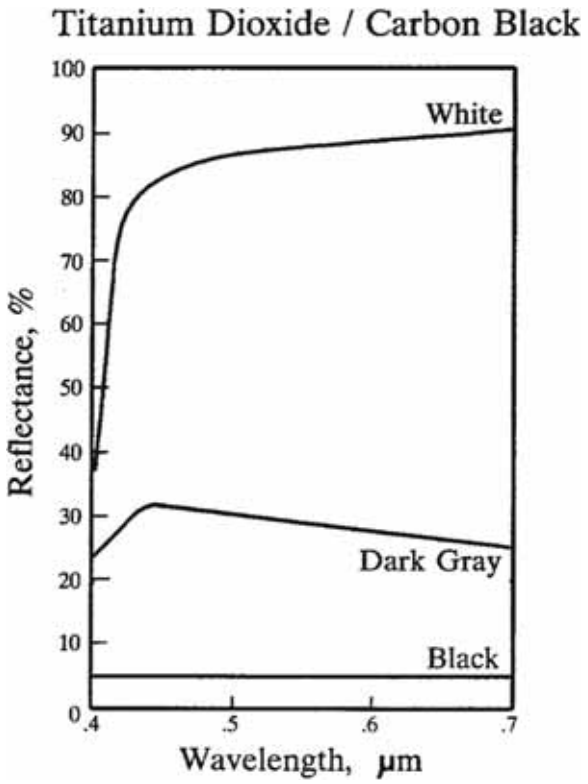

Fig. 8—Reflectance of white, gray, and black paints. From Braun, J. H., "Introduction to Pigments," Monograph in the Federation Series on Coatings Technology, Federation of Societies for Coating Technology, United States, 1993.

report their results in any of several color coordinates. The L**a***b** system[21] seems particularly well suited to describe variations on the theme of white.

HAZARDS

TiO_2 pigment is a benign chemical. Its hazards, and the relative lack thereof, are detailed in Material Safety Data Sheets that must accompany any United States shipment. TiO_2 presents no pronounced health hazards; it is neither corrosive nor acutely toxic and does not appear to be a significant carcinogen nor embryo toxin in the workplace. As a dry powder, TiO_2 can become a nuisance dust that may require control.

TiO_2 pigment cannot burn nor explode, either as a dry powder or as aqueous slurry. Neither the dry pigment nor the slurry is corrosive or reactive. The hazards of pigment dispersions in organic liquids reflect the characteristics of the dispersion liquids.

Pigment Performance

The TiO_2 industry sells light scattering for the price of TiO_2 because there is no better and cheaper way to achieve effective hiding by thin films that are white or light in color. Thus, optical effectiveness is the primary performance characteristic of the pigment. However, TiO_2 pigment is well optimized and functions near its theoretical potential. Between products developed for similar end use, light scattering differences are too small to matter or to be measured. Thus, secondary performance characteristics can be commercially decisive.

[21] CIELAB (Commision International de l'Eclairage, 1978) metric of color.

HIDING AND OPACITY

Pigment sells by weight but scatters light, that is, functions, by its volume. The particle size of TiO_2 for white pigment applications was optimized for the scattering of visible light, first experimentally, later confirmed by theory. Commercial grades perform near theoretical potential. A rutile particle of about 0.2 μm diameter is optimal for green light, the wavelengths of greatest sensitivity of the human eye.

Fig. 1 illustrates the relationship between scattering power and particle diameter. The Mie theory can specify the optimal diameter for the scattering of an electromagnetic wave by a dielectric particle with great precision, but the result is limited to single spheres. This complex and abstract theory must be translated (1) from a sphere into a real particle of elongated, angular shape, (2) from a single, isolated particle to assemblies of massive numbers, and (3) from monosize particles to particle-size distributions. The task is formidable, yet significant progress has already been made.

Fig. 9 is an illustration of the effects of pigment concentration on hiding of a paint film. At first, hiding increases in direct proportion to concentration. Then, the crowding of pigment particles causes the increase to diminish, to reach a maximum, and to decrease toward the critical pigment volume concentration. Beyond the critical pigment volume concentration, dry hiding, that is, light scattering at air/ pigment interfaces, causes hiding to increase again.

Crowding of pigment particles diminishes light scattering substantially [4] (Fig. 10). Effects become apparent at pigment volume concentrations above about 8 vol %. More than half of a pigment's scattering effectiveness can be lost between 8 vol % and the critical pigment volume concentration. A simple optical model explains the effects [5]. Improvements in pigment effectiveness achieved through control of crowding are likely to be fairly insignificant [6].

The optics within paint films are quantified by the Kubelka-Munk theory that combines for thin films the effects of light scattering (usually by white pigment) and light absorption (usually by color pigment). The model serves exceedingly well in spite of some theoretical limitations. Kubelka-Munk equations provide a basis or an explanation for most performance measurements: hiding, opacity, and tinting strength.

MEASUREMENTS OF LIGHT SCATTERING

Until recently, pigments and paint films were evaluated by visual comparisons, for example, ASTM D332, Standard Test Method for Relative Tinting Strength of White Pigments by Visual Observation. The eye was more sensitive than available instruments, and the mathematics of Kubelka-Munk was too complex for routine calculations. Two developments make quantitative evaluation of pigments more appropriate: (1) Optical instruments have become more sensitive and more reliable than the eye, and (2) the least of computers can calculate results on the spot.

Light scattering and light absorption of paint films can be quantified independently using light reflectance or transmission measurements of thin[22] films drawn over black and white substrates. In addition, film thickness or film weight and composition must be measured. ASTM

[22] Thin enough to show obvious contrast between regions drawn over black and white backgrounds but thick enough to look uniform rather than mottled.

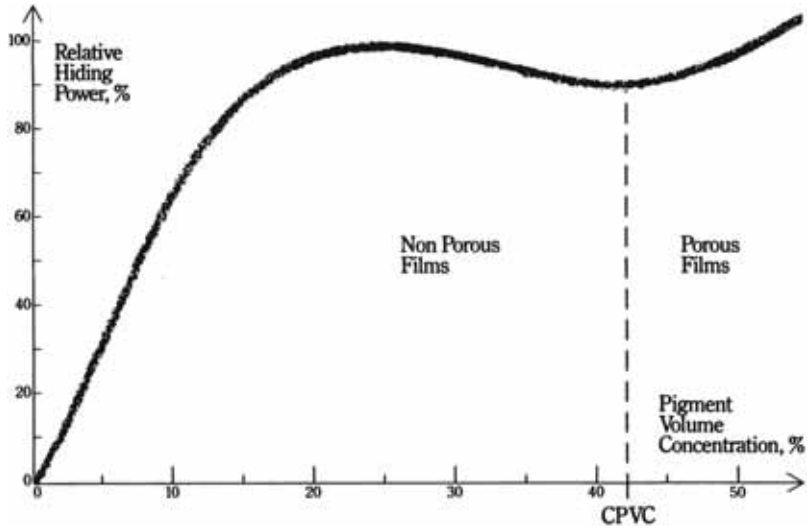

Fig. 9—Hiding power of paint films. From Braun, J. H., "Introduction to Pigments," Monograph in the Federation Series on Coatings Technology, Federation of Societies for Coating Technology, United States, 1993.

D2805, Standard Test Method for Hiding Power of Paints by Reflectometry, describes such a test.

Relatively inexpensive and very reliable spectrophotometers can measure reflectances in any specific and narrow wave band. By measurements, wave band-by-wave band across the spectrum of visible light, applicability of hiding power measurements is extended from black and white to color. Paints of different hues can be compared and results expressed separately for performances of white and color pigments. Computer programs are available for data evaluation.

Tinting strength tests, ASTM D2745, Standard Test Method for Relative Tinting Strength of White Pigments by Reflectance Measurement, measure the relative light scattering of a white pigment by overwhelming the slight intrinsic absorptions of binder and pigment with a massive absorption by a standardized addition of colorant. Measured are thick films of infinite hiding.[23] The same test serves for the evaluation of color pigment. Here, the slight intrinsic scattering of the color pigment is overpowered by the massive scattering from standardized addition of a white pigment.

Absorption of light within the paint film increases the hiding power of the film. The effect is quite pronounced, and either pigment or binder can cause it. When caused by TiO_2 pigment of low brightness, this low-purity product can get undeserved credit for a hiding power advantage over purer products. Also, off-color extenders and colored polymers can boost hiding power incidentally or deliberately. This hiding improvement comes at the expense of brightness.

DISPERSIBILITY

To make paint, dry powder has to be distributed in liquid composed of binder and solvent. The process is called dispersion or paint grinding. The ease with which a powder can be dispersed in a liquid depends primarily on its particle size. As pigments go, TiO_2 at 0.2 μm size is large and easy to disperse, almost as easy as extenders, much easier than most color pigments. For all but glossy coatings, TiO_2 can be stirred into liquids with high-speed agitators. High-gloss finishes require more powerful equipment: media, roll, or ball mills.

Dispersing a pigment involves four distinct stages during which most of the energy of grinding converts to heat:

1. *Liquid replaces air-solid interfaces with liquid-solid interfaces.* The ease of wetting depends on (a) energy characteristics of the surface of the solid and (b) the chemical affinity between solid and liquid. TiO_2's high-energy surface wets well. By contrast, the low-energy surfaces of organic color pigments wet only with difficulty.
2. *Bonds between particles are broken.* TiO_2 crystals are not broken in ordinary mills. Bonds between crystals range in strength from strong within aggregates to weak within agglomerates. Weak aggregates can be broken in the high-energy mills of pigment and plastics technologies, not, though, by equipment common in coating technology. Agglomerates break in high-speed dispersers.
3. *Particles are distributed throughout the liquid.* The more viscous the liquid, the more power that is required to mix and distribute materials and the more effective is the grind.

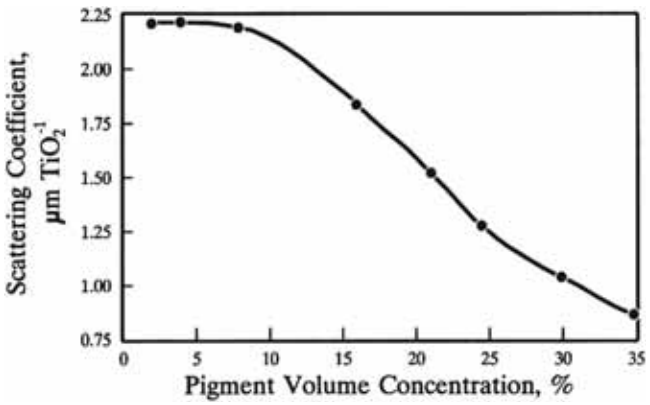

Fig. 10—Scattering coefficient of TiO_2 [4].

[23] Sufficiently thick that a further increase in thickness does not affect reflectance.

4. *The distribution of particles has to be stabilized against reversible flocculation.* Nonaqueous systems flocculate by Brownian motion and are stabilized against flocculation by surfactants that provide steric hindrance. Aqueous dispersions flocculate by (1) electrostatic attraction and by (2) Brownian collisions. They are charge stabilized by ionic dispersants.

Rheology matters decisively. When grinding in a shear-thickening rheology regime, dilatent grinding is highly effective. By contrast, shear-thinning rheology of the grind charge absorbs energy into reversible bonding, wasting much of it as heat. High viscosity helps the energy transfer from mill to particulate. Thus, other parameters equal, grinding "viscous" is more effective than grinding "thin," and grinding "well cooled" is more effective than grinding "hot."

Flocculation degrades optical performance. White pigments can lose only a moderate fraction of hiding, rarely as much as 30 %. By contrast, color pigments can lose most of their color. Excessive or inappropriate grinding does not degrade TiO_2. Optical performance does not improve with grinding because most of the pigment is dispersed very early in the grind cycle. A few parts per million of undispersed grit, however, can degrade film fineness from "excellent" to "inadequate."

MEASUREMENT OF DISPERSIBILITY

This author knows of no reliable and useful measurement of dispersibility. Granted, it is possible to use standardized procedures to establish a ranking of pigment samples against specific performance requirements. Such a ranking cannot be quantified and does not translate from one application to another. In one such scheme, paint is made by a minutely standardized, low-shear dispersion procedure. The paint is then tested for grit by one of several conventional fineness gages.

The "residual grit" aspect of dispersion is usually evaluated by fineness-of-dispersion gages, for example, ASTM D1210, Standard Test Method for Fineness of Dispersion of Pigment-Vehicle Systems by Hegman-Type Gage. The gages are shallow, tapered channels that are precision machined into steel blocks. A paint sample is scraped into the channel. The surface of the paint wedge is then examined to see at what depth the diameters of largest agglomerates exceed the depth of the channel. This point is visible as a transition from smooth to streaked paint surface.

PIGMENT EFFECTS ON PAINT FILM DURABILITY

Durability is the continuance of decorative and protective performance of paint films and their components under the influence of weathering. Lack of weathering resistance manifests itself as (1) oxidation of polymer ultimately to carbon dioxide and water, (2) discoloration and fading of color pigments, and (3) chalking of the TiO_2 with concomitant erosion and gloss loss. Instability of substrates introduces additional degradation effects.

For paint films with TiO_2, concerns involve the weathering resistance of the films themselves. Exposure to sunlight, moisture, and oxygen changes the appearance of paint films. Some films chalk and eventually erode to their substrates; others discolor and fade well before chalking becomes a problem. Degradation of coatings occurs because paint films are slowly oxidized by air. Sunlight triggers the degradation reactions. In the dark, paint films can last for centuries, even millennia. In light, durability depends on binders, pigments, and the conditions of exposure. High humidity, particularly condensation, aggravates degradation.

Only the ultraviolet radiation (UV) portion of sunlight causes degradation directly because it has energy content sufficient to break chemical bonds. The degradation of UV-A and UV-B radiation[24] is irreversible for polymers and for all organic and some inorganic pigments. A few inorganic pigments are thermodynamically stable. Titanium dioxide is stable, but UV above 3.08 eV activates its catalytic characteristics. In effect, the band gap of TiO_2 [25] is within the energy levels present in sunlight. All white pigments share some of this attribute. Extenders are stable and inert. Their band gaps are too large to be activated by the UV components of sunlight.

Titanium dioxide affects the durability of paint films in two distinct and opposing ways. (1) As a strong UV absorber, TiO_2 protects the paint film, and (2) as a UV-activated oxidation catalyst, TiO_2 degrades binders [7].

Three characteristics of TiO_2 are functionally disparate but are manifestations of a single fundamental characteristic of dielectric matter: (1) its unique refractive index, which makes TiO_2 the best white pigment, (2) its extreme UV absorptivity, and (3) UV catalytic activity of the TiO_2 surface.

Radiation of more than 3.08 eV, water, and oxygen are all essential for the TiO_2-catalyzed degradation of binder. Their reactions combine into a cycle that generates two free radicals from each active UV photon [8].

$$H_2O + O_2 + h\nu_{(UV)} \rightarrow \cdot OH + \cdot HO_2 \text{ (in presence of } TiO_2)$$

The hydroxyl and peroxyl free radicals are highly reactive agents that oxidize and thus degrade essentially any organic polymer:

$$2 \cdot HO + 2 \cdot HO_2 + CH_4 \rightarrow CO_2 + 4H_2O$$

The chain of chalking events is cyclic with respect to TiO_2, and it can be disrupted by exclusion of either UV, water, or oxygen.

DURABILITY CONTROL

The TiO_2 industry inhibits the catalytic activity of the TiO_2 surface and improves the weathering resistance of its products by encapsulation in amorphous silica. The shell that forms is a true silica glass precipitated from aqueous solution by technology invented by DuPont in the 1960s [9]. Encapsulation of TiO_2 made it practical to paint automobiles in white and bright colors. Meanwhile, binders were improved so that less effective deactivation of the TiO_2's

[24] UV-A is the UV wavelength region near to visible radiation or light, UV-B is the medium UV region, and UV-C is the far (shortest wavelength) UV light. Sunlight contains little UV-B and essentially no UV-C.

[25] The band gap is the "forbidden" energy gap between the valence band and the conduction band of a semiconductor. In the language of physics: "UV radiation induces semiconductor characteristics in TiO2;" in the language of chemistry: "UV radiation reduces colorless TiO_2 to black Ti_2O_3."

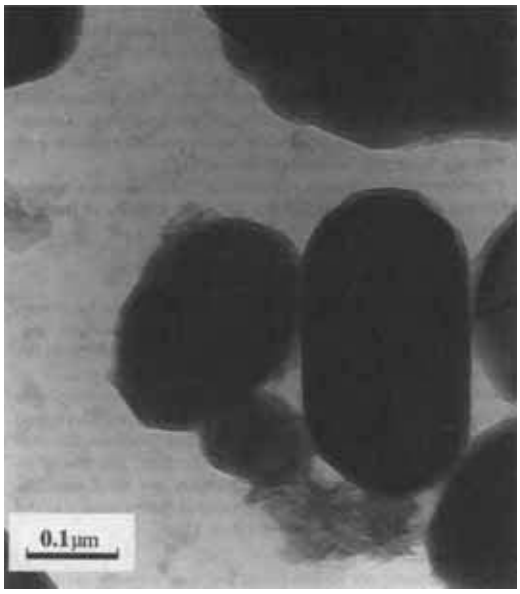

Fig. 11—Encapsulated TiO_2 pigment.

catalytic activity suffices and provides satisfactory performance of automotive finishes in temperate climates.

The SiO_2 glass prevents contact between the catalytic surface of rutile and the organic vehicle and provides a surface for recombination of free radicals. Fig. 11 is a depiction of superdurable pigment particles. Their silica sheaths are barely visible on the transmission electron micrograph. The silica sheaths themselves, after the TiO_2 was dissolved out, are shown in the transmission electron micrographs of Fig. 12. Even the holes are visible through which the rutile cores were dissolved.

Intermediate levels of weathering resistance are attained by partial encapsulation of the rutile in silica and/or alumina with or without zirconia and by bulky coatings of hydrous aluminum and silicon oxides on rutile.

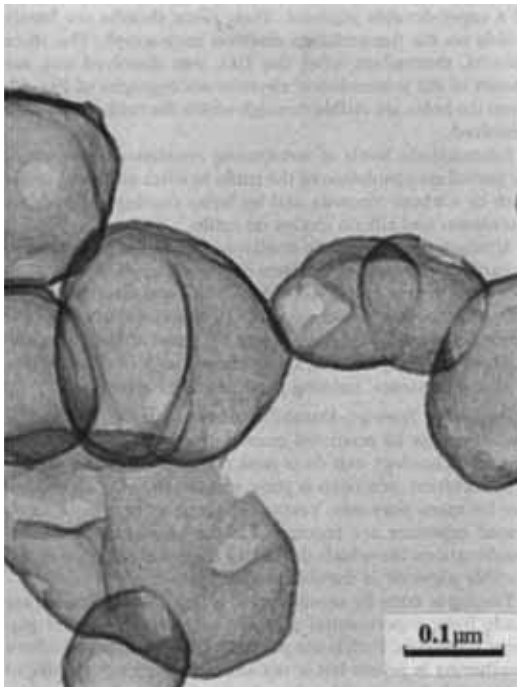

Fig. 12—Silica shells from encapsulated pigment.

Alternate approaches to chalking control are less effective or cause performance problems in coating applications. They involve attempts to (1) recombine holes and electrons at the TiO_2 surface by semiconductor mechanisms whereby the products are slightly yellow and (2) prevent the hydroxylation of the TiO_2 surface, i.e., interfere with one step of the chalking sequence, causing products to be gritty.

DURABILITY TESTING

Durability of coatings can neither be measured nor be predicted quantitatively. The best state-of-the-art technology can do is rank coatings. Costs per sample are exorbitant, precision is poor, and the time lag is prohibitive for many purposes. Years of outdoor or months of accelerated exposure are required for the pigment and binder combinations for which durability is important to yield useful information, that is, for durable pigment in durable binder.

Testing is done by simulation of a "real" world. Paints are made from experimental pigment and usually several pigment standards. Panels are painted. They are exposed where weathering is severe but is not necessarily representative of the intended application. Certain appearance characteristics are regularly measured and often chalk, color, gloss, etc., are noted. Finally, data are reduced, correlated, and compared. Reproducibility is barely sufficient to tell an interior grade pigment from a durable grade without testing replicates. Experimental durability differences within grades are not generally detectable [10].

Results from one binder system cannot be extrapolated quantitatively to binders involving different polymer chemistry, nor can a single acceleration factor predict outdoor performance from accelerated exposures [11]. Pigment manufacturers supplement their exposure testing by science-based analyses of the catalytic activity of the pigment.

PIGMENT EFFECTS ON GLOSS

Powders do not have a gloss; only surfaces can be glossy. Within surfaces, particulates affect gloss, for example, pigments in paint films. They are detrimental, particularly to the dimension of gloss perceived by the human eye. Naturally glossy surfaces occur on liquids and amorphous solids.[26] Particulates in paint film, pigments, extenders, and some additives reduce gloss because they roughen the film surface. The more particulate there is in the film, the lower its gloss. Clear paint films are glossy if they are sufficiently thick. Thin films can telegraph the roughness of the substrate to the surface of the paint film, reducing its gloss.

Since the volume concentration of white pigments in paint films must be much higher for hiding than the concentration of color pigments and blacks, the burden of improvement falls on TiO_2 producers. They have increased gloss performance for grades that serve the automotive and industrial markets.

Gloss matters are complicated because a fundamental difference exists between the measured gloss that guides

[26] Single crystals are an exception, but their surfaces are generally small. Glass is an amorphous solid. Polished surfaces are not "natural." Incidentally, only liquids, amorphous solids, and single crystals can be transparent.

coatings formulation and the perceived gloss that sells automobiles [1]. These two operational definitions of gloss, one based on instrumental measurement of an intensity of image and the other on the human perception of a distinctness of image, differ profoundly in substance. However, they correlate well enough to guide quality control and pigment development by incremental improvement. The fundamental difference between measured and perceived gloss can, however, misdirect the strategy of product development, for example, a development strategy focus on increasing refractive index. A mechanism by which pigment causes the surface roughness that degrades gloss explains [1] that pigments diminish gloss by an interplay between the surface tension of the wet film with the compressive strength of a particulate bed and a gel structure that develops within the film while it cures. While the film is fluid, surface tension maintains the surface at a molecular smoothness that results in "perfect" intensity-of-image gloss. As the film dries, the structure within the wet film strengthens until it overcomes the surface tension that maintains gloss. Shrinkage of the partially cured film continues, but now shrinkage becomes uneven on a microscopic scale because only the binder/solvent combination, not the pigment, shrinks. Thus, micro-roughness develops and diminishes gloss.

GLOSS MEASUREMENT

Gloss measurement has long been routine, and one technique is described in ASTM D523, Standard Test Method for Specular Gloss. Many conventional gloss meters are on the market. Most perform well for coatings pigmented with white and color pigments.[27] They come with measuring heads for three specular angles, generally 20°, 60°, and 85°. High-gloss surfaces are best measured at low (20° specular angle), medium glosses at medium angle, and matte surfaces at grazing angle, 85°. The selection of the proper specular angle improves instrumental precision.

The conventional gloss meters measure the intensity of light reflected by a surface, the intensity-of-image component of gloss. The human eye, by contrast, perceives the distinctness-of-image[28] component of gloss. Thus, haze and so-called distinctness-of-image data are used to supplement the conventional gloss measurements.

COMPATIBILITY

Usually, TiO_2 is used in combination with other pigments. Interactions between pigments can occur and are detrimental to performance. Often, hiding is decreased, color strength is lost, and chroma is reduced; occasionally, the hue shifts slightly.

Most interaction problems involve surface chemistry. The immediate cause of the problem is flocculation. Either the white or one of the color pigments has flocculated. Almost inevitably, the color pigment is at fault.

Most color pigments enter the market as toners, lakes, or dispersions, that is, complex composites that can contain more surfactants and modifiers than colorant. These additives are chemically reactive and can interact detrimentally with the surfactants or additives of the paint formula. Dry TiO_2 pigments,[29] by contrast, contain no surfactants and are inert and chemically less complex with far fewer possibilities of adverse interactions.

Chemical interactions between pigments are problems of the past caused by reactive pigments. White lead, for example, was incompatible with TiO_2 because UV exposure could cause gross, though temporary, discoloration. Few modern pigments are susceptible to these problems.

Problems between TiO_2 pigment and polymers or additives do, however, occur occasionally because many paint films contain much higher concentrations of TiO_2 than of additives or of color pigments. Components of TiO_2 pigment can thus have significant leverage even if present in relatively small concentrations on the pigment. Problems are usually quite specific to the paint formula. Several such problems have been recognized and are resolved through specialized TiO_2 grades made, for example, for electrocoating primers and for acid-catalyzed paints.

Product Types

ASTM D476, Standard Classification for Dry Pigmentary Titanium Dioxide Products, distinguishes four types of TiO_2 pigments (Table 2)—one anatase type and three rutile types: interior, exterior, and pigment for paints formulated above the critical pigment volume concentration. The standard was formulated in 1939 with two classes of pigments. In the years since, the design of pigments has progressed to where the coatings industry can now select the most suitable pigment grade for a specific application from far more than two or four TiO_2 types. Granted, a single TiO_2 grade could serve diverse needs but would do so only moderately well. Optimal performance in any application demands specialized pigment grades that satisfy specific requirements of optics, surface chemistry, and dispersion technology. Some of these requirements can be met only through compromise.

The diversity of products can be described in terms of four specific performance dimensions such as durability, gloss, dispersibility, and undertone. Then there are products aimed at specific applications such as enamel paints, dry hiding paints, pigment slurries, acid-catalyzed coatings, electrocoated primers, etc. Finally, pigment grades are designed for the specific requirements of whole industries such as coatings, plastics, paper, and ink.

These are the products designed to specific performance dimensions in coatings.

- *Durability: Interior—Exterior—Severe Exposure.* Interior grades are unfit for exterior applications except when used underneath top coatings that absorb all radiation with wavelengths below 400 nm. All-purpose pigments are exterior durable in appropriately durable vehicles at moderate severity of exposure and for moderate appearance requirements. Severe exposure grades are intended for satisfactory performance including high gloss at exceptionally severe conditions, for example, at the horizontal position in the humid subtropics. Durability must be manufactured into the pigment surface.
- *Gloss: Conventional—Flashy.* Conventional pigments satisfy the gloss requirements of most architectural and

[27] For coatings that contain flake pigments, the interpretation of angle-dependent reflectance measurements is complicated.

[28] The distinctness-of-image instrument is really an intensity-of-image meter sensitized toward distinctness of image.

[29] Slurry grades do contain some organic surfactant.

TABLE 2—Excerpt from ASTM D476: Specification for titanium dioxide pigments				
	Type 1	**Type II**	**Type III**	**Type IV**
	Anatase Free Chalking	Rutile Medium Chalk Resistant	Rutile Medium Chalk Resistant	Rutile Highly Chalk Resistant
Typical application	White exterior house paint, interior use	Low-medium PVC enamels and lacquers	Medium-high PVC enamels; alkyd and emulsion flat wall paints	Highly chalk-resistant exterior coatings requiring excellent durability and gloss retention
TiO_2, min.%	94	92	80	80

trade-sales applications and of many industrial coatings. High-gloss pigments are aimed at automotive and some flashy industrial finishes. High-gloss applications call for pigments of small agglomerate size and low oil absorption.

- *Dispersibility: Conventional—Low Shear.* Conventional pigments are designed to be dispersed by equipment developing moderate to high shear:[30] media mills, ball mills, roller mills, and high-speed dissolvers at low rates of throughput. Special pigments are available for low-shear, high-rate dispersion by high-speed dissolvers and for stir-in with screening. Dispersibility is promoted by surface treatments at some detriment to gloss. Unlike many color pigments, TiO_2 pigments are sufficiently dispersible to not require predispersion.
- *Undertone: Neutral—Blue.* In coatings applications, the undertone of the pigment, blue, neutral, or red, is rarely an issue. Thus, most coating grades have a neutral undertone. Blue undertone pigments are preferred in applications at very low pigment volume concentration. Red undertone pigments do not appear to be in demand. Undertone is affected by pigment volume concentration and controlled by the size of the primary TiO_2 particle, small for blue, intermediate for neutral, and large for red.

There are also specific coatings applications addressed by special product designs.

- *Grades intended for coatings below the critical pigment volume concentration.* Most TiO_2 pigments, conventional interior and exterior grades, conventional and high-gloss products, conventional and low-shear dispersible pigments, the neutral and blue undertone pigments, are all suitable for applications below the critical pigment volume concentration.
- *Grades intended for applications above the critical pigment volume concentration.* Heavily treated, low-gloss products perform better in dry-hiding paints than grades made for high and moderate gloss. In effect, the pigment contains its own, exceptionally effective ex tender.
- *Slurries intended for waterborne paints.* Aqueous slurries are suited only for waterborne applications. The costs of dispersion operations are borne by pigment manufacturers. For medium- and large-scale operations, savings from the elimination of a process step outweigh the costs of slurry-handling facilities.
- Other specialized grades are made as opportunities are recognized and solutions developed.

[30] High shear within coatings technology. The plastics industry uses several more powerful mills.

Finally, specific products targeted for industries other than coatings.

- *Plastics.* Plastics are pigmented by products most of which are optimized for performance at PVCs of less than 1 vol %. Durability and dry-flow characteristics can be important to the plastics industry. High-gloss and low-shear dispersibility are usually not required.
- *Paper.* The wet-end stage of papermaking uses aqueous slurries. Slurry handling and optics are important: Low-shear dispersibility, high gloss, and durability are irrelevant.
- *Ink.* Inks require pigments that are high in gloss. Compatibility with a wide range of solvents and vehicles is often an important factor.
- *Miscellaneous end uses.* Pigmentary applications (floor coverings, elastomers, roofing granules, fibers, fabrics, sealants, food additives, etc.) and nonpigmentary applications where pigment is used for its TiO_2 content (ceramics, welding rods, etc.) or as a low-cost, mono-disperse particulate (for example, as catalyst support).

Also, the same products can be packaged in different ways, bag, semibulk, or bulk, or analyzed for special purposes, for example, food additive purity. Each such product may enter commerce under its own grade designation.

The wrong grade of TiO_2 pigment for any specific application will still be inert, white, and will hide well. But, the inappropriate pigment will fall short of expectations on secondary performance characteristics such as durability, gloss, or rheology. This is in marked contrast to most color pigments, where a grade inappropriate to an application is likely to fail grossly.

Matters of pigment classification are complicated by interactions among requirements.

1. Certain requirements are mutually exclusive. For example, aqueous pigment slurries are obviously suitable only for waterborne applications.
2. Some industry requirements overlap. Paper coatings resemble dry hiding paints and are served by similar products.
3. Optimal performance in one dimension can come at the expense of performance in another dimension. Flashy gloss can be attained only at the expense of pigment characteristics that promote stir-in dispersibility.
4. Premium performance can require additional process steps, increasing the cost of manufacture. Pigments for severe exposure and grades for flashy finishes are sold at a premium because they are more expensive to make.
5. Identical performance objectives can be achieved by different product designs.

TABLE 3—Commercial TiO_2 pigment grades

Product Type	Intended PVC[a]	Intended Gloss	Intended Exposure	Pigment Delivery	Intended Dispersion
1	Low[b]	Flashy[c]	Indoors	Dry	High Shear[d]
2	Low[b]	Flashy[c]	Indoors	Slurry[e]	Dispersed
3	Low[b]	Flashy[c]	Outdoors	Dry	High Shear[d]
4	Low[b]	Flashy[c]	Outdoors	Slurry[e]	Dispersed
5	Low[b]	Flashy[c]	Extreme[f]	Dry	High Shear[d]
6	Low[b]	Flashy[c]	Extreme[f]	Slurry[e]	Dispersed
7	Low[b]	Discreet[g]	Extreme[f]	Dry	Low Shear[h,i,j]
8	Low[b]	Discreet[g]	Extreme[f]	Slurry[e]	Dispersed
9	Low[b]	Discreet[g]	Extreme[f]	Dry	Low Shear[h,i,j]
10	Low[b]	Discreet[g]	Extreme[f]	Slurry[e]	Dispersed
11	Low[b]	Discreet[g]	Extreme[f]	Dry	Low Shear[h,i,j]
12	Low[b]	Discreet[g]	Extreme[f]	Slurry[e]	Dispersed
13	High[k]	Discreet[g]	Indoors[l]	Dry	Low Shear[h,i,j]
14	High[k]	Discreet[g]	Indoors[l]	Slurry[e]	Dispersed

[a]Pigment volume concentration, pigments plus extenders, in the paint film.
[b]Always below the critical pigment volume concentration.
[c]Application for which gloss is maximized at direct or indirect expense.
[d]Media mills and the like at moderate or low throughput, optimized mill base.
[e]Aqueous slurries.
[f]Including horizontal exposure to tropical and subtropical levels of ultraviolet radiation.
[g]Gloss levels from flat through semi-gloss to high gloss but excluding extremely high gloss.
[h]High shear is generally not required for less than extremes levels of gloss.
[i]High speed dispersers and the like.
[j]The film qualities of low-shear dispersion are generally not satisfactory for flashy finishes.
[k]Above the critical particulate volume concentration.
[l]Coatings above the critical pigment volume concentration are usually not suited for outdoors.

Nevertheless, I have attempted classification of state-of-the-art products in terms of six performance parameters and intended applications: concentration, gloss level, exposure, optics, slurry, and dispersion. Permutations of these requirements make for 72 potential product niches for coatings applications alone. Commercial products occupy 14 of the niches. They are shown in Table 3. All major manufacturers sell at least several of these products as specific grades or by equivalent subclassifications within grades.

About two-thirds of the potential product niches appear to serve no practical purpose. For example, aqueous pigment slurries are not suited for solvent-based paints, and high-PVC paint films are not made to have flashy gloss. Obviously, the multiplicity of grades creates costs and incentives for the development of universal grades. Lately some of these attempts have been partially successful, and a few "universal" products have appeared on the market. Conspicuously absent from this table are anatase pigments. They and the extended TiO_2 grades that used to dominate TiO_2 markets are no longer used in coatings.

OTHER WHITE PIGMENTS

In coatings, only void hiding competes with TiO_2. The classic white pigments—lithopone, zinc sulfide, zinc oxide, and white lead—are far less cost effective. White lead is also too toxic. Pigmentary zinc oxide is still being used in paint, not as a white pigment but as a mildewstat.

Extenders—colorless ground minerals and precipitated particulates—are sometimes described as pigments and are advocated as supplements for true white pigments.[31] Extenders are formulated into coatings to reduce costs by replacing expensive polymer with cheaper mineral. Below the critical pigment volume concentration, that is, in films with excess polymer, extenders do not scatter light because their refractive indices are too low. In films with excess particulates (films above their critical pigment volume concentration), extenders hide indirectly by creating pores. Only in very porous films do extenders scatter light at the particulate/air interface.

In colonial times, calcium carbonate ($CaCO_3$) was used as a white pigment. The pigment was made *in situ* by the reaction of atmospheric carbon dioxide with "whitewash," a brushed-on slurry of calcium hydroxide. The pigment was held together by minimal amounts of binder. Light was scattered at the $CaCO_3$/air interface. Because the service life of the coating was minimal, whitewashing ceased when wages increased with industrialization.

[31] They do not "impart black or white or a color to other materials," thus they do not meet Webster's definition of a pigment.

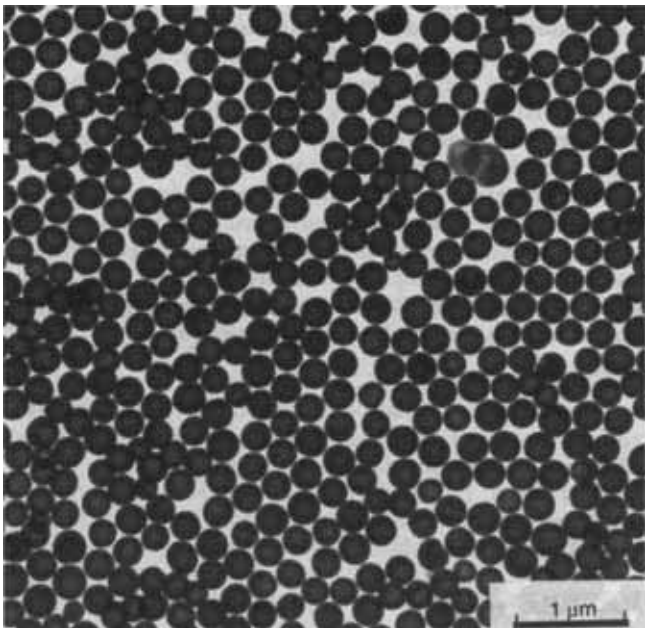

Fig. 13—Rhopaque®. From Braun, J. H., "Introduction to Pigments," Monograph in the Federation Series on Coatings Technology, Federation of Societies for Coating Technology, United States, 1993.

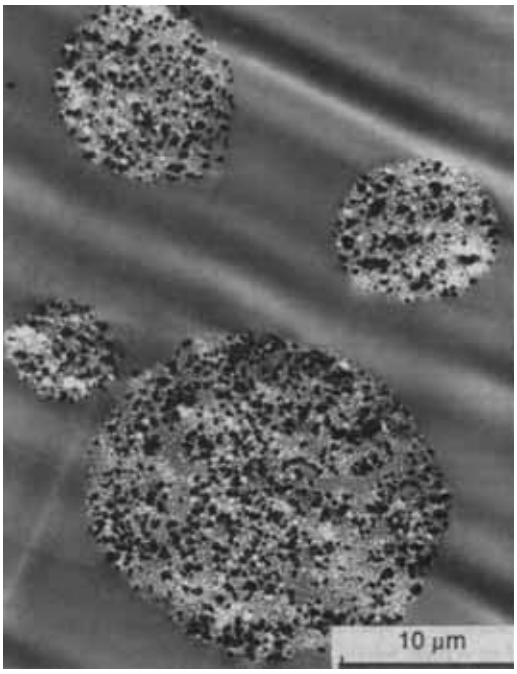

Fig. 14—Vesiculated beads. From Braun, J. H., "Introduction to Pigments," Monograph in the Federation Series on Coatings Technology, Federation of Societies for Coating Technology, United States, 1993.

Void Pigments

Air-filled voids in a paint film can either act as if they were pigment particles or enhance the effectiveness of a true pigment. Both mechanisms have been implemented in coatings.

Pigmentary and subpigmentary voids contribute to hiding of all dry hiding paints films, that is, films starved of binder. Somewhere above the critical pigment volume concentration voids join into an interconnected network of pores. The pores become stress concentrators that degrade the mechanical qualities of the paint film. The network conducts chemical contaminants into the paint film and to the substrate, diminishing the chemical and protective qualities of the film.

It is through the creation of pores that extenders contribute to light scattering. This scattering comes at the expense of film qualities. Problems can be avoided if the voids are sealed and spherical.

Voids of pigmentary size scatter light like particles, about as effectively as pigmentary zinc sulfide but not nearly as well as TiO_2 pigment. Unlike interconnected pores that degrade paint films, sealed spherical voids are not, *per se,* detrimental to mechanical and chemical film qualities.

One commercial product, Rhopaque® (Fig. 13), generates sealed, spherical air voids in paint films from plastic beads that have one concentric void. The beads are added to the paint as an aqueous dispersion of water-filled resin balloons that lose their water as the film dries. These voids are protected by the thickness of their own plastic shells from the crowding that diminishes the scattering effectiveness of conventional white pigment. Their direct light scattering effectiveness is only 12 % of scattering by the same volume of rutile. Immunity to crowding increases the effective light scattering of voids.

Another, less-successful product, Pittment®, generated pigment-sized air voids in paint films by evaporation of droplets of an organic solvent emulsified in the paint. If the voids are of subpigmentary size, small enough to lose their individual optical identity, they do not scatter much light but collectively decrease the refractive index of the matrix. A composite refractive index of polymer and air takes the place of the index of polymer alone. This decrease of matrix refractive index has a potent effect on the scattering of any true pigment present in the paint film.

A product composed of vesiculated and pigmented polymer beads makes use of this effect. The product, Spindrift® (Fig. 14), is suitable only for low-sheen paints because the beads act as a flatting agent. They have to be larger than TiO_2 particles because each bead has to accommodate several pigment particles plus voids and some binder.

A third approach to void hiding, the use of stretched foam, is very efficient. Hiding can be achieved without any pigment with less polymer on the substrate than by any conventional paint. But foam coatings are pressure sensitive.

They are too sensitive for paint applications but are suitable for opacification of textiles, curtain fabrics in particular.

ACKNOWLEDGMENTS

I am indebted to my former colleagues for advice, counsel, and the insights I developed during my career in DuPont's white and color pigments businesses. Special thanks go to A. Baidins and R. E. Marganski, my co-authors in a literature review of TiO_2 technology, and to D. A. Holtzen and R. C. Craft-Tulloch, who helped review and revise the manuscript.

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Black Pigments

Frank R. Spinelli[1,2]

BLACK PIGMENTS FALL INTO THREE CLASSES [1] as described in Table 1. The first two classes derive their color characteristics from the element carbon, the third class from ferrous oxide, Fe_3O_4. Class 1 blacks are carbon blacks that are composed of 90 % or more elemental carbon. Class 2 blacks may be referred to as "carbonaceous pigments" and these contain from 8 % to 88 % elemental carbon.

CARBONACEOUS PIGMENTS (CLASS 2)

This class of blacks, perhaps the least important for paints and coatings, is composed of two main types, mineral blacks and bone blacks.

Mineral Blacks

Mineral blacks are finely ground derivatives of coal and shale, and they are mixtures of carbon, aluminum silicates, silica, and iron oxides. They can be characterized as having poor jetness (see later description), very low tinting strength, low oil absorption, very brown undertone, and poor dispersibility. Consequently, they are rarely used in the paint industry.

Bone Blacks

Bone blacks are made by the destructive distillation of solvent-extracted cattle and sheep bones and contain only from 8 % to 17 % carbon with the remainder of the composition mostly calcium phosphate. During the "calcination," thermal treatment for 8 h at 800°C, the organic matter is decomposed and the resulting carbon forms a thin, porous film on the surface of the mineral network, creating a large carbon surface area per unit of weight. Consequently, bone blacks have high color and great adsorptive ability, but they have very weak tinting strength. Oil absorption is quite low, and aqueous dispersibility is excellent. Bone blacks are used only in specialty finishes where high color with low oil absorption is essential.

IRON OXIDE BLACKS (CLASS 3)

Naturally occurring as the mineral magnetite, iron oxide blacks are synthesized by reacting ferrous sulfate, $FeSO_4$, with alkali and then oxidizing to ferrous oxide, Fe_3O_4 (black magnetic oxide). Having the highest density of the black pigments as well as excellent light fastness and chemical resistance, these blacks are chiefly used in the paint industry in metal-protective primers. It should be noted that black iron oxide, Fe_3O_4, will oxidize at high temperatures to red or brown ferric oxide, Fe_2O_3. Iron oxide blacks have very poor color and strength properties compared to carbon blacks.

CARBON BLACKS (CLASS 1)

Carbon black is the most important black pigment for paints and coatings. This unique, strictly manmade material offers great versatility in end use performance. Through variation in key properties, by careful control of manufacturing conditions, a broad range of grades is commercially available. To provide a better understanding of carbon black as a pigment in paints and coatings, the effects of carbon black property variations on its optical functioning in dispersed media are herein defined. This involves some discussion of how carbon black is formed as well as identification of its key parameters. Following is an elucidation of the mechanisms of carbon black's optical function and how they are influenced by variations in each of the key parameters. Based on this knowledge, certain guidelines for selection of a grade of carbon black are enumerated. As a corollary, the subjects of achieving optimal quality dispersion and its importance to end use performance are addressed. Finally, techniques for measurement of carbon black coating's optical performance properties are outlined with reference to the appropriate ASTM tests where applicable.

Carbon Black Optical Function

GENERAL NATURE OF CARBON BLACK

1. *Principles of formation*—The formation of carbon black requires the application of thermal energy to a hydrocarbon, usually by incomplete combustion (limited oxygen supply), which results in the rupture of C—H bonds [2]. This first stage is often called "cracking" [Fig. 1(a)]. The reaction products are aromatic radicals and dicarbon radicals, highly reactive species, which combine to form hexagonal lattices in a planar configuration. Several "layer planes" then tend to stack and form crystallites [Fig. 1(b)]. These crystallites tend to form spherical prime particles that continue to grow, forming primary aggregates that are the characteristic units of carbon black (Fig. 2). Both prime particle and primary aggregate distributions are typically broad since a great number of layer planes and crystallites are going through the described processes, but not in phase. Those particles and aggregates that began formation earlier in the process have longer growth times and would be larger in character. By choice of hydrocarbon feedstock and careful control of reaction conditions, the key properties of prime particle

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[2] *This chapter is from the previous edition. The ASTM documents have been updated and increased in number through a table that has specifications and test methods of interest. In certain cases the editor has added small amounts of information.*

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TABLE 1—Classification of Black Pigments [1]

Type	Source	ASTM Specification[a]	Color Index; Name
Class 1—Carbon Blacks			
(a) Furnace	Oil	. . .	. . .
(b) Channel	Gas	D561	77226; Pigment Black 7
(c) Lamp	Oil	D209	77226; Pigment Black 7
(d) Thermal	Gas and Oil	. . .	. . .
(e) Acetylene	Gas	. . .	. . .
Class 2—Carbonaceous			
(a) Mineral	Coal	. . .	
(b) Bone	Bones	D210	77267; Pigment Black 9
Class 3—Iron Oxides			
(a) Synthetic	Chemical Reaction	D769	77499; Pigment Black 6
(b) Natural	Magnetite Ore	D3872	77499; Pigment Black 6

[a]ASTM D561, Standard Specification for Carbon Black Pigment for Paint.
ASTM D209, Standard Specification for Lampblack Pigment.
ASTM D210, Standard Specification for Bone Pigment.
ASTM D769, Standard Specification for Black Synthetic Iron Oxide.
ASTM D3872. Standard Test Method for Ferrous Iron in Iron Oxide.

size, primary aggregate size, porosity, structure, and surface chemistry are varied to create the spectrum of commercial carbon blacks.

2. *Types/processes* [3]—There are five types of industrial carbons that fall in the general category of carbon black. Included are lampblack, channel black, furnace black, thermal black, and acetylene black. Each of these is made by a different process and, consequently, has certain unique properties (Table 2).

Lampblack Process: Oils or resins are burned in shallow pans in an enclosure with a restricted air supply, and the smoke is passed through settling chambers prior to venting. Carbon black deposited on the cool walls of the chambers is subsequently scraped off by motor-driven ploughs. The principal feedstocks are coal tars or petroleum residual oils. Lampblack's major usage in the coatings industry is as a tinting pigment. It exhibits excellent antiflocculation properties and an extremely blue undertone. Although lampblacks have been replaced by furnace blacks to some extent on a tinting strength basis, substantial quantities are still produced for special applications.

Channel Process: Until about 1975, this process was the leading source of carbon blacks for the coatings industry. Its demise was brought about by two principal factors: (1) the escalating cost of natural gas and (2) the increasing stringency of air pollution regulations.

The process (Fig. 3) involves partial burning of natural gas with insufficient air. Small fan-shaped flames from gas burner tips (2,000 or more) are housed in sheet metal buildings or "hot houses" and are arranged so that they impinge

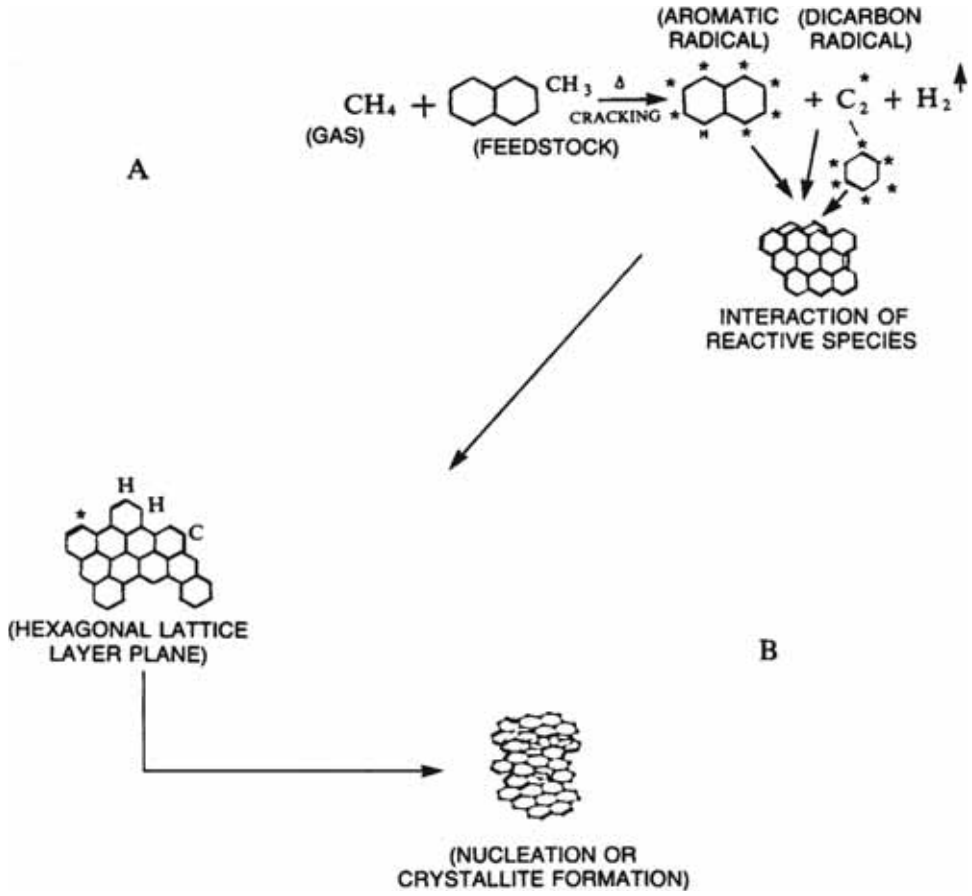

Fig. 1—Formation of carbon black. Asterisks indicate active sites.

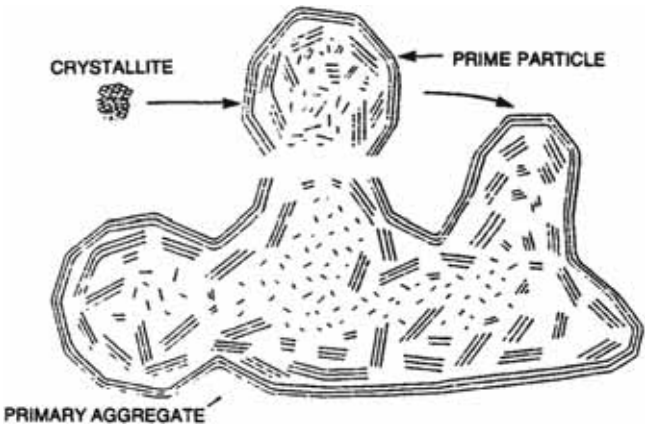

Fig. 2—Growth to particles and aggregates

on channel irons suspended above hoppers. Using scrapers and a reciprocating action of the channel irons, the deposited carbon is collected in the hoppers and passed through a collection system. Yields are characteristically very low, reaching a maximum of about 5 % with the coarser grades. This process can produce carbon blacks with particle sizes ranging from about 30 nm to less than 10 nm. The resultant blacks typically have higher volatile contents (chemisorbed oxygen complexes on the surface) because of the presence of oxygen during formation than other blacks. Though channel blacks have virtually disappeared from industry, a variant called "roller process blacks," made from feedstocks other than natural gas, are still produced in limited quantities in Germany.

Furnace Process Blacks: These products are made by partial combustion of a hydrocarbon in a closed reactor (or furnace) under well-defined conditions. The precursors of modern oil furnace blacks were the gas furnace blacks, which are no longer produced.

Oil Furnace Process: A hot flame is first created by burning gas with air inside a closed furnace, and then a liquid hydrocarbon is atomized into the hot flame zone. Furnace designs and reactor configurations vary considerably, but the principle is the same [Fig. 4(*a*) and (*b*)]. The feedstock is usually a medium molecular weight aromatic oil that must be heated to 200–250°C to have sufficient fluidity for processing. Yields are high (30 %–60 %), air pollution is virtually nil, and it offers superior process control capability. Blacks ranging in prime particle size from 100 nm down to about 10 nm, with variations in structure level (degree of aggregation of prime particles), can be produced by varying furnace conditions, feedstock properties, residence time in the hot zone, and quench distances (how far downstream the cooling sprays are introduced into the furnace).

Oil Furnace Carbon Blacks: These pigment blacks essentially satisfy all requirements of industrial blacks and account for 95 % of all the carbon black produced today.

Thermal Cracking or Thermal Decomposition: This category of carbon black processes uses thermal cracking or thermal decomposition of a gaseous hydrocarbon in the absence of flame. This includes thermal blacks and acetylene blacks, which are not used in the coatings industry.

MECHANISMS OF INTERACTION WITH LIGHT [4]

Since coatings vehicles are usually transparent polymer-containing solutions, the function of a pigment in rendering

TABLE 2—Typical analysis of carbon black grades from five different processes. Note: Adapted from data in Encyclopedia of Chemical Technology, Volume 4, 3rd ed.

Property	Type Black, Symbol, ASTM D3053-08b, "Standard Terminology Relating to Carbon Black"					
	Furnace; HAF; N-330	Thermal; MT; N-990	Thermal; FT; N-880	Acetylene; —;—-	Channel; EPC; S300	Lampblack; Lb;—-
Average particle diameter, nm	28	500	180	40	28	65
Surface area (BET) m^2/g	75	47	13	65	115	22
DBPA,[a] ml/100 g	103	36	33	250	100	130
Tinting strength,[b] % SRF[c]	210	35	65	108	180	90
Benzene extract, %	0.06	0.3	0.8	0.1	0.00	0.2
pH	7.5	8.5	9.0	4.8	3.8	3.0
Volatile material, %	1.0	0.5	0.5	0.3	5	1.5
Ash, %	0.4	0.3	0.1	0.0	0.02	0.02
Composition						
% Carbon	97.9	99.3	99.2	99.7	95.6	98
% Hydrogen	0.4	0.3	0.5	0.1	0.6	0.2
% Sulfur	0.6	0.01	0.01	0.02	0.20	0.8
% Oxygen	0.7	0.1	0.3	0.2	3.4	0.8

[a] *n*-dibutyl phthalate [see ASTM D2414-09, "Standard Test Method for Carbon Black—Oil Absorption Number (OAN)"].
[b] See ASTM D3265-07, "Standard Test Method for Carbon Black-Tint Strength."
[c] SRF is semi-reinforcing furnace black.

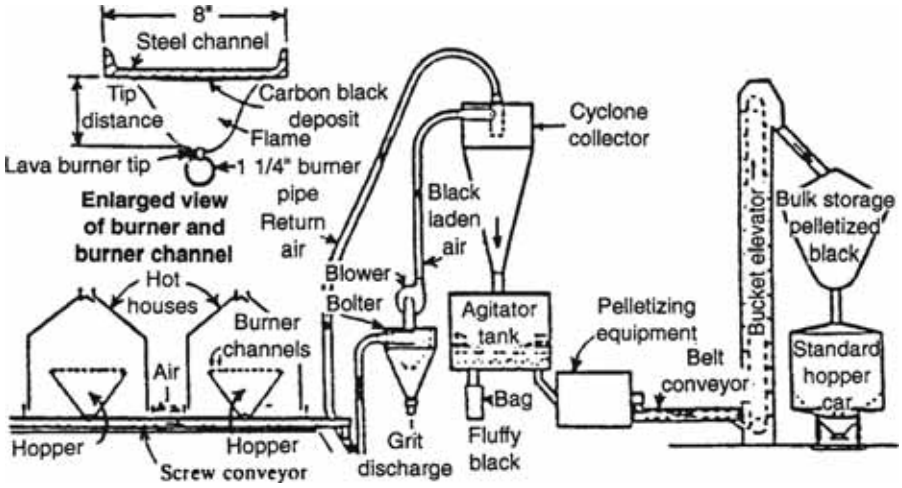

Fig. 3—Channel process for carbon black manufacture.

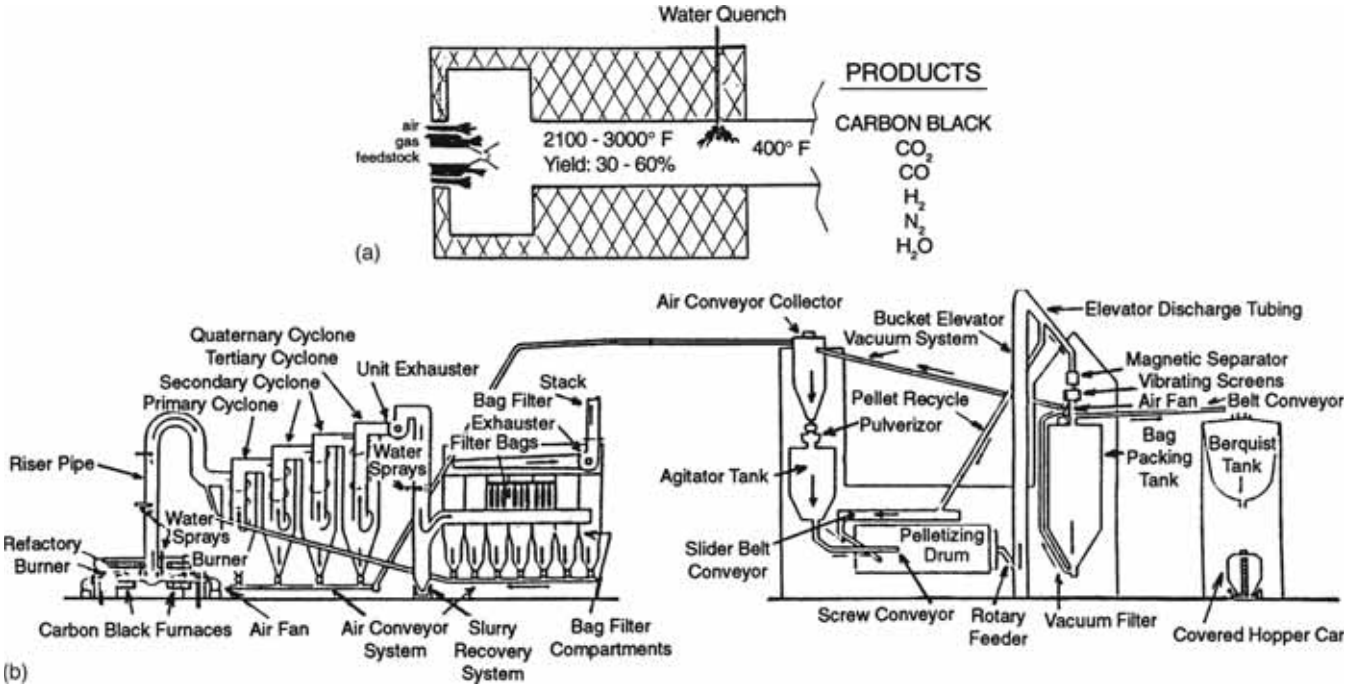

Fig. 4—(a) Oil furnace reactor. (b) Oil furnace plant.

the coating opaque and imparting a desired color is to intercept and modify incident visible light.[3] Carbon black accomplishes this by means of two mechanisms: light absorption and light scattering.

1. Light Absorption—By nature of its quasigraphitic microstructure, carbon black strongly absorbs visible light across the spectrum. In dispersed media, because of its relatively fine particle size and high surface area, it is an extremely efficient light absorber and thus appears black. To achieve opacity, it is necessary to have a sufficient number of carbon black aggregates distributed throughout the polymeric matrix to intercept virtually all of the incident light (Fig. 5). This condition is often referred to as the opacity loading level and translates to about 2 %–3 % carbon black by weight in most vehicle systems. Loadings of carbon black above the opacity loading level will not further enhance the depth of color (blackness).
2. Light Scattering [5]—Another factor that contributes to carbon black's appearance is its relatively weak light-scattering ability. When dispersed in a vehicle, individual aggregates of carbon black are much too fine to be efficient scatterers [6]. Nevertheless, light scattering plays a significant part in the details of carbon black optical performance.

[3] Strictly speaking, the term "visible light" is redundant, since by definition, light is the "visible radiation" that occurs between 400 and 750 nm. However, in common usage, the term visible light is often used.

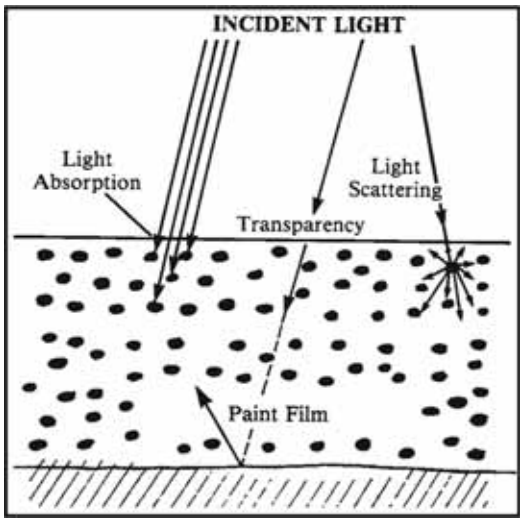

Fig. 5—Optical function of carbon black. This diagram is an oversimplification of how carbon black functions in that primary aggregates are depicted as spherical and of roughly the same size. In reality, the aggregates are irregular in shape and occur as a distribution of sizes, which complicates the optical functioning considerably. However, the fundamental processes as shown still represent the theoretical basis for more complete treatments of the subject.

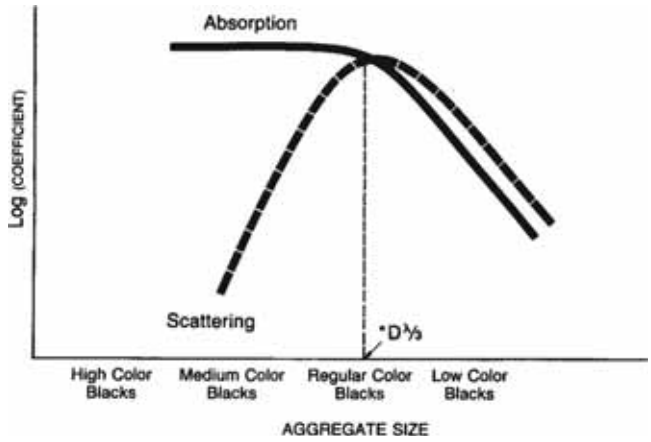

Fig. 6—Carbon black optics. *Dλ/3 is an aggregate size equal to one-third the wavelength of the incident light.

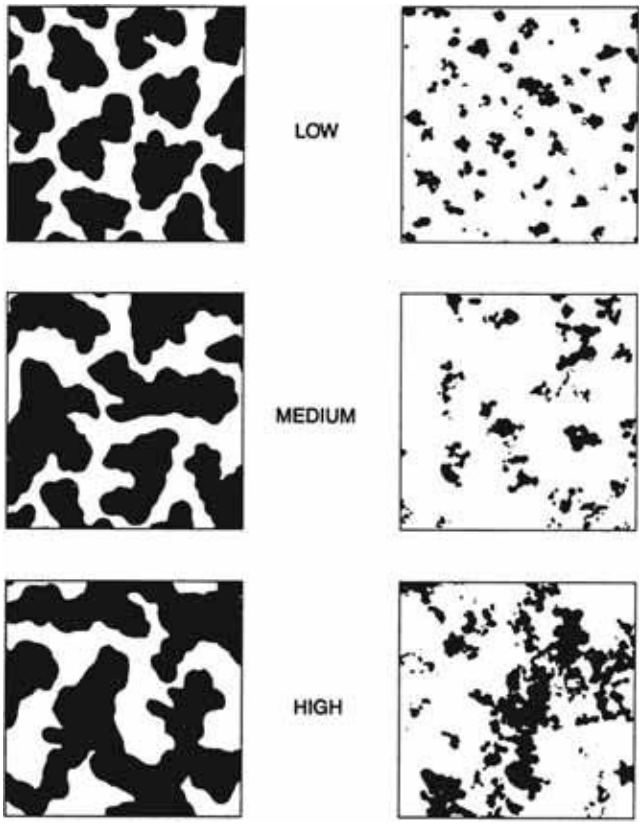

Fig. 7—Structure comparison.

Carbon Black Parameters Affecting the Optical Function

GENERAL PRINCIPLES

When dispersed in a transparent vehicle, the primary aggregates of carbon black are the optically functional units. Thus, the optical function is affected by variations in the two key carbon black parameters that determine aggregate size: prime particle size and structure.

As primary aggregates decrease in size, the specific surface area increases and incident light must penetrate more carbon, which results in increasing light absorption. Both absorption and scattering efficiencies (per unit weight of carbon black) increase with decreasing aggregate size (Fig. 6) down to a size equal to about one third the wavelength of the incident light, *D* (about 180 nm for "white light"). Further decreases in aggregate size show a leveling off of absorption efficiency and a decrease in scattering efficiency. As size decreases, electrical conductivity, ultraviolet radiation protection, tint, and blackness all increase but dispersibility decreases.

The size of the prime particles determines the size of the primary aggregate at a fixed level of aggregation. The level of aggregation is known in the carbon black industry as "structure." It is a parameter that not only indicates the average number of prime particles composing a primary aggregate, but also the degree of anisometry, branching, and chaining or shape irregularity (Fig. 7). The higher the degree of structure the greater the void space within and around a primary aggregate. In fact, the extent to which a carbon black absorbs oil or dibutylphthalate (DBP), which fills the void spaces, is a common industry measure of its structure. As structure is increased, blackness and tint are reduced, but electrical conductivity, viscosity, and dispersibility are improved.

JETNESS

The industry term for degree of "blackness" is "jetness," which increases with decreasing aggregate size for two reasons: (1) increasing light absorption efficiency and (2) decreasing light-scattering efficiency. As primary aggregates become smaller, incident light must penetrate more carbon, resulting in more light absorption per unit weight of black. Also, despite the individual variations of absorption and scattering efficiencies per unit weight, as shown in Fig. 6, the ratio [4] of absorption efficiency to scattering efficiency, *A/S,* essentially increases continuously with decreasing aggregate size. Thus both mechanisms, absorption and scattering, are synergistic with respect to jetness, and the degree of jetness is controlled by the *A/S* ratio. The smaller the aggregate, the higher the *A/S* ratio and the jettier the black.

Structure can also be a measure of aggregate size for a given prime particle since it reflects the number of prime particles composing a primary aggregate. In this sense it is also an indicator of scattering efficiency. Low-structure blacks have smaller primary aggregates, exhibit less scattering, and have higher *A/S* ratios. High-structure blacks have larger primary aggregates, exhibit more scattering, and have lower *A/S* ratios. Given two carbon blacks of comparable prime particle size, the black of lower structure (smaller, more compact primary aggregates) will show the higher jetness because of a higher *A/S* ratio.

TINTING STRENGTH

Carbon black's primary tinting application is to make gray colors by blending with a white pigment. Addition of a fixed amount of a number of different carbon blacks to a titanium dioxide, TiO_2, dispersion, for example, will result in various depths of gray color. The darkest gray will represent the carbon black highest in tinting strength. Since even a dark gray surface reflects a great amount of light relative to a black surface, the increment of light scattered by the carbon black is insignificant. For this reason, the controlling mechanism in tinting strength is light absorption [7]. Finer primary aggregate size, which favors increased absorption, will enhance tinting strength (Fig. 8). As the primary aggregate size is determined both by prime particle size and structure, higher tinting strength is favored by fine particle size, lower structure blacks. However, as shown in Fig. 6, at an aggregate size equal to one-third the wavelength of incident light, the absorption efficiency, and consequently tinting strength, levels off and becomes independent of further decreases in size. This phenomenon can be seen in Fig. 8 as well.

OPACITY

The extent to which a coating will cover or "hide" a substrate is a function of the nature of the pigment and its loading level. As mentioned earlier, the opacity loading level of carbon black in a coating system is usually 3 % or less by weight for normal paint film thicknesses (around 1.0 mil). With much thinner films, higher loadings would be required to achieve opacity. In other words, there must be a sufficient number of primary aggregates dispersed throughout the film to prevent any significant amount of incident light from passing through the film.

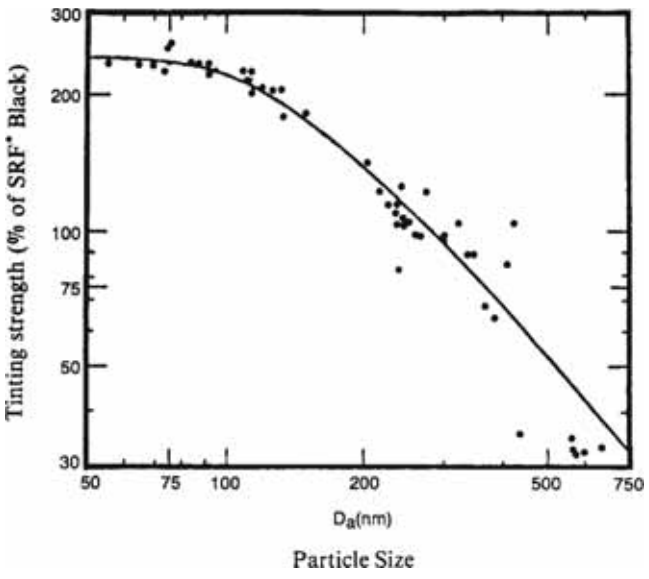

Fig. 8—Tinting strength of a range of carbon blacks.

Carbon black creates opacity through the two mechanisms cited earlier, absorption and scattering of visible light. In fact, opacity of carbon black can be considered as being directly proportional to the sum of the absorption coefficient and the scattering coefficient, $(A + S)$. This means simply that light that is either absorbed or scattered is not transmitted through the film. From this relationship, it is also possible to predict that optimum opacity, as a fixed loading, would be rendered by blacks having an aggregate size close to one-third the wavelength of incident light (in short, blacks in the regular to medium color categories for white light of 180 nm, as per Fig. 6).

One convenient way to express the opacity of films is to use the parameter called optical density. This is a function of the percent of incident light transmitted as follows:

$$\text{optical density} = -\log_{10} T_\lambda$$

where:

T_λ = transmitted light/incident light and
λ = wavelength of incident light

An optical density of 1.0 would indicate a transmission of 1 % (0.01), 2.0 would indicate a transmission of 0.1 % (0.001), etc. Since T_λ will vary somewhat with wavelength, it is necessary to use the subscript notation to denote the wavelength of the incident light. Further, there is a logarithmic relationship with film thickness, F (expressed as weight of coating per unit area, g/m^2), for a fixed carbon black loading, i.e.,

$$\text{optical density} = -\ln(F)$$

UNDERTONE

In the carbon black industry, blacks are visually characterized as having a blue or brown undertone or some gradation in between when dispersed in a coating system. In a black coating, it is called mass tone and in a gray it is called tint tone. The phenomenon of undertone results from the fact that both scattering and absorption efficiencies of carbon black vary with wavelength [8]. Preferential absorption of blue light tends to make the unabsorbed light reaching the observer favor the red end of the spectrum (browner tone). The degree of preferential absorption/scattering of the blue end of the spectrum increases with decreasing aggregate size. Thus, in a gray finish, where the absorption mechanism is in control, the finer the aggregates the browner the tint tone. In mass tone, we have the more complex situation wherein both preferential scattering and preferential absorption, each with a separate wavelength dependency, contribute to undertone.

GLOSS

The term gloss is generally taken to mean the specular reflectance of a surface measured at some specific angle (for example, 60°—ASTM D523, Standard Test Method for Specular Gloss). As with any pigment added to a transparent vehicle, the gloss of the dried film will be influenced by the loading and the properties of the carbon black. Starting with an unpigmented coating having optimal gloss in the

dried film and adding a given carbon black incrementally (assuming excellent dispersions), a point will be reached where gloss begins to deteriorate until eventually the finish becomes flat. Since it is the polymers in the dry film that create the smooth surface for reflection, the addition of particulate substances, such as pigments or fillers in significant concentrations, can only interfere with the "smoothness" of the surface.

The properties of carbon black that affect the gloss of a coating are aggregate size, structure, and surface chemistry. Other factors being constant, the finer the aggregate size, the less the effect on surface texture. The finer aggregate blacks tend to result in coatings with higher gloss when properly dispersed. Higher structure, which means more void space and therefore higher oil absorption, tends to work against gloss. This is because more vehicle is "tied up" for a given loading of black in comparing a higher structure with a low structure black. Once again we must emphasize the importance of quality of dispersion. Since higher structure blacks are somewhat easier to disperse, the effect of structure can only be properly observed in cases where optimal dispersion has been achieved. Higher-structured carbon blacks results in improved electrical conductivity.

Surface chemistry generally refers to the amount of volatile content or chemisorbed oxygen complexes on the surface, that is, hydroxylic, carboxylic, quinonic, or lactonic groups. Carbon blacks often are chemically oxidized after formation, a process termed "after treatment," to increase volatile content. While this is usually done to improve rheological properties (for example, flow and viscosity), it normally creates improved gloss as well. The volatile content acts as a built-in dispersing agent and serves to reduce the amount of vehicle needed to completely wet the surface of the black.

The Effect of Dispersion Quality

GENERAL PRINCIPLES

The influence of the key carbon black parameters on dispersibility must first be defined [9]. As the primary aggregates of carbon black become finer, dispersion becomes more difficult for two reasons: (1) more energy is required to "wet" the higher surface areas and (2) to overcome the greater attractive forces between aggregates because more particles per unit weight of carbon black means smaller interaggregate distances.

Structure plays a key role as well. Low-structure blacks allow closer "packing" (higher density), which results in smaller interaggregate distances and stronger attractive forces and more difficulty in dispersion. Higher structure means more void space (lower density), which reduces interaggregate attractive forces and provides greater accessibility to vehicle penetration or greater ease of dispersion. While lower-structure blacks are more difficult to disperse ultimately, they contain less occluded air (lower density) to be displaced so that they incorporate or "wet-out" more readily than high-structure blacks.

Surface chemistry can be a factor in dispersion both as volatile content or simply as adsorbed moisture. Higher volatile content, acting as a built-in dispersing agent, tends to favor easier dispersion. Adsorbed moisture, present in all carbon blacks in proportion to surface area and ambient conditions in limited amounts, has proven to be beneficial to dispersion in liquid systems.

Density, bulk density, and physical form of carbon black also influence dispersibility. Carbon black as produced is extremely "fluffy" and must be substantially densified (removal of occluded air by agitation), usually to over 10 lb/ft^3 for handling purposes. When the densification is done by rotary agitation in drums, either wet or dry, the result is spherical pellets, which offer ease of handling and reduced dusting. Densification packs agglomerates more closely, increasing interaggregate attraction and making dispersion a more difficult process. Pelletization adds the dimension of pellet hardness, which must be overcome prior to actual dispersion. However, pelleted blacks "wet-out" very quickly and therefore are suitable for use in certain types of equipment (Table 3).

Optimal dispersion of carbon black can be defined as that condition in which all agglomerates are broken down into their constituent primary aggregates; each aggregate is separated from the others, and the surface of each is completely covered by the polymeric species. Primary aggregates are the characteristic units of carbon black and are not broken down under normal dispersion conditions. The steps involved in the dispersion process are as follows.

1. *Incorporation* (*Wetting*)—This step involves the displacement of occluded air and covering the surface of agglomerates with the vehicle being used, yielding a workable dispersion mix. Sometimes this is referred to in the coatings industry as premixing.
2. *Pellet Breakdown*—When pelleted black is used, step 1, incorporation, is easier since initial mixing causes little, if any, pellet fracture. Thus, at the worst, larger pellet fragments need to be "wetted" by vehicle. Pellet breakdown must then be accomplished by the application of additional energy (for example, longer mixing) after step 1.
3. *Deagglomeration*—This is the principal step in achieving optimal dispersion and the one that consumes most of the applied energy. Interaggregate attractive forces must be overcome to break down agglomerates into their constituent primary aggregates.
4. *Stabilization*—To stabilize the deagglomerated aggregates at this stage of the process, each of the aggregates must adsorb sufficient vehicle to completely deactivate its surface.

This process can often be facilitated by the use of dispersing agents.

To function efficiently in an optical sense, carbon black must be optimally dispersed. The primary aggregates, which characterize carbon black, must be separated from

TABLE 3—Preferred form of carbon black for various processes

	Preferred Form	
Equipment	**Fluffy (Powdered)**	**Pellets (Beads)**
Two-roll mill	. . .	X
Three-roll mill	X	. . .
Steel ball mill	. . .	X
Attritor	X	. . .
Disk disperser	X	. . .
Sand/shot mill	X	X

TABLE 4—Suggested vehicle solids to carbon black ratios for mill base compositions

Type	Nitrogen surface area, m^2/g	Suggested ratio, vehicle solids/carbon black
High color	230–560	3.5/1.0 to 4.5/1.0
Medium color	200–220	2.5/1.0 to 3.0/1.0
Regular color	45–140	1.5/1.0 to 2.0/1.0
Low color	25–40	1.0/1.0

one another and distributed fairly uniformly throughout the vehicle matrix to be most efficient at intercepting incident light. Choosing a grade with high surface area for high color applications, for example, must be combined with designing an effective dispersion system to ensure full color development. Mill base formulations, grade selection, physical form of carbon black (fluffy or pellets), and premixing as needed all play a part in ensuring quality dispersion. Perhaps the most important factors in mill base formulation are (1) providing sufficient vehicle solids to accommodate the carbon black surface (Table 4) and (2) adjusting viscosity to a level suitable for the chosen dispersion equipment.

DISPERSION MECHANISMS

Available liquid system dispersion equipment utilizes either or both of the two main dispersion mechanisms: (1) shearing force and (2) collision of agglomerates with each other and with dispersion media particles. These mechanisms describe the manner in which energy is applied to carbon black agglomerates during the dispersion process. For example, disk dispersers and three-roll mills use shearing force while ball mills, sand mills, and attritors rely on collisions.

DISPERSION QUALITY TESTING

It is possible to stabilize carbon black dispersions at various levels of deagglomeration. The term "macrodispersion" is applied to very moderate levels of deagglomeration at which only the larger agglomerates are fractured. "Microdispersion," on the other hand, refers to levels of deagglomeration approaching the ideal of single primary aggregates.

The most accurate way to measure dispersion quality is microscopically. Using 100-power optical micrographs, it is possible to set up a classification system. However, this is costly and time consuming as well as somewhat impractical for production control. More commonly used in the coating industry is the grind gage (Hegman gage, paint club gage, etc.). These devices do not measure microdispersion. Since it is microdispersion that largely determines color performance, it is possible to have two identical mill bases, both "off-scale" on a grind gage, one of which is significantly poorer in dispersion quality. The better dispersed system would be blacker (jettier) and glossier. This leads to the most practical indirect method, that is, using color and/or gloss development, properties that are extremely sensitive to small variations in degree of microdispersion.

Selecting a Grade of Carbon Black for Coloring BLACK COATINGS

For coloring purposes, a grade of carbon black should be selected that is as low as possible in surface area, but consistent with end use color specifications. This enables the formulator to take advantage of the greater ease of dispersion and lower cost associated with the lower surface area. The desired structure level should be high enough to give acceptable dispersibility, but not so high as to adversely affect gloss or rheology. In some cases, the use of after-treated grades will give an edge in dispersion and gloss as well as protect the working rheology at higher loadings. Normally, at opacity level loadings, rheology is only a problem when more concentrated mill bases are used.

Implicit in the selection of a grade of carbon black is the choice of the fluffy (also termed "powdered") or pelleted (also termed "beaded") form. The choice is usually made on the basis of dispersion equipment available or on ease of incorporation or both. Listings of preferred forms for best results with each of the major pieces of equipment are useful (Table 3) to formulators. Regarding ease of incorporation, if, for example, a steel ball mill, which is a very effective disperser, is to be used, the edge in dispersion provided by the fluffy form is not really needed, so it is wise to consider the pelleted form, which will "wet in" quickly and which creates less dust during handling.

Candidate grades must be dispersed in the specific formulation in which they are intended to be used. Keeping in mind the sensitivity of color and gloss development to dispersion quality, it is useful to evaluate jetness and gloss both at the end of the prescribed grind cycle and again after an extended cycle. This technique not only identifies which of the candidates will provide the color and gloss levels needed, but also indicates whether or not full color value from a given grade will be achieved under the prescribed dispersion conditions. The factors of carbon black cost and dispersibility must be weighed against desired color and gloss levels in making a final decision. Some commonly used oil furnace grades for the coatings industry are listed in Table 5.

Black Tinted Coatings

While selecting a black for tinting purposes involves the principles mentioned earlier under *General Natures of Carbon Black* on mass tone color, some key points need emphasis. The selection depends upon required tinting strength (see Table 5), tint tone, and relative ease of dispersion.

Tint tone (see under the topic Carbon Black Parameters Affecting the Optical Function the section on *Undertone*) refers to the color undertone in tinting. If very blue undertone is needed, grades such as LCF 2 and LCF 3 are suggested. Sometimes it is necessary to sacrifice some tinting strength by going to grades with larger aggregate size to maximize blue tint tone (for example, going from LCF I to LCF 2). High-tint-strength blacks tend to give browner undertone, which is desirable in some applications.

Finally, where dispersion stability (that is, flocculation resistance) is critical, after-treated blacks can be helpful. Medium-flow furnace black, for example, exhibits excellent stability and high tinting strength and is often used for tinting in relatively poor wetting vehicles.

Measuring Appearance Properties of Carbon Black Coatings

A black coating pigmented with carbon black at the opacity level (less than 3 % by weight) will probably reflect only about 1 % of the incident light. This presents some unique

TABLE 5—Oil furnace black color grades for coatings. Note: The data are typical of commercial I grades representative of the indicated categories [11]

Property									
		ASTM Standard Test Method							
	N/A	D3037	N/A	D2414		D3265	D1620	D1513	
				DBPA Absorption, cc/100 g				Density, lb/ft³	
Grade	Jetness index[a]	Surface area (BET), m_2/g	Particle size, nm	Fluffy (powdered)	Pellets (beads)	Tinting strength, %	Volatile content, %	Fluffy (powdered)	Pellets (beads)
High Color									
HCF 3	60	560	13	90	80	100	9.0	17	27
HCF 2	64	560	13	100	90	100	9.5	16	25
HCF 1	69	340	16	105	100	116	9.5	11	24
Medium Color									
MC 4	70	230	15	70	64	120	2.0	14	29
MC 3	74	220	16	112	105	122	1.5	8	21
MC 2	73	210	17	74	68	120	1.5	15	28
MC 1	78	200	18	122	117	118	1.5	9	19
Flow Grades									
Low, LFF	83	138	24	60	55	112	5.0	15	32
Med., MFF	84	96	25	72	69	112	3.5	14	30
Regular Color									
RCF 4	83	112	24	65	60	116	1.0	15	31
RCF3	84	94	25	70	65	110	1.0	19	28
RCF 2	87	80	27	85	72	104	1.0	13	29
RCF 1	90	85	27	100	. . .	92	1.0	12	. . .
Low Color									
LCF 4	93	43	37	37	. . .	80	1.0	11	. . .
LCF 3	95	42	41	41	121	62	1.0	. . .	22
LCF 2	96	35	50	50	90	60	1.0	. . .	27
LCF 1	99	25	75	75	64	58	0.5	18	33

[a]Based on Nigrometer scale values, so lower numbers mean higher jetness.

problems in trying to make absolute instrumental measurements since the sensitivity of available instruments is simply not adequate. For this reason, it has been traditional in the carbon black industry and even among end users to depend upon visual judgments of appearance properties in many cases. While no one challenges the incredible sensitivity and versatility of the human eye, it has the drawback of not being able to quantify its observations. Nevertheless, using special techniques, it is possible to obtain quantitative measurements on all appearance properties as outlined below.

JETNESS

Jetness or blackness is a function of surface area, i.e., a parameter that is inversely proportional to aggregate size (Fig. 9). Traditionally, the industry assigned nigrometer "scale" values, which are a direct function of the amount of light reflected by dispersed samples (coatings, plastics, etc.).

Smaller "scale" values indicated jettier carbon blacks. However, the modern approach is to measure the spectral reflectance of a black dispersion, which is made possible by the enhanced sensitivity of current instrumentation. The spectral reflectance curves can then be converted to Hunter L, a, b; or CIE coordinates [10] to quantitatively measure jetness and mass tone as well.

UNDERTONE

The mass tone is measured as described above in the section concerned with jetness. This is an important tool because visual ratings of jetness are usually influenced by the undertone variations among blacks being rated. Tint tone, on the other hand, can normally be measured directly

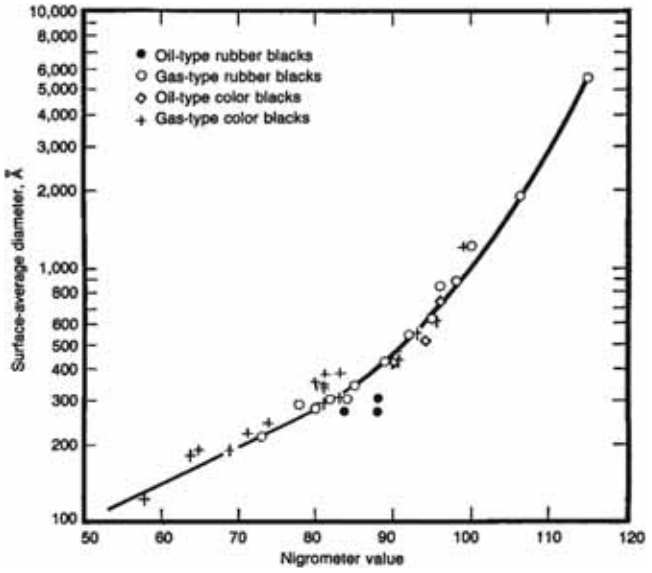

Fig. 9—Nigrometer values versus particle size for a range of carbon blacks.

via absolute reflectance (versus a white standard) using a spectrophotometer or a colorimeter. However, common practice is to measure against a gray standard (ASTM D3265, Test Method for Carbon Black-Tint Strength).

TINTING STRENGTH

As illustrated in Fig. 8, tinting strength increases with decreasing particle size. The differential measurement technique, described above, is used to assign tinting strength values. The procedure, ASTM Test D387, Test Method for Color and Strength of Color Pigments with a Mechanical Muller, involves dispersing carbon black together with a white pigment in wetting oil or other suitable vehicle. The reflectance of this dispersion versus a standard gray tile or gray vitreous enamel is then a measure of its tinting strength. While it was customary in the carbon black industry for many years to report tinting strength as a percent of a reference black (for example, IRB No. 4), some suppliers are now using an independent tinting strength index, allowing strength comparisons only within their own product lines.

GLOSS

Clearly, the property of gloss and the manner in which it is measured is not unique for carbon black coatings. Whether the pigmentation is black or any other color, the test (for example, for 60° gloss) is the same.

TESTING

A number of ASTM documents dealing with standard test methods and/or specifications have been mentioned in the above text and in certain tables. Table 6 is a supplemental list of such ASTM documents that may be of interest to readers or people working in the area of black pigments. The list does not contain all existing ASTM documents related to carbon black—more than 200 such documents exist.

SUMMARY

Individual key carbon black parameters have been viewed from the standpoint of their influence on the optical

TABLE 6—Supplemental ASTM documents (some duplication with previous use in chapter)

ASTM Designation	Title
D305	Standard Test Method for Solvent Extractable Material in Black Pigments
D387	Standard Test Method for Color and Strength of Chromatic Pigments with a Mechanical Muller
D561	Standard Specification for Carbon Black Pigment for Paint
D1506	Standard Test Method for Carbon Black-Ash Content
D1509	Standard Test Methods for Carbon Black-Heating Loss
D1510	Standard Test Methods for Carbon Black-Iodine Adsorption Number
D1511	Standard Test Method for Carbon Black-Pellet Size Distribution
D1512	Standard Test Methods for Carbon Black-pH Value
D1513	Standard Test Methods for Carbon Black-Pelleted-Pore Density
D1619	Standard Test Method for Carbon Black-Sulfur Content
D2414	Standard Test Methods for Carbon Black-Oil Absorption Number (OAN)
D3037[a]	Standard Test Methods for Carbon Black-Surface Area by Nitrogen Absorption (WITHDRAWN 1999)
D3053	Standard Terminology Relating to Carbon Black
D3265	Standard Test Method for Carbon Black-Tint Strength
D3313	Standard Test Method for Carbon Black-Individual Pellet Hardness
D3493	Standard Test Method for Carbon Black-Oil Absorption Number of Compressed Sample (COAN)
D3849	Standard Test Method for Carbon Black-Morphological Characterization of Carbon Black Using Electron Microscopy
D4122	Standard Practice for Carbon Black-Evaluation of an Industry Reference Black
D4527	Standard Test Method for Carbon Black-Solvent Extractables
D4820[a]	Standard Test Methods for Carbon Black-Surface Area by Multipoint B.E.T. Nitrogen Absorption (WITHDRAWN 2000)—See ASTM D6556 below.
D4821	Standard Guide for Carbon Black-Validation of Test Method Precision and Bias
D5230	Standard Test Method for Carbon Black-Automated Individual Pellet Hardness

TABLE 6—Supplemental ASTM documents (some duplication with previous use in chapter) (*continued*)

D5816[a]	Standard Test Methods for Carbon Black—External Surface Area by Multipoint Nitrogen Absorption (WITHDRAWN 2000)—See ASTM D6556 below.
D5817	Standard Practice for Carbon Black, Pelleted-Reduction, Blending, and Drying of Gross Samples for Testing
D6086	Standard Test Method for Carbon Black-Void Volume (W)
D6556	Standard Test Method for Carbon Black and External Surface Area by Nitrogen Adsorption
D6602	Standard Practice for Sampling and Testing of Possible Carbon Black Fugitive Emissions or Other Environmental Particulates, or Both
D6915	Standard Practice for Carbon Black—Evaluation of Standard Reference Blacks
E284	Terminology of Appearance

[a]Withdrawn document—included for historical purposes.

function blacks. It is important to emphasize, however, that these parameters do not operate independently. The effect on optical functioning, and therefore on pigmentary properties, is a combined effect. When varied, each parameter influences the other parameters, which are also varying. Thus the situation is dynamic and complex.

Dispersion quality and its importance in realizing the full optical potential of a given grade has also been addressed. Therefore, in the grade selection process, the physical form of carbon black as well as key parameters must be considered in relation to the chosen dispersion technique.

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Colored Organic Pigments*

Paul Merchak[1]

DEFINITION OF A PIGMENT

BEFORE ENTERING INTO ANY DISCUSSION RELATING to pigments, it is first necessary to clearly define what is understood to be an organic pigment as opposed to a dyestuff. In many earlier texts on color and articles concerning the use of color, the terms "pigment" and "dyestuff" are used almost interchangeably and often incorrectly.

A definition of a pigment has been proposed by the Color Pigments Manufacturers Association (CPMA)[2] in response to a request from the Toxic Substance Interagency Testing Committee. This definition was developed specifically to enable differentiation between a dyestuff and a pigment with the intention of forever ending the confusion surrounding these two terms. As such, it is worthwhile reproducing this definition in its entirety:

> "Pigments are colored, black, white, or fluorescent particulate organic and inorganic solids which usually are insoluble in, and essentially physically and chemically unaffected by, the vehicle or substrate in which they are incorporated. They alter appearance by selective absorption and/or by scattering of light.
>
> Pigments are usually dispersed in vehicles or substrates for application, as for instance in inks, paints, plastics, or other polymeric materials. Pigments retain a crystal or particulate structure throughout the coloration process. As a result of the physical and chemical characteristics of pigments, pigments and dyes differ in their application; when a dye is applied, it penetrates the substrate in a soluble form, after which it may or may not become insoluble. When a pigment is used to color or opacify a substrate, the finely divided insoluble solid remains throughout the coloration process."

Additionally, the older terms "lake" and "toner" may be encountered when dealing with pigments. American terminology, applied to pigments, defines a toner as an organic pigment that is free of inorganic extender pigments or carriers; as such, the pigment is unadulterated and exhibits maximum tinting capacity for the pigment type. A lake, conversely, is an organic colorant that has been combined with an inorganic substrate or extender such as barium sulfate (Blanc Fixe) or alumina. In European terminology, toners are considered to be water-soluble acid or basic dyestuffs that are converted into insoluble pigmentary forms by appropriate precipitation with an inorganic compound. As such, Barium Lithol red (C. I. Pigment Red 49:1) and the phosphotungsto molybdic acid (PTMA)-based Rhodamine (C.I. Pigment Violet 1) are considered toners. In the coatings industry, the term "toner" may be used to refer to a secondary color that is added to alter the primary hue of the paint. The term "lake" now has an accepted definition as that used in America.

A most confusing European term, the use of which should be discouraged, is "pigment dyestuff." This term is meant to refer to insoluble organic pigments devoid of salt-forming groups, for example, Benzimidalone Orange (C. I. Pigment Orange 36).

INTERNATIONAL NOMENCLATURE—THE COLOUR INDEX (C. I.) SYSTEM

In any publication discussing either organic or inorganic pigments, it is highly likely that the author will make use of the coding system as published as a joint undertaking by the Bradford Society of Dryers and Colourists in the United Kingdom and the Association of Textile Chemists and Colorists in the United States.

This system is known as the "Colour Index," [1] and, as such, is a recognized trademark, hence the retention of the "u" in "colour" whenever reference is made to a "Colour Index" name or number.

The Colour Index (C. I.) identifies each pigment by giving the compound a unique "Colour Index Name" and a "Colour Index Number." This description is proving to be most valuable to persons within the coatings industry responsible for assembling data on the composition of a coatings formulation for documents such as Material Safety Data Sheets, shipping information, product composition, or hazard data sheets. As such, the identification of a pigment by mention of its C. I. name and number unequivocally identifies the chemical composition of the pigment in a manner acceptable to meet government bodies. For example, DNA Orange has the Colour Index name of Pigment Orange 5 (PO 5) and the Colour Index Number of 12075.

The Colour Index Name for a pigment is abbreviated as:
PB—Pigment Blue
PBk—Pigment Black
PBr—Pigment Brown
PG—Pigment Green
PM—Pigment Metal
PO—Pigment Orange

* Modification of original chapter by Peter A. Lewis.

[1] *Merchak Sun Chemical Corporation, 5020 Spring Grove Ave., Cincinnati, OH 45232.*

[2] Color Pigments Manufacturers Association, Inc., Suite 102, 300 N. Washington St., Alexandria, VA 22314; www.pigments.org.

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PV—Pigment Violet
PR—Pigment Red
PW—Pigment White
PY—Pigment Yellow

CLASSIFICATION OF PIGMENTS BY CHEMISTRY

Pigments in paints and coatings may be broadly divided into opaque or hiding whites and colored toners. All the opaque whites are inorganic compounds and, as such, fall outside the contents of this chapter. For the sake of clarity, it should be noted that such compounds include the following:

Lithopone (co-precipitate of barium sulfate and zinc sulfide)
Zinc oxide
Antimony oxide
Titanium white (mixture of titanium dioxide and blanc fixe)
Titanium dioxide (rutile form)

The colored pigments as covered in this section are all organic in nature and, as such, contain a characteristic grouping or arrangement of atoms known as a "chromophore," which imparts color to the molecule. In addition, the molecule is likely to feature a number of modifying groups called "auxochromes" that alter the primary hue of the pigment in a more subtle way—such as shifting a red to a more yellow shade or a blue to a more red shade while still maintaining the primary hue of red or blue rather than pushing the hue over to an orange or a violet. The entire colored molecule may be referred to as the "chromogen."

Perhaps the most important of the chromophores is the azo chromophores (—N═N—). The naphthol reds, monoarylide and diarylide yellows, benzimidazolone yellows and oranges, pyrazolone reds and oranges, and azo condensation pigments are all examples of organic pigments that feature the azo chromophore. Of equal importance is the phthalocyanine structure based on the compound tetrabenzotetra-azaporphin. Halogenation of this compound results in a major shift in hue from a blue to a green. Pigments are also derived from heterocyclic structures as perylene, diketopyrrolopyrrole, quinacridone, and carbazole dioxazine violet. Finally, there are pigments that result from the vat dyestuffs and miscellaneous metal complexes.

CLASSIFICAITON OF PIGMENTS BY COLOR

Reds

METALLIZED AZO REDS

Many reds used in the coatings industry contain the azo chromophore (—N═N—) and, as such, are termed "azo reds." A further subdivision is possible into acid, monoazo metallized pigments such as Strontium Red 2B (PR 48:3), Manganese Red 2B (PR 48:4), and non-metallized azo reds such as Toluidine Red (PR 3), and the very popular naphthol reds (PR 170; PR 188).

Typically, each of the metallized types contains an an ionic grouping such as sulfonic (–SO_3H) or carboxylic acid (–COOH), which will ionize and react with a metal cation such as calcium, manganese, strontium, or barium to form an insoluble metallized azo pigment. Conversely, non-metallized azo reds do not contain an anionic group in their structure and, therefore, cannot complex with a metal cation.

All azo reds contain one or more azo groups and are all produced via a similar reaction sequence involving diazotization and coupling. Diazotization involves the reaction of a primary aromatic amine with nitrous acid to yield a "diazonium salt," which is immediately "coupled" to the other half of the molecule, called the coupler, to yield the colored pigment. It is usual practice to produce the nitrous acid "in-situ" from the addition of hydrochloric or sulfuric acid to sodium nitrite. This serves to explain the presence of inorganic salts such as sodium chloride or sodium sulfate in the unwashed pigment, salts that have to be removed by washing at the filtration state prior to discharging the pigment from the filter. It is at the coupling stage that the colored, insoluble pigment is formed. Careful control of the reaction rate by control of *p*H, temperature, concentration, addition rates, agitation, etc., are critical at this stage to produce the desired particle size pigments. Once the insoluble pigment is produced, the particle size, crystallinity, or morphology may be altered either by a thermal treatment of the pigment slurry or after isolating the pigment by subjecting it to a solvent or thermal treatment. Fig. 1 illustrates the structure of a series of metallized azo reds that are of considerable commercial importance and that find some, albeit limited, use within the coatings industry. Each of these structures feature a molecule based on the coupling of a naphthalene ring structure to a

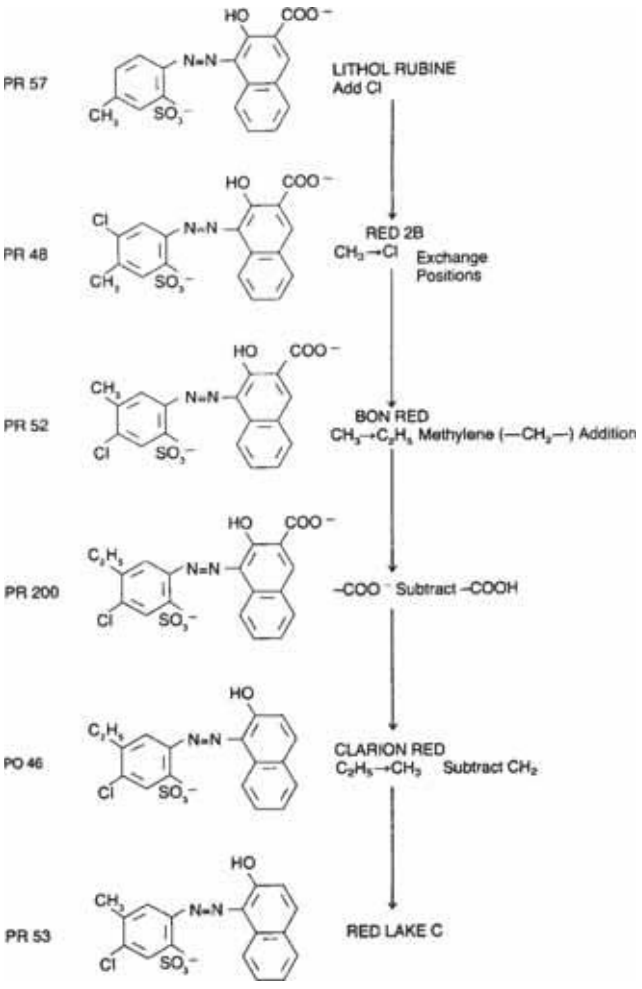


Fig. 1—Structure of metallized azo reds.

benzenoid structure. A brief description of the more common metallized azo reds is as follows:

Lithol Reds—Barium Lithol PR 40:1, C. I. Number 15630:1; Calcium Lithol PR 49:2, C. I. Number 15630:2

This pigment was discovered in 1899 and its major use is in the printing ink industry and finds only limited application within the coatings industry at masstone levels, that is, at a level where the tinting strength of the pigment is not diluted with a white-tint base. Examples of the use of this pigment are for such reds as those used on tool boxes, fire extinguishers, gas cylinders, oil filters, and the less expensive lawn mowers where the fastness properties of the pigment are acceptable.

The pigments are bright reds with high tint strength and good dispersion characteristics; the barium salt is lighter and more yellow in shade than the calcium salt, which may best be described as a medium red. Neither pigment can be recommended for outdoor exposure applications, since their exterior durability is inadequate for such situations. Additionally, they cannot be used in situations that require pigments to withstand an environment that is highly acidic or highly alkaline since Lithol Reds under such conditions give weaker, yellower shade products, resulting from an exchange of the alkaline earth salt by neutralization of the pigment acid functional groups or exchange with the added base agent.

Permanent Red 2B—Barium Red 2B, PR 48:1, C. I. Number 15865:1; Calcium Red 2B, PR 48:2, C. I. Number 15865:2; Strontium Red 2B, PR 48:3, C. I. Number 15865:3; Manganese Red 2B, PR 48:4, C. I. Number 15865:4.

Discovered in the 1920s, the Red 2B pigments are azo reds prepared by coupling diazotized 1-amino-3-chloro-4-methyl benzene sulfonic acid (2B acid) with 3-hydroxy-2-naphtholic acid (BONA).

A major end use of the barium and calcium pigments is in baked industrial enamels, where outdoor fastness properties are not a prerequisite of the application. Their use in alkaline systems is again severely restricted due to the tendency of these metal salts to exchange ions in highly alkaline environments. The barium salt is characterized by a clean, yellow hue as compared to the bluer calcium salt. The barium salt has a poorer light fastness and weaker tinting strength, but a slightly better bake stability as compared to the calcium salt.

The Manganese Red 2B has sufficiently improved light fastness to allow its use in implement finishes and aerosol spray cans for touchup paints. This salt is bluer, dirtier, and less intense as compared to the calcium salt. Extension of the manganese pigment with any pigment such as titanium dioxide or Molybdate Orange (PR 104) to an amount greater than 15 % is not recommended since the durability of the pigment will be adversely affected.

The term "light fastness" used throughout this chapter refers to the pigment's stability to withstand exposure to light, both direct and indirect, natural or artificial, without suffering any visible change in appearance. The most damaging component of light appears to lie in the ultraviolet region of the electromagnetic spectrum and, as such, a rapid evaluation of a pigment's likely reaction to long-term exposure of such radiation can be assessed using exposure equipment that maximizes exposure to ultraviolet radiation. Many high-performance pigment's are exposed under application conditions in specially maintained areas of Florida to more fully evaluate their "fastness," that is, their behavior on outdoor exposure involving intense sunlight, high humidity, and changing weather conditions.

Lithol Rubine Red—Calcium Lithol Rubine, PR 57:1, C. I. Number 15850:1.

This pigment is made by coupling 3- BONA with diazotized-2-amino-5-methyl benzene sulfonic acid (4B acid). This blue-shade red was discovered in 1903 and has found widespread use in the printing ink industry ever since the process "magenta" of the four-color printing process, for offset, gravure and flexographic printing.

A clean blue-shade red with high tint strength, its major application in the coatings industry is for interior applications calling for an inexpensive red with both good solvent and heat resistance. Again, this pigment must be used at near masstone levels to maximize its fastness properties.

BON Reds—Calcium BON Red, PR 52:1, C. I. Number 15860:1; Manganese BON Red, PR 52:2, C. I. Number 15860:2.

These reds are manufactured by coupling diazotized 1-amino-4-chloro-3-methyl benzene sulfonic acid onto BONA. The pigments were first commercialized in 1910. They are characterized by outstanding cleanness, brightness, and color purity. The manganese salt offers a very blue-shade red with improved light fastness as compared to the calcium salt. As such, the manganese salt is suitable for outdoor applications and, as with the Manganese Red 2, can be used in blends with Molybdate Orange (PR 104) to give bright, economical reds.

BON Maroon—PR 63:1, C. I. Number 15880:1

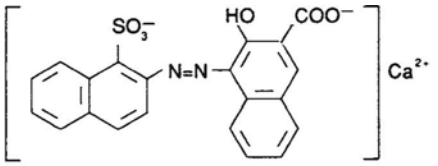
Illustrated in Fig. 2, BON Maroon was first synthesized in 1906 by Ernest Gulbransson of Farbwerken Meister, Lucius, and Bruning. The manganese salt is the only one that finds commercial significance rather than the calcium or barium variations. Its light fastness is such that the pigment can be used at masstone levels for implementation and bicycle finishes. Over 50 years ago, when specifications were not as demanding as today, BON Maroon actually found application in automotive finishes.

NON-METALLIZED AZO REDS

As implied by their classification, the non-metallized azo reds do not contain a precipitating metal cation and, as such, offer increased stability as they do not suffer from neutralization or ion exchange problems in highly acidic or alkaline environments, as compared to the metallized azo red previously discussed.

Toluidine Red—PR 3, C. I. Number 12120.

This pigment, described in Fig. 3, was first synthesized in 1905 and is chemically the reaction product from coupling the diazonium salt of 2-nitro-4-toluidine (MNPT) onto 2-naphthol (beta naphthol). Various shades of Toluidine Red are commercially available and these are described



2-naphthylamine-1-sulfonic acid ⟶ 3-hydroxy-2-naphthoic acid (BON)

Fig. 2—Structure of BON Maroon, PR 63:1.

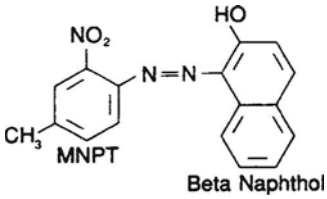


Fig. 3—Structure of Toluidine Red PR 3.

as "very light," "light," "medium," "dark," and "very dark." These are also graded as offering "haze resistance" and being "easy dispersing."

Almost the entire worldwide production of Toluidine Red is consumed by the coatings industry. The pigment provides a bright, economical red of acceptable light fastness when used in full shade coupled with a high degree of color intensity and good hiding power. However, the pigment is not fast to white over-striping since it will blend through, turning white into pink, and it shows a marked tendency to bleed in high Kauri-Butanol solvents.

Toluidine Red is used almost exclusively at masstone levels, that is, in full shade without the addition of opaque extenders such as titanium dioxide or zinc oxide. Usage extends to such applications as farm implements, lawn and garden equipment, and bulletin paints where a bright, economical red of moderate light fastness is required to fill the user specification. Because of the pigment's poor durability in tinted shades, a reduced or extended pigment with an opaque white is rarely used at reduced levels.

Para Reds—Para Red, PR 1, C. I. Number 12070; Chlorinated Para Red, PR 4, C. I. Number 12085; Parachlor Red, PR 6, C. I. Number 12090.

Each of these three pigments, which are shown in Fig. 4, is based on the coupling of a primary amine to betanaphthol. The position of the –chloro or –nitro auxochromes on the molecule controls the shade of the pigment. In fact, Chlorinated Para Red differs from Parachlor Red only in the position of the –nitro and –chloro groups on the benzene ring. As such, these pigments are isomers.

Use of these pigments in the coatings industry has declined rapidly due to the ever-increasing and exacting demands placed on colored finishes by the industry. All of these pigments will bleed in solvents typically used in the coatings industry and, as such, cannot be used in any finish that requires over-striping.

As a class of insoluble azo reds, they are characterized by intense shades of red through scarlet. Their good alkali resistance, light fastness, and durability when considered as a function of their cost recommends them for use in latex paints and outdoor signs. At temperatures above 270°F (121°C), the pigments will sublime. Light fastness of tints is significantly inferior to that of the pigments at full shade.

Naphthol Reds—Naphthol Reds are chemically defined as monoazos of 2-hydroxynaphtholic acid N-arylamides without anionic, salt-forming groups. Their individual properties are dependent on the specific composition of the pigment, in addition to the conditioning steps used in their manufacture. As a class, they are pigments that exhibit good tinctorial properties combined with moderate fastness to heat, light, and solvents. The Naphthol Reds are extremely acid-, alkali-, and soap-resistant pigments. Such

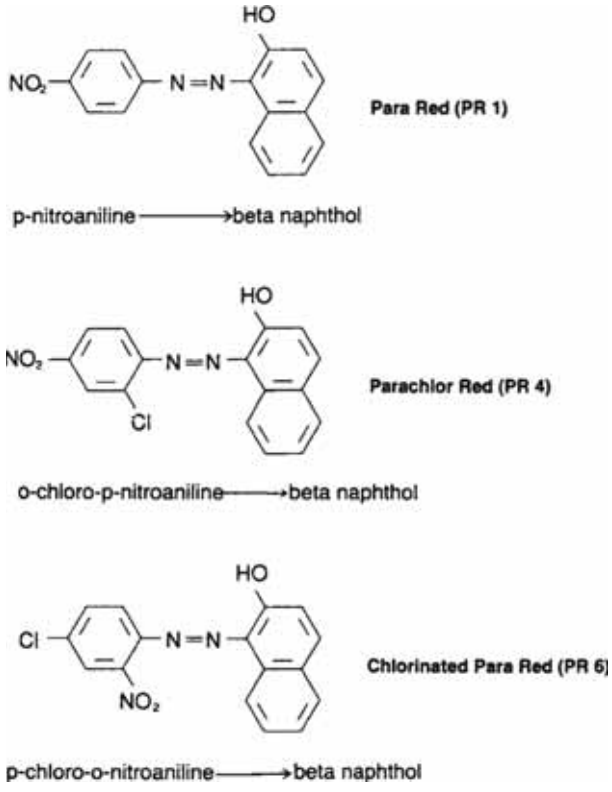


Fig. 4—Structure of para reds.

properties lead to their use in masonry paints and latex emulsions that are formulated under alkaline conditions.

Naphthol Reds may be described as "medium performance" reds since they exhibit properties that fall somewhere between Toluidine Red and Quinacridones with a cost that corresponds accordingly. Fig. 5 illustrates the generic structure of the naphthol molecules and gives the chemistry of several of the types described below. Those Naphthol Reds of commercial significance that should be briefly covered are:

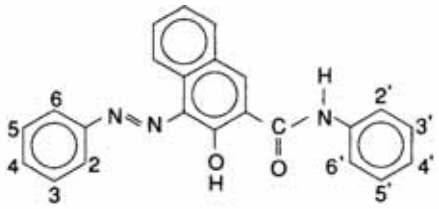
Pigment Red 22, C. I. Number 12315—a light yellow shade Naphthol used in air-drying alkyds and aqueous systems that can be satisfied with this pigment's marginal light fastness.

Pigment Red 112, C. I. Number 12370—a Naphthol Red that possess a very clean, yellow hue and that finds uses in both industrial and architectural coatings. The tendency of the pigment to bloom at high concentrations and its poor over-striping fastness has limited its more widespread use. In Europe, this pigment finds a major outlet in store tinting systems. Light fastness at both tint and full shade is rated good.

Pigment Orange 38, C. I. Number 12367—is a very yellow shade, bright red pigment with good solvent fastness. It can be used in baking enamels at high concentrations without showing any tendency to bloom.

Pigment Red 5, C. I. Number 12490—has only marginal fastness to heat and solvents. Nevertheless, it finds application in implement coatings. The opaque grade of this pigment can be combined with iron oxide to give an economical red with high hiding.

Pigment Red 146, C. I. Number 12485—is a very blue-shade red that finds its major use in interior architectural



Colour Index Name	Colour Index Number	Substituents 2	4	5	2′	4′	5′
PR 2	12310	Cl	H	Cl	H	H	H
PR 7	12420	CH_3	Cl	H	CH_3	Cl	H
PR 9	12460	Cl	H	Cl	OCH_3	H	H
PR 10	12440	Cl	H	Cl	H	CH_3	H
PR 14	12380	NO_2	Cl	H	CH_3	H	H
PR 17	12390	CH_3	H	NO_2	CH_3	H	H
PR 22	12315	CH_3	H	NO_2	H	H	H
PR 23	12355	OCH_3	H	NO_2	H	H	NO_2
PR 112	12370	Cl	Cl	Cl	CH_3	H	H

Fig. 5—Generic structure and key to the naphthol reds.

applications. Its poor exterior durability makes the pigment unsuitable for outdoor finishes.

Pigment Red 170, C. I. Number 12475—is a medium-performance, moderately priced red. It is available as both a transparent and an opaque grade. Manufacturing techniques are used to produce the pigment in two crystal phases, each exhibiting a unique hue. The opaque grade finds use in farm tractor and implement finishes. Its use with iron oxides allows a practical approach to formulating reds with acceptable light fastness, hiding, and economics. It is a fair statement that this pigment finds use in just about every paint and coatings application method practiced in the United States, from water-based through powder-coating products. Blends with quinacridones are used in automotive refinish paints where durability requirements are not as exacting as those for the original factory-applied finishes. In a color sense, the pigment is almost identical to the diketopyrrolopyrrole pigment PR 254.

Pigment Red 187, C. I. Number 12486—is a transparent pigment with excellent heat fastness, moderate durability, and good bleed resistance. Its uses extend to bicycle, coil, and powder coatings.

Pigment Red 188, C. I. Number 12467—is a yellow, clean-shade red with acceptable durability at all depths of shade. It is fast to over-striping at temperatures below 160°C and therefore finds use in higher-quality industrial finishes. A Naphthol Red with a shade that is almost an orange, PR 188 is used in the in-store tinting systems that are popular at hardware-type outlets throughout the United States.

High-Performance Reds

These types of pigments may be briefly defined as products that will meet the exacting demands of the automotive industry with respect, particularly to the outdoor exposure requirements demanded by controlled exposure in Florida and Arizona for as little as two, and as long as, five years.

The high-performance reds considered fall into five basic classes:

Quinacridone red and violet
Vat dyestuff-based reds as the perylenes
Benzimidazolone reds
Disazocondensation reds
Diketopyrrolopyrrole

QUINACRIDONE REDS

These pigments are heterocyclic in nature since their structure comprises a fused ring in which the ring atoms are dissimilar and being a combination of carbon and nitrogen rather than only carbon as has been the case with the previous pigments discussed. The addition of differing auxochromic groups such as methyl (—CH_3) and chlorine (—Cl) gives Pigment Red 122 and Pigment Red 202, respectively, both described as magentas.

The theory behind the superior durability of pigments with the quinacridone structure is that considerable hydrogen bonding occurs between molecules through the carbonyl (═C═O) and imino (═N—H) ring atoms (see Fig. 6).

As a group of pigments, the quinacridones find their primary uses in automotive, industrial, and exterior coatings. A minor use is in the preparation of quality furniture stains and finishes. The pigments combine excellent tinctorial properties with outstanding durability, solvent resistance, light fastness, heat fastness, and chemical resistance. Table 1 lists those shades currently commercially available. Possibly the only potential drawback exhibited by the quinacridones is their poor rheology in high solids, solvent-based coating formulations used for original equip-

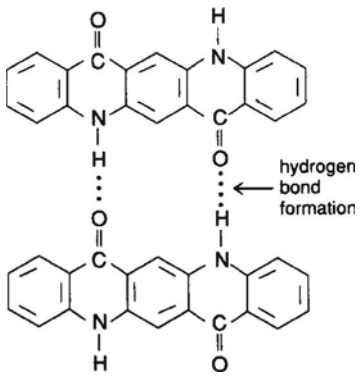


Fig. 6—Translinear quinacridone showing proposed hydrogen bonding mechanism.

TABLE 1—Classifications of quinacridone pigments

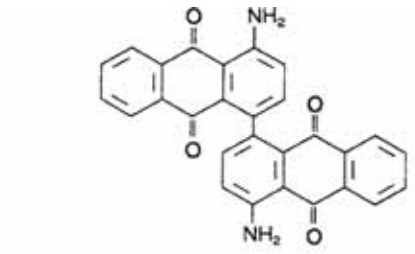
Colour Index Name	Hue	Comments
PO 49	Gold	Quinacridone quinone
PR 122	Magenta	2,9-dimethyl
PR 192	Red-yellow	Mono methyl
PR 202	Magenta	2,9-dichloro
PR 206	Maroon	Solid solution
PR 207	Scarlet	4,11-dichloro
PR 209	Red-yellow	3,10-dichloro
PV 19	Violet-blue	Beta crystal
PV 19	Red-yellow	Gamma crystal
PV 42	Maroon	Solid solution

ment manufacturer (OEM) automotive applications. When the formulator is working with such high pigments bases, it is often impossible for levels as high as 20 % pigment to be achieved with many quinacridones available in today's marketplace due to poor flow and thixotropic properties that can be a feature of these pigments. Poor rheology, resulting in a heavy-bodied paint, is often the limiting factor in achieving a highly concentrated mill base when quinacridones are used as a major component of red formulations. As pressures increase to reduce the volatile organic content that is part of a solvent-based paint, the need for pigments that can be dispersed at high levels with minimal effect on the flow properties of the mill base will only increase proportionately. Fortunately, this class of pigments does not appear to give similar flow problems when formulated into a water-based OEM coating. Thus, they continue to be used as aqueous systems are developed as an alternative to high solids, solvent-based coatings. The rheology problem, however, is replaced with the situation color stylists face when trying to create an exact match in an aqueous system for a style that was made using solvent- based paint. A point worthy of note is that 2,9-dichloroquinacridone magenta (PR 202) is inherently considerably better in rheology than is the 2,9-dimethylquinacridone magenta (PR 122). Ironically, as more water-based formulations are developed, the Pigment Red 202, so vital in high-solids solvent systems, is being replaced by Pigment Red 122 since rheology is not an issue, and the Red 122 offers a better hue than does the Red 202 in the water-based systems.

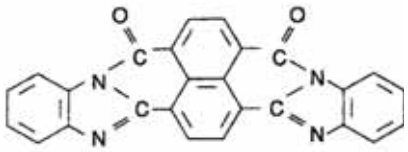
VAT REDS

Vat Red pigments based on anthraquinone include such structures as Anthraquinone Red (PR 177), Perinone Red (PR 194), Brominated Pyranthrone Red (PR 216), and Pyranthrone Red (PR 226) as described in Fig. 7. The term "vat pigments" originates from the fact that this class of pigments is related to the vat dyestuffs used originally in the dying of cotton. Only their high cost limits the more widespread use of the pigments throughout the coatings industry.

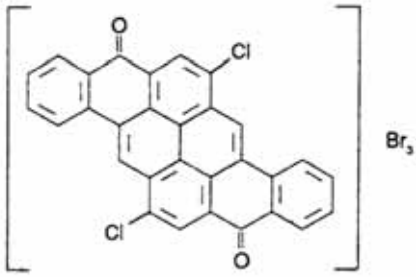
Anthraquinone Red, PR 177, C. I. Number 65300. This is a medium-shade red with excellent all-around fastness



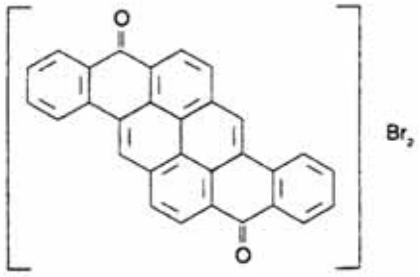
Anthraquinone Red (PR 177)



Perinone Red (PR 194)



Brominated Pyranthrone Red (PR 216)



Pyranthrone Red (PR 226)

Fig. 7—Structure of typical vat reds.

properties. Again, it finds major use in the automotive industry for the production of clean, bright red coatings.

Brominated Pyranthrone Red, PR226, C. I. Number 59710. This pigment is a yellow shade red that can be classed as an automotive-grade pigment because of its excellent fastness properties. Neither light nor dark shades will suffer on prolonged exposure to Florida atmospheres. Transparency is generally not adequate for this pigment to be used in metallic or mica finishes.

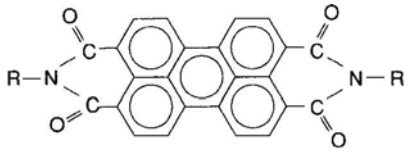
Perylene Reds

These pigments provide pure, transparent shades and novel styling effects when used in metallic aluminum and mica finishes. The perylenes offer improved flow characteristics when used in high-solids formulations. Perylenes may

also be described as vat pigments and in fact are the only class of such pigments that were developed specifically for the pigment marketplace rather than as dyestuffs. These pigments are generally not clean enough for use as a self-shade, accordingly they most often find use in blends with such compounds as the quinacridones to produce clean, transparent finishes. Almost all of the perylenes have a structure as shown by the generic formula given as Fig. 8, that is, they are based on *N*, *N'*-substituted perylene-3, 4,9.10-tetracarboxylic di-imide. An exception of note is Pigment Red 234, Fig. 9, which is derived from the perylene tetra carboxylic dianhydride.

Benzimidazolone-Based Reds

This subdivision of reds includes such pigments as Pigment Reds 171, 175, 176, 185, and 208. Benzimidazolone-based reds are azo reds that contain the Benzimidazolone structure as part of their makeup. These reds all possess the generic structure based on a central naphthol molecule as illustrated in Fig. 10. Such structures exhibit a significantly high molecular weight that greatly influences durability and fastness properties of the pigment.



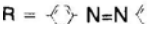
R = $-C_6H_3OC_2H_5$	PR 123	Vermillion
R = $-C_6H_3(CH_3)_2$	PR 149	Scarlet
R = $-CH_3$	PR 179	Maroon
R = $-C_6H_5OCH_3$	PR 190	Red
R = $-H$	PBr 26	Bordeaux
R = $-C_6H_5Cl$	PR 189	Yellow Shade Red
R = 	PR 178	Red

Fig. 8—Structure of typical perylene.

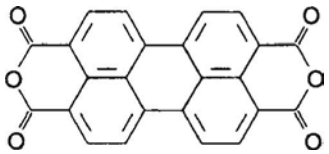
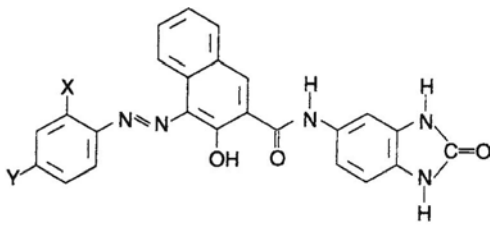


Fig. 9—Structure of Pigment Red 224.



Colour Index Name	X	Y
PR 171	OCH_3	NO_2
PR 175	$COOCH_3$	H
PR 176	OCH_3	$CONHC_6H_5$
PR 185	OCH_3	SO_2NHCH_3
PR 208	$COOC_4H_9$	H

Fig. 10—Structure of the benzimidazolone reds.

Benzimidazolone reds are primarily used in the coloring of plastics because of their outstanding heat stability, although some uses are found within the coatings marketplace. They have excellent fastness to light at all depths of shade, good weather resistance, and excellent fastness to over-spraying at elevated temperatures. They all find use in coil coatings, power coatings, camouflage paints, automotive refinish, and farm implements where less-expensive, less-stable pigments would be inadequate.

Pigment Red 175 is a highly transparent red with good light fastness that finds application in the automotive base-coat/clear-coat systems since it is not sufficiently durable for top-coat systems without a clear coat to provide additional protection to the pigment. Pigment Red 171 is also a transparent pigment, but it has a maroon shade that finds use in industrial systems. Pigment Reds 176, 185, and 208 find considerable use in quality printing ink applications but currently no use in the paint and coatings industry.

Disazo Condensation Reds

These types of pigments have been commercially available in Europe since 1957 and in the United States since 1960. Their outstanding fastness properties have resulted in their use in high-quality industrial finishes. Fig. 11 illustrates three typical structures of the disazo condensation reds. The figure merely serves to show the size and variation of the structures of pigments within this class.

Pigment Red 242, C. I. Number 20067, Fig. 12, is a bright yellow shade disazo condensation pigment with excellent fastness properties that is finding increased use in high-quality industrial finishes and as a lead replacement pigment for those high-qualtiy coatings that now must be formulated lead free.

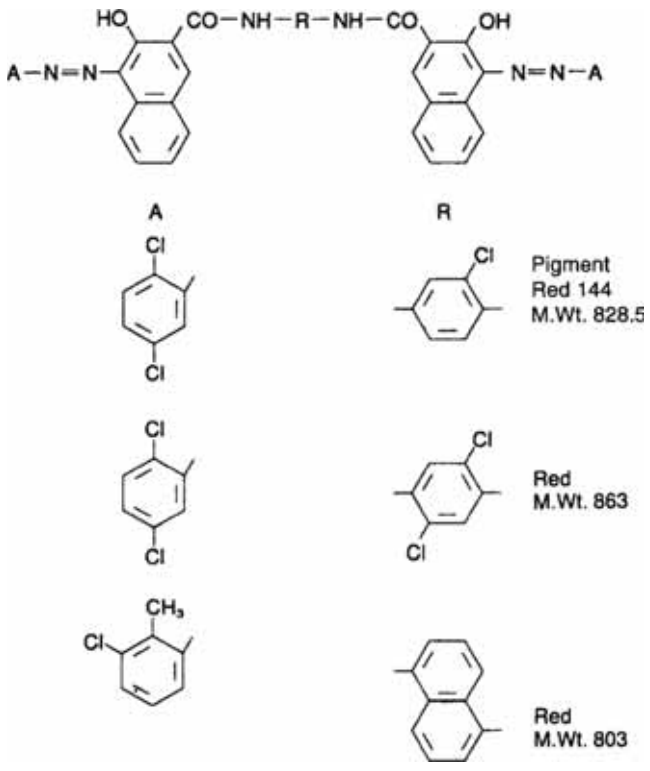


Fig. 11—Structure of the disazo condensation reds.

Pigment Red 214, C. I. Number 200660, Fig. 13, is another example of a disazo condensation red with properties similar to those of Pigment Red 242.

THIOINDIGOLD REDS

The thioindigold serves as a nucleus for a wide range of red to violet pigments including such pigments as Pigment Reds 86, 87, 88, 181, and 198 (see Fig. 14). These pigments are all noted for their brightness of shade and generally good fastness properties, resulting in their use in the coatings industry. Many of these pigments have been discontinued. Pigment Red 88, at one time widely used in automotive finishes, has been withdrawn from the marketplace for environmental reasons. Formulators wishing to find a match for the shade of PR 88 should attempt a match by blending quinacridone violet (PV 19) with perylene violet (PV 29) beginning with a ratio approaching 8 parts of the quinacridone to 1 part of the perylene as a starting point.

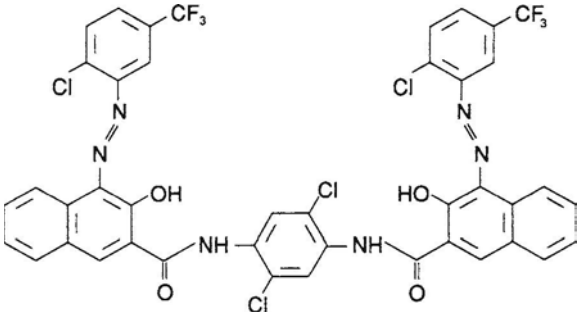


Fig. 12—Structure of Pigment Red 242.

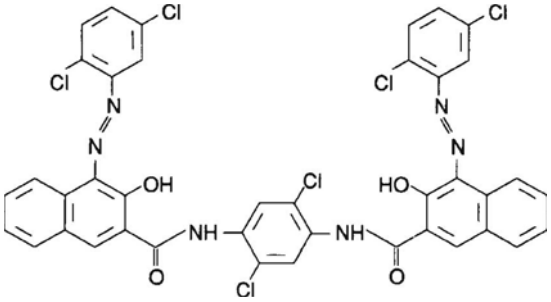


Fig. 13—Structure of Pigment Red 214.

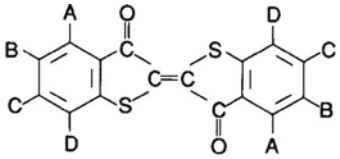
DIKETOPYRROLOPYRROLE REDS

An essential feature common to these pigments, which have been synthesized in hues from scarlet to a very blue shade red, is the two fused five-membered ketopyrrole rings. Reds based upon this structure are currently finding widespread use in both automotive and industrial systems to provide brilliant, saturated red shades of outstanding durability, and are used alongside quinacridones and perylenes. Grades and chemistries in the marketplace are outlined in Table 2. By control of the particle size, diketopyrrolopyrrole pigments may be produced as transparent or opaque grades. Yet again, the excellent fastness properties provided by a pigment of such low molecular weight is explained by the significant intermolecular hydrogen bonding shown to exist throughout the crystal lattice [3]. These pigments also find use in plastics and high-performing printing ink applications.

NOVEL HIGH-PERFORMANCE REDS

In recent years, several novel organic reds have been commercialized and targeted exclusively to meet the requirements of the coatings marketplace.

Pigment Red 257, C. I. Number 562700, Fig. 15, is a nickel complex with a red-violet masstone and a magenta undertone that exhibits fastness properties similar to that of quinacridone. Pigment Red 257 is particularly useful in the formulation of high-quality industrial and automotive coatings. The pigment also exhibits excellent rheological properties in highly pigmented systems.



A	B	C	D	
$-CH_3$	–H	–Br	–H	PR 86
–H	–H	–H	–Cl	PR 87
–Cl	–H	–H	–Cl	PR 88
$-CH_3$	–H	–Cl	–H	PR 181
–Cl	–H	–H	$-CH_3$	PR 198
–H	–Cl	–H	$-CH_3$	PV 36
$-CH_3$	–Cl	–H	$-CH_3$	PV 38

Fig. 14—Structure and key thioindigold reds.

TABLE 2—Listing of current "diketopyrrolopyrrole" based pigments including oranges and reds

Colour Index Name	Colour Index Number	Composition	Comments
PR 254	56110	1-chloro-pyrrolopyrrole	Used in powder and automotive coatings
PR 255	561050	Un-substituted pyrrolopyrrole	Used in industrial and automotive coatings
PR 264	561300	Dibenzyl-pyrrolopyrrole	Very blue shade, automotive and powder
PR 270	N/A	Not declared	Transparent red
PR 272	561150	Methyl-pyrrolopyrrole	Bright red for fibers and plastics end uses
PO 71	561200	Benzyl cyanide- pyrrolopyrrole	Transparent orange for metallic finishes and textile printing
PO 73	561170	Trimethylphenyl-pyrrolopyrrole	Opaque, bright orange for decorative and industrial finishes

Pigment Reds 251 and 252 are both based on the pyrazoloquinazolone structure as described in Fig. 16. These pigments are monoazo compounds derived from pyrazolo(5,1-b)quinazolones as the coupling compound and substituted anilines or polycyclic amines as the diazo component. Each pigment exhibits excellent brightness of hue at full shades, good gloss retention, and high scattering power combined with good light and weather fastness. As such, they are finding increased use in industrial and automotive coatings.

Blues

COPPER PHTHALOCYANINE BLUE

The most important and most widely used blue throughout all applications of the coatings consuming industry is copper phthalocyanine blue, Pigment Blue 15, C. I. Number 74160, Fig. 18.

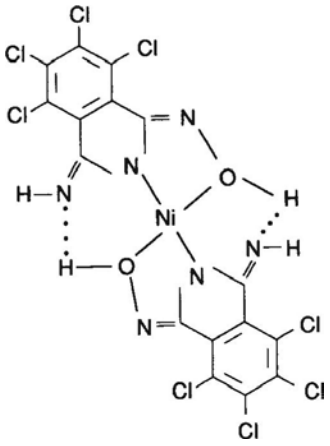


Fig. 15—Structure of Pigment Red 257.

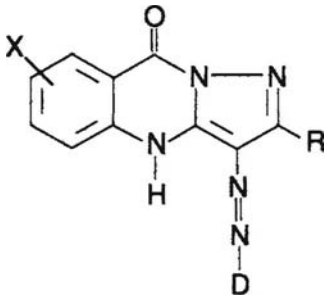


Fig. 16—Generic structure of pyrazoloquinazolone (basis of Pigment Red 251 and 252).

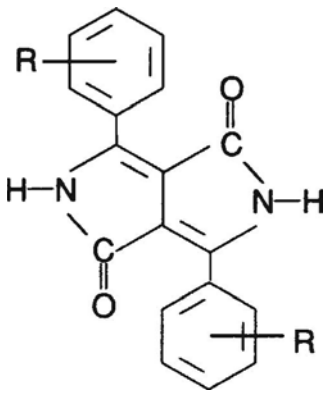


Fig. 17—Generic structure of pyrrolo-pyrrole.

First described in 1928 by chemists working for the Scottish Dye Works, this pigment has steadily increased in importance to become a product with worldwide significance. The only metal derivative of significant commercial use is that of copper, derivatives of other metals having been shown by research to have less desirable shade or fastness characteristics. Metal-free phthalocyanine, Pigment Blue 16, C. I. Number 74100, once found an outlet as a green shade blue. However, this pigment's inferior heat stability and poorer chemical resistance, coupled with the significant higher price than that of the copper-containing pigment, has resulted in a rapid decline in its consumption for all but very special applications. The newer aluminum phthalocyanine, Pigment Blue 79, C. I. Number 741300, has found use in aqueous ink applications where the presence of copper is a problem.

Copper phthalocyanine is predominantly available in two crystal forms, the alpha and the beta forms. The alpha crystal is described as Pigment Blue 15, 15:1, and 15:2. It is a clean, bright red shade of blue. The beta crystal is described as Pigment Blue 15:3 and 15:4, and is a clean green or peacock shade. The beta form is the most stable crystal form and readily resists re-crystallization. The alpha form, conversely, is the least stable form, which readily converts to the more stable, green shade, beta crystal. As such, the crystal requires special proprietary treatments to produce a red shade product that is stable to both crystallization and flocculation.

Copper phthalocyanine gives excellent performance in most coatings applications, but there is considerable variation between the surface treatments employed to stabilize the alpha crystal types. The coatings formulator should bear this in mind when choosing a grade for a specific application. Use of any of the unstabilized grades in strong solvents or in systems that experience heat during dispersion or application will result in a shift in shade to the greener side and a loss of strength as re-crystallization takes place within the unstabilized crystal.

Pigment Blue 15, C. I. Number 74160, is a red shade, alpha crystal. It is the least stable of the family and as such is referred to as "crystallizing red shade blue."

Pigment Blue 15:1 is a modified alpha crystal also having a red shade, but with modification to stabilize the structure against phase transformation to the beta crystal. In some instances, the molecule is chlorinated to the extent of one molecule of chlorine per molecule of copper phthalocyanine to give "monochlor" blue (C. I. Number 74250).

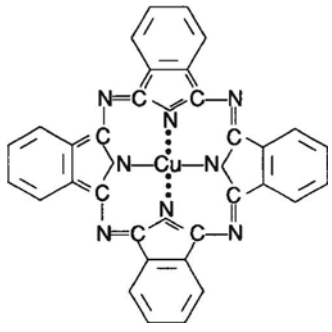


Fig. 18—Copper phthalocyanine, PB 15.

Pigment Blue 15:2, described as "non-crystallizing non-flocculating" red shade blue, is an alpha crystal that is stabilized against both flocculation and crystallization by using additive technology. Such additives are introduced during the manufacturing or blending operation, and are essentially derivatives of copper phthalocyanine that confer stability by a steric hindrance mechanism.

Pigment Blue 15:3 represents the most stable crystal, green shade, beta copper phthalocyanine.

Pigment Blue 15:4 is a descriptive of a beta blue that has been modified with phthalocyanine-based derivatives that are designed to be system specific to confer flocculation resistance to the pigment after the dispersion process.

Other specialized, more expensive crystal modifications also exist such as Pigment Blue 15:6, a very red shade, epsilon crystal.

Copper phthalocyanine is a pigment that offers brightness, cleanness, strength, and economy with all-around excellent fastness properties. The only drawback to this pigment is its tendency to change to a coarse, crystalline nonpigmentary form when used in strong solvent systems. If the crystal has not been adequately stabilized, it has a tendency to flocculate from white pigments such as titanium dioxide when used to tine such paint and lacquer systems. Another negative is the fact that copper phthalocyanine blues exhibit the phenomenon of bronzing when applied at masstone levels, deep tints, and in metallic systems.

Miscellaneous Blues and Violets

Indanthrone Blue—Pigment Blue 60, C. I. Number 69800. Belonging to the class of pigments described as "vat pigments," Indanthrone Blue is a very red shade, nonbronzing flocculation-resistant pigment with outstanding fastness properties. Two crystal modifications are available on the market, the more common α-modification and the more recently introduced even redder shade δ-modification. This pigment is used in paint systems requiring high durability of an intense red shade blue as a shading pigment at low levels where the expense of using the pigment is justified.

Carbazole Violet—Pigment Violet 23, C. I. Number 51319. A pentacyclic structure, intense violet shade pigment that possesses excellent fastness properties. It has found use in virtually all applications including paint, plastics, and inks, though use in the automotive industry has diminished as a result of increasing demands for durability. The pigment typically has a very high surface area and provides high tinctorial strength.

Yellows

MONOARYLIDE YELLOWS

These are azo pigments whose manufacture is based on the diazotization and coupling sequence as mentioned when dealing with azo reds. The structures of the major monoarylide yellows are illustrated in Fig. 19.

Hansa Yellow G, Pigment Yellow 1, C. I. Number 11680. This is a bright yellow pigment that is made by coupling diazotized 2-nitro-4-methyl aniline onto acetoacetanilide. It has a major use in trade sales, emulsion, and masonry paints. Its major disadvantages are its poor bleed resistance in most popular solvents, poor light fastness in tint shades, and very inferior bake resistance due to its tendency to sublime.

Hansa Yellow 10G, Pigment Yellow 3, C. I. Number 11710. This pigment is a very green shade yellow that is made by coupling the diazo of 4-chloro-3-nitro aniline onto 2-chloro acetoacetanilide. Greener in shade than Pigment Yellow 1, this pigment is used in the same types of applications and suffers from the same deficiencies as Pigment Yellow 1 with the exception that Pigment Yellow 3 is suitable for use in exterior applications at high tint levels.

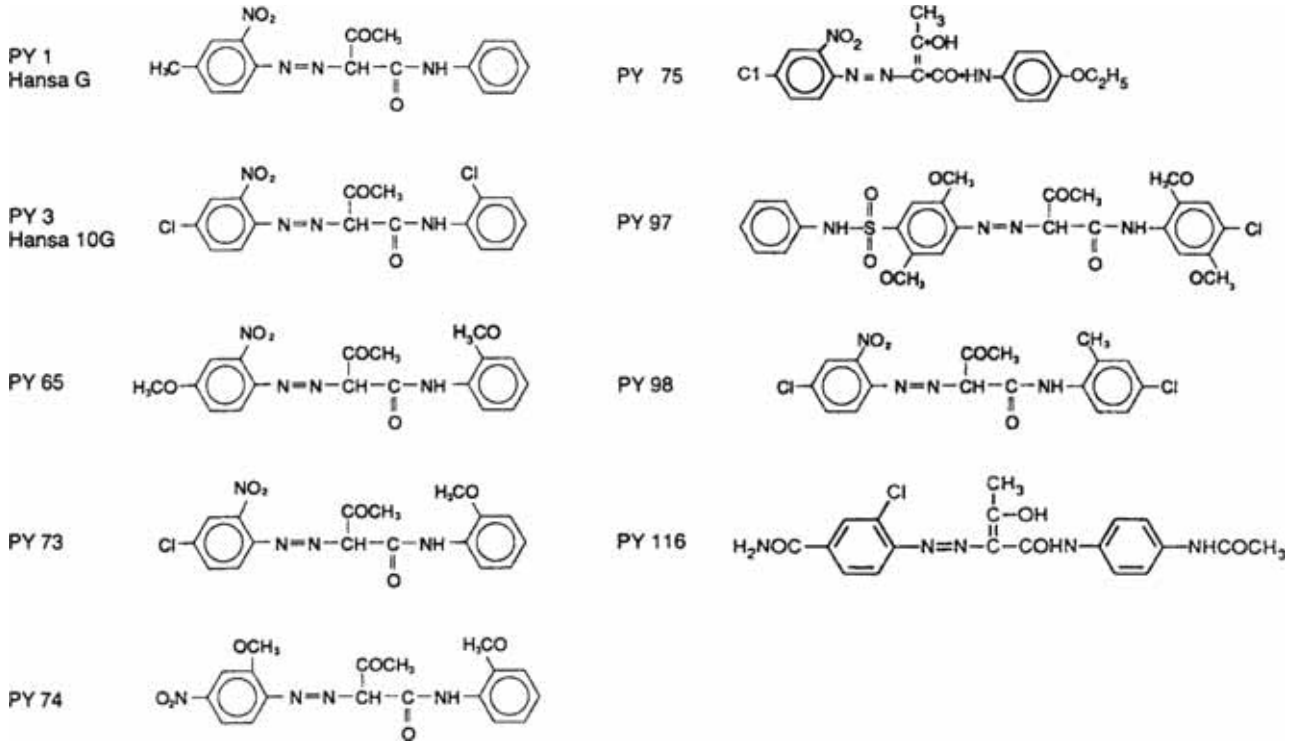


Fig. 19—Structures of the major monoarylide yellows.

Pigment Yellow 65, C. I. Number 11740. This is a monoarylide pigment produced by coupling diazo 2-nitro-methoxy aniline with 2-acetacetanlaidine. It has a redder shade than the two yellows previously discussed. Pigment Yellow 65 is used in trade sales, latex, masonry paints, and road traffic marking paints that are specified as being lead free. The bleed resistance and baking stability are little improved over PY 1 and PY 3.

Pigment Yellow 73, C. I. Number 11738. This pigment is prepared by coupling diazo 3-chloro-2-nitro aniline onto 2-acetoacetanisidine. It has a shade close to that of Pigment Yellow 1 that finds use in a similar application. Not considered durable enough for exterior application, Pigment Yellow 73 nevertheless plays an important role in interior inter-mix systems due to its stability against re-crystallization in the presence of glycols and wetting agents used in latex systems.

Pigment Yellow 74, C. I. Number 11741. This is the produce obtained from the coupling of diazo 4-nitro-2-anisidine onto 2-acetoacetanisidide, which offers the user a pigment suitable for outdoor applications that is considerable stronger and somewhat greener than Pigment Yellow 1. Major outlets, as with all the monoarylide yellows, are in latex trade sales and masonry paints. Additionally, an opacified grade is available that is optimized for its exterior durability, although of lower tint strength than the normal transparent grade.

Pigment Yellow 73 and the opaque grades of Pigment Yellow 74 show the least tendency to crystallize in organic solvent systems.

Pigment Yellow 75, C. I. Number 11770. This is a pigment produced by the coupling of 4-chloro-2-nitroaniline onto acetoacetophenetidide. It is a red shade yellow that has found use in traffic paint.

Pigment Yellow 97, C. I. Number 11767. This yellow is derived from the coupling of diazo 4-amino-2,5-dimethoxy-benzene sulphoanilide to 4-chloro-2,5-dimethoxy acetoacetanilide. It surpasses the Hansa yellows in solvent bleed and light fastness, especially in reduced shades. This yellow is finding use in high-quality decorating paints.

Pigment Yellow 98, C. I. Number 11727. Similar in shade to Pigment Yellow 3, but considerably stronger and more heat stable, this pigment has only met with limited commercial success in trade sales, masonry, and decorative paints. Manufacture is accomplished by coupling diazo 4-chloro-2-nitro aniline onto 4-chloro-2-methyl acetoaceta-nilide.

Pigment Yellow 116, C. I. Number 11790. This is a product from the coupling of diazo 2-chloro-5-carbamoyl aniline onto 4-acetylamino acetoacetanilide. It is similar in shade to light chrome yellow (PY 34) and has improved

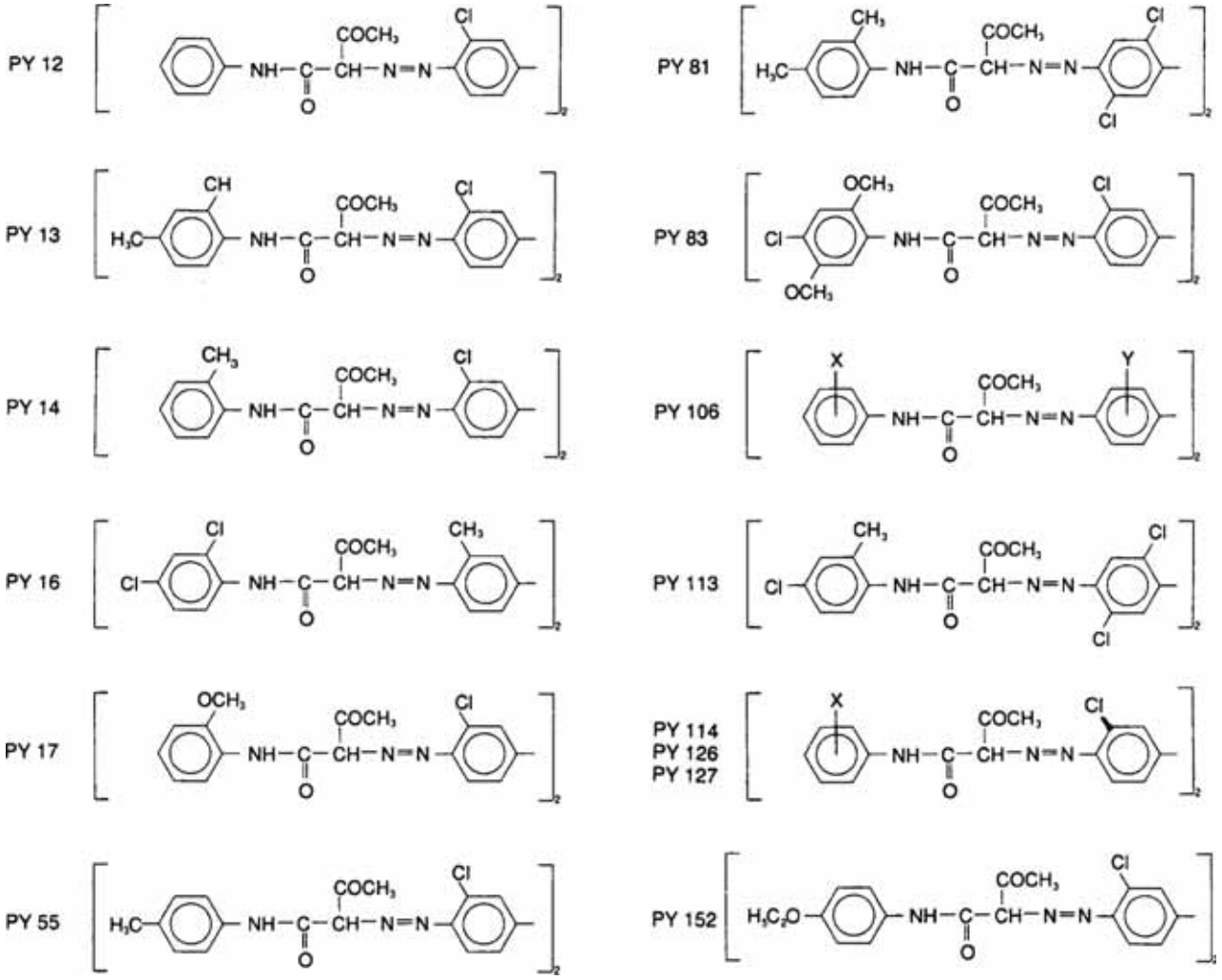


Fig. 20—Structures of the major diarylide yellows.

light, heat, and solvent fastness as compared to the other monoarylide yellows. As may be expected from its shade, this pigment's major use is in lead-free coatings.

METALLIZED AZO YELLOWS

Pigment Yellow 62, C. I. Number 13940, Calcium Salt. Pigment Yellow 62 is rather unique in that it is a metallized azo yellow that finds use in coloration of rubber, low density polyethylene, poly(vinyl chloride), and polypropylene fibers. This pigment is a calcium-based azo yellow produced from the diazotization and coupling of 4-amino-3-nitro benzene sulfonic acid onto acetoaceto-toluidide followed by conversion of the sodium salt to that of calcium. The pigment is a green shade yellow with good economy and moderate fastness properties to light, acids, and alkali. The maximum heat stability is rated at 475°F, measured at 0.1 % pigment with 1.9 % TiO_2 and a 5-min. dwell time. It is for this reason that Pigment Yellow 62 may have application in certain powder coating applications where economics are key.

DIARYLIDE YELLOWS

The structures of this commercially important range of organic yellows are shown in Fig. 20. This figure clearly shows the similarity between each of these pigments, which are principally a backbone structure centered on 3,3′-dichlorobenzidine with modifications to the shade and properties by variation of the coupling component used in the pigment's manufacture. Table 3 contains a summary of the properties of the major diarylide yellow pigments of commercial significance.

Each of the diarylide yellows offer low cost, reasonable heat stability, and moderate chemical resistance. The major worldwide market for this class of yellows is the printing ink industry. These yellows are approximately twice as strong as the monoarylide yellows dealt with above. Furthermore, they offer improved bleed resistance and heat fastness. Nevertheless, none of the diarylide yellows have durability properties that would allow for their use in exterior situations and, as such, should never be considered for outdoor applications. Minor applications exist in the area of toy enamels and pencil coatings, especially if a lead-free formulation is specified.

A range of opacified diarylide yellows is available. They undergo an after treatment that reduced their surface area and, consequently, opacity was increased. These specific types also exhibit improved fastness properties when compared against their non-opacified, transparent counterparts.

BENZIMIDAZOLONE YELLOWS

These yellows are illustrated in Fig. 21. They take their name from the fact that each features the 5-acetoacetylaminobenzimidazolone molecule as the coupler component. These pigments have exceptional fastness to heat, light, and over-striping. These properties are directly attributed to the benzimidazolone group within the pigment's structure. They were first described in 1964 and offered to the marketplace in 1969. They were initially used for the coloring of plastics, but the pigments are finding increased use in the coatings industry where their excellent fastness properties are demanded. Table 4 gives a summary of the properties of this class of pigments.

HETEROCYCLIC YELLOWS

All these yellow pigments contain a heterocyclic molecule within their structure as illustrated by the examples presented

TABLE 3—Properties of the major diarylide yellows

Colour Index Name	Common Name	Properties
PY 12	AAA Yellow	Poor lightfastness and bleed resistance. Major use is in printing inks.
PY 13	MX Yellow	Redder shade than PY 12, improved heat stability and solvent fastness. Major use is in printing inks.
PY 14	OT Yellow	Green shade, some use in interior finishes, poor tint light fastness.
PY 16	Yellow NCG	Bright green shade, with good heat and solvent fastness. Used in full shade for coatings.
PY 17	OA Yellow	Green shade. Some use in interior finishes. Poor light fastness.
PY 55	PT Yellow	Red shade. Some use in interior finishes, poor light fastness. Isomer of PY 14.
PY 81	Yellow H10G	Bright green shade. Same shade but much stronger than PY 3.
PY 83	Yellow HR	Very red shade. Improved transparency, heat stability, and light fastness over PY 12. Some interior finish use.
PY 106	Yellow GGR	Green shade. Poor tint light fastness. Major use in packaging inks.
PY 113	Yellow Hi0GL	Very green shade. More transparent than PY 12 and offering better heat and solvent fastness. Some interior use.
PY 114	Yellow G3R	Red shade. Improved solvent and light fastness over PY 12. Major use in oil-based inks.
PY 126	Yellow DGR	Similar shade to PY 12 but offering improved heat and solvent fastness. Major use is in printing inks.
PY 127	Yellow GRL	Bright red shade. Poor light fastness. Major use is in offset inks.
PY 152	Yellow YR	Very red, opaque pigment. Poor light fastness. Some use in interior finishes as a lead-chrome replacement.

in Fig. 22. Even with their molecular complexity, these new high-performance yellows continue to be used to satisfy the exacting demands of the coating industry. Pigments such as Isoindoline Yellow (PY 139) and Quinophthalone Yellow (PY 138) are typical examples of such complex, novel chromophores introduced in 1979 and 1974, respectively.

All of these pigments find application in high-quality coatings where the end-use can justify the price of these high-performing products. Table 5 summarizes the properties of the heterocyclic yellows available that find some use within the coatings industry.

Oranges

Table 6 lists those orange pigments that have significance in today's marketplace.

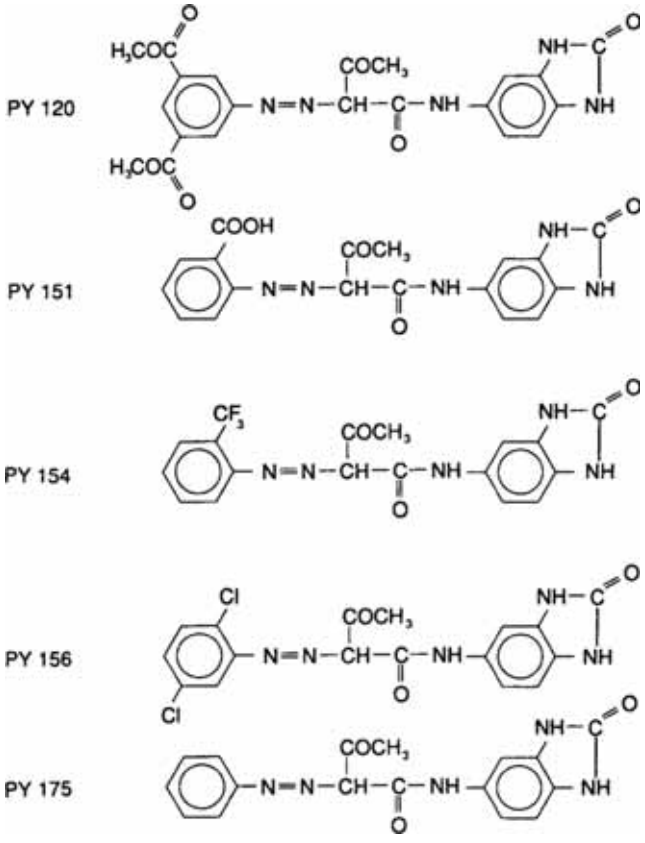


Fig. 21—Structures of the benzimidazolone yellows.

AZO-BASED ORANGES

These oranges show considerable variation in structure as can be seen from Fig. 23. All, however, have the azo chromophore (—N═N—) featured within the molecule. The benz-imidazolone oranges all feature the azo chromophore in addition to all being produced using 5-acetoacetylaminobenzimidazolone as the coupling agent.

Orthonitroaniline Orange, Pigment Orange 2, C. I. Number 12060. This pigment is prepared by the chemical diazotization and coupling technique used for all azo pigments. It is the product of coupling diazo orthonitro aniline onto beta-naphthol. Its major outlet is in printing inks, and its use is not recommended in coatings due to the pigment's poor resistance to solvents and inferior light fastness.

Dinitroaniline Orange, Pigment Orange 5, C. I. Number 12075. Coupling diazo dinitroaniline onto beta-naphthol produces Pigment Orange 5. This pigment has good light fastness in full tone and moderate solvent fastness under this condition. As such, Pigment Orange 5 finds outlets in latex paints and air-dry architectural and industrial finishes. Its poor baking stability rules out its use in high temperature baking enamels.

Pyrazolone Orange, Pigment Orange 13, C. I. Number 21110, is synthesized by coupling tetrazotized 3,3′-dichlorobenzidine onto 3-methyl-1-phenyl-pyrazol-5-one. The pigment is a bright, clean yellow shade product that may be used for interior coatings, particularly as a replacement for lead-based orange pigments such as Molybdate Orange.

Dianisidine Orange, Pigment Orange 16, C. I. Number 21160, is a diarylide orange produced by coupling tetrazotized 3,3′-dimethoxybenzidine onto acetoacetanilide. It finds usage in baking enamels and interior coatings at full shade.

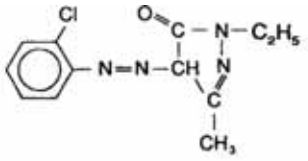
Tolyl Orange, Pigment Orange 34, C. I. Number 21115. This is a diarylide pigment manufactured by coupling tetrazo 3,3′-dichlorobenzidine onto 3-methyl-1-(4′methylphenyl (-pyrazol-5-one). This orange is a bright, reddish shade offering moderate light fastness and good alkali resistance, but poor solvent fastness. As such, the pigment is used in interior coating applications, particularly where a lead-free formulation is specified.

Pigment Orange 46, C. I. Number 15602. A metallized azo pigment manufactured by coupling diazotized 2-amino-5-chloro-4-ethyl benzene sulfuric acid onto beta-naphthol followed by reacting this product with barium to yield the barium salt of the pigment. The pigment is not recommended for coatings due to its poor light fastness,

TABLE 4—Properties of benzimidazolone yellows

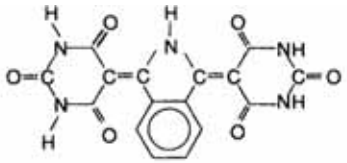
Colour Index Name	Common Name	Properties
PY 120	Yellow H2G	Medium shade, good solvent fastness, excellent light fastness, used in industrial finishes.
PY 151	Yellow H4G	Greener shade with good solvent fastness, excellent light fastness. Industrial and refinish applications.
PY 154	Yellow H3G	Green shade, but redder than PY 151. Good solvent fastness, excellent light fastness. Industrial and automotive refinish.
PY 156	Yellow HLR	Redder shade, transparent, good exterior durability in full shade and tint. All exterior coatings and refinish areas.
PY 175	Yellow H6G	Very green shade. Good solvent fastness, excellent light fastness. Used in all exterior coatings and refinish areas.

PY 60



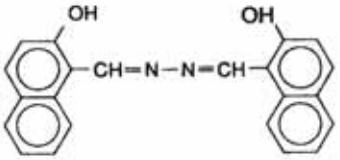
Arylide Yellow

PY 139



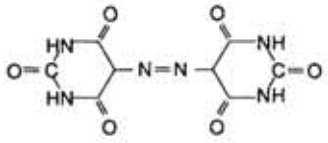
Isoindoline Yellow

PY 101



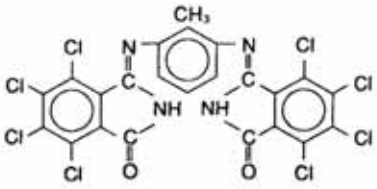
Methine Yellow

PY 150



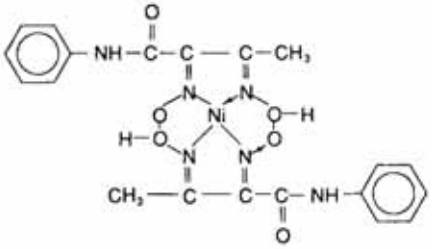
Pyrimidine Yellow

PY 109



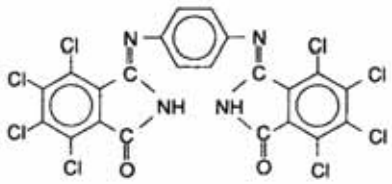
Tetrachloro Isoindolinone Yellow

PY 153



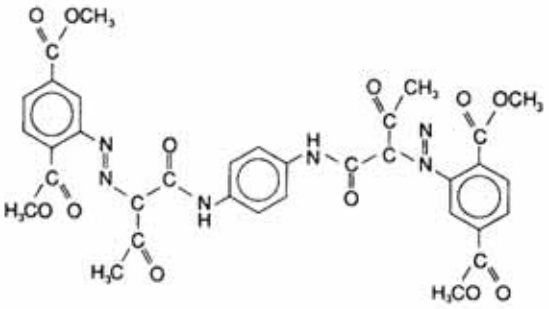
Nickel Dioxine Yellow

PY 110



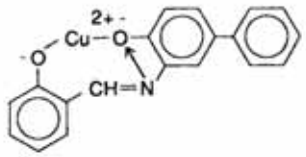
Tetrachloroisoindolinone Yellow

PY 155



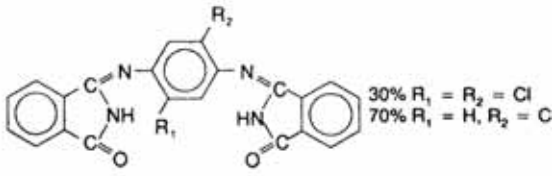
Azo Condensation Yellow

PY 117



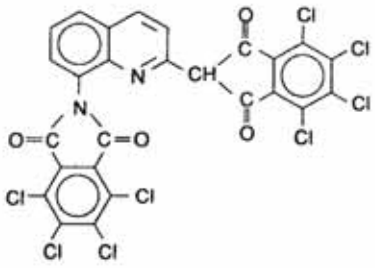
Azomethine Yellow

PY 173



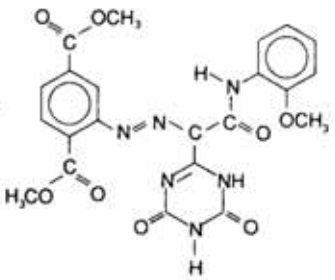
Isoindolone Yellow

PY 138



Quinophthalone Yellow

PY 182



Triazinyl Yellow

Fig. 22—Structures of the heterocyclic and azo condensation yellows.

TABLE 5—Properties of the heterocyclic yellows	
Colour Index Name	**Properties**
PY 60	Arylide Yellow. Very red shade. Moderate light and solvent fastness. Good acid and alkali fastness Trade sales, latex, and masonry paints.
PY 101	Methine Yellow, bright yellow. Highly transparent and exceptionally brilliant. Industrial finishes and specialty coatings. Moderate bleed and alkali resistance.
PY 109	Tetrachloroindolinone. Green shade with excellent brightness, strength, and durability. Automotive finishes.
PY 117	Greenish yellow copper complex of an azomethine. Excellent chemical, light and heat fastness. Specialty finishes.
PY 139	Azomethine Yellow, very green shade. Excellent chemical, light, and heat fastness. Industrial and specialty coatings.
PY 138	Green shade quinophthalone. Clean hue and excellent overall fastness properties. High-quality industrial and automotive areas.
PY 139	Red shade Isoindoline. Similar in masstone to medium chrome (PY 34). Excellent light and solvent fastness. Industrial and automotive coatings.
PY 150	Pyrimidine Yellow. Very green shade. Good heat and light fastness. Industrial coatings.
PY 153	Red shade nickel dioxine. Excellent fastness properties except poor acid resistance. Specialty coatings and baking enamels.
PY 155	Azo Condensation Yellow. Green shade, excellent fastness properties in full shade. Industrial and specialty coatings.
PY 173	Isoindolone Yellow. Very green shade with excellent fastness properties. Industrial and specialty finishes.
PY 182	Triazinyl Yellow. Medium shade with excellent fastness properties at masstone levels. Industrial finishes.

TABLE 6—Orange pigments of significance in the coatings industry		
Colour Index Name	**Colour Index Number**	**Chemical Type**
PO 2	12060	Azo
PO 5	12075	Azo
PO 13	21110	Bisazo
PO 16	21160	Bisazo
PO 31	20050	Bisazo condensation
PO 34	21115	Bisazo
PO 36	1780	Benzimidazolone (Azo)
PO 38	12367	Azo
PO 43	71105	Perinone
PO 46	15602	Azo
PO 48	73900/73920	Quinacridone
PO 49	N/A	Quinacridone
PO 60	11782	Benzimidazolone (Azo)
PO 61	11265	Tetrachloroisoindolinone
PO 62	11775	Benzimidazolone (Azo)
PO 64	12760	Heterocyclic hydroxy
PO 67	12915	Pyrazoloquinazolone

inferior alkali resistance, and inadequate solvent fastness. It finds its major outlet in the printing ink marketplace.

Benzimidazolone Oranges, Pigment Orange 36, C. I. Number 11780. This product is formed from the coupling of diazo 4-cloro-2-nitroaniline to 5-acetoacetylamino-benzimidazoloe. It is a bright red shade orange with high tint strength. In its opacified form, this pigment offers excellent fastness to both heat and solvents and a hue similar to Molybdate Orange (PR 104). As such, the pigment is used in automotive and high-quality industrial finishes that must be lead free and that were formerly made using the lead-based pigment Molybdate Orange.

Pigment Orange 60, C. I. Number 11782. This is a transparent, yellow shade orange that also exhibits excellent heat and solvent fastness with an exterior durability that allows the pigment to be used in automotive and high-performance industrial finishes. It is made by coupling acetoacetylamino-benzimidazolone to 4-nitro-analine.

Pigment Orange 62, C. I. Number 11775. This is a relatively new member of the benzimidazolone oranges. It is a yellow shade pigment that shares the light fastness properties of PO 36 and PO 60, but has inferior solvent fastness and exhibits a slight bleed in alkaline systems. Currently, the pigment is being used in oil-based inks and artists' colors. Its use in the coatings industry is being explored.

MISCELLANEOUS ORANGES

Fig. 24 illustrates the structures of those oranges that fall into a "miscellaneous" category as far as such structures have been declared. Table 7 summarizes the properties of

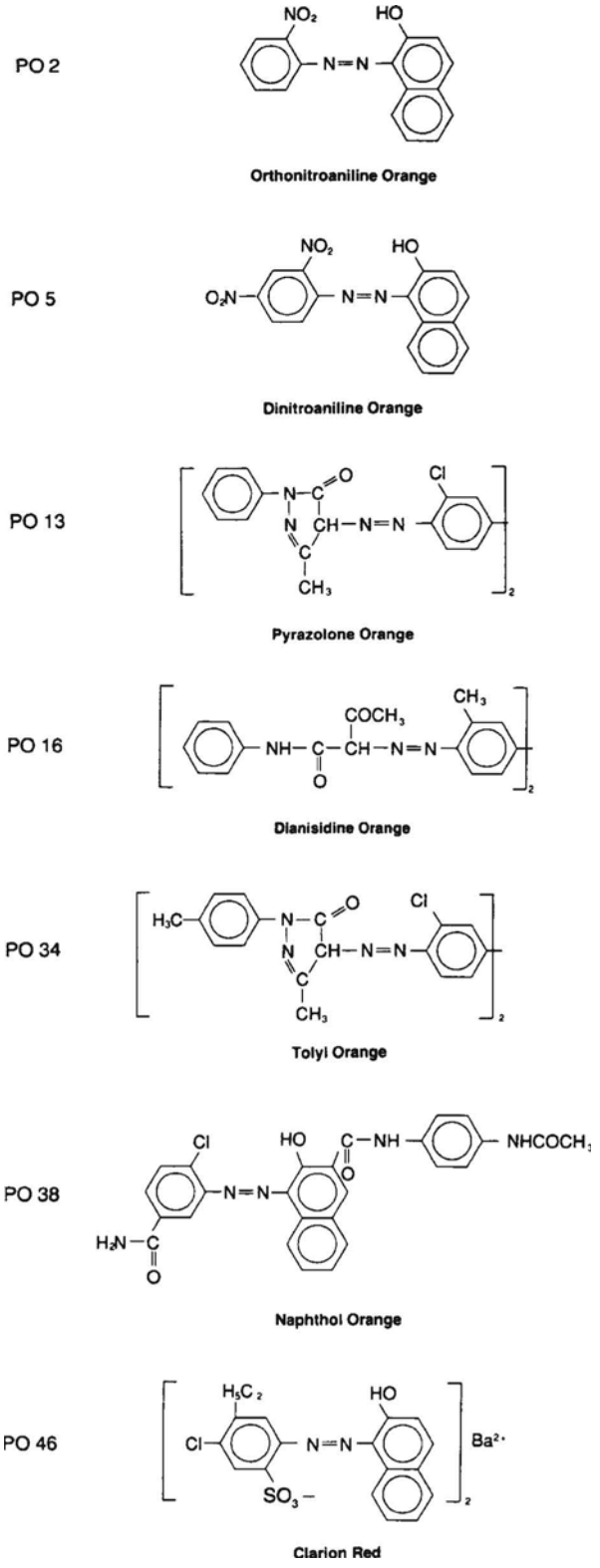


Fig. 23—Structures of azo-based oranges.

this series of pigments, each of which is finding increased usage within the coatings industry.

Greens

COPPER PHTHALOCYANINE GREEN

When a self-shade green is required, rather than a green produced by mixing blue and yellow, copper phthalocyanine is the green of choice. This pigment is based on halogenated crude copper phthalocyanine involving either chlorine or a mixture of chlorine and bromine. The chlorinated product is Pigment Green 7, whereas the mixed chlorine/bromine product is Pigment Green 36.

Pigment Green 7 is a blue shade green made by introducing 13–15 chlorine atoms into the copper phthalocyanine molecule, whereas Pigment Green 36 is a yellow shade green based on a structure that involves progressive replacement of chlorine in the phthalocyanine structure with bromine. Fig. 25 illustrates the proposed structures of the phthalocyanine greens. The most highly brominated product, Pigment Green 36, sometimes is referred to as "green 6Y" or "green 8G." It has an extreme yellow shade and contains 12–13 chlorine atoms.

Both greens exhibit outstanding fastness properties to solvents, heat, light, and outdoor exposure. They can be used equally effectively in both masstone and tints down to the very pale depth of shades. Metallic automotive paints may feature phthalocyanine green at all shade depths.

MISCELLANEOUS GREENS

Table 8 contains a brief summary of the properties of other commercially available organic green pigments that may find some use in the coatings industry. It should be noted, however, that green blends such as Brunswick Green (PF 15) and Mineral or Phthalo Chrome Green (PG 13), once widely used in industrial coatings, are now being replaced by the more economic organic green—phthalocyanine green.

Pigment Greens 1, 2, and 4 are triphenyl-methane-based dyes complexed with PTMA to allow their use as pigments. Their fastness properties are inadequate for most applications.

Pigment Green 8, C. I. Number 10006, is the bisulfide complex of 1-nitroso-2-naphthol reacted with ferrous sulfate and then with sodium hydroxide. It is one of the oldest chelate-based pigments that maintain some minor commercial significance as a colorant for cement. Exhibiting excellent alkali stability, this pigment suffers from poor acid fastness.

Testing of Pigments for Use in Coatings

Many tests can be applied to a pigment to assess its suitability in a coating formulation. However, it is of paramount importance that the formulator is satisfied that the tests have a clear relationship to the end use of the coating. It is pointless to evaluate a pigment's interior performance only to then use the pigment in an exterior application. For a pigment to be merely the shade and opacity as required by the customer is not an adequate safeguard that the pigment will perform as expected once the product is employed in its intended end use. In today's marketplace, more than at any other time in the past, with quality relationships being of such commercial significance, it is vital that the user and supplier have a full understanding of what is expected of any coating formulation that is in commercial production. The coatings business is under constant change and review, and it is in this atmosphere of change that care must be taken to ensure "fitness for use" of any colored organic pigment is fully explored.

Many types of tests will be run on a pigment that are not specific to an application but which are a property of

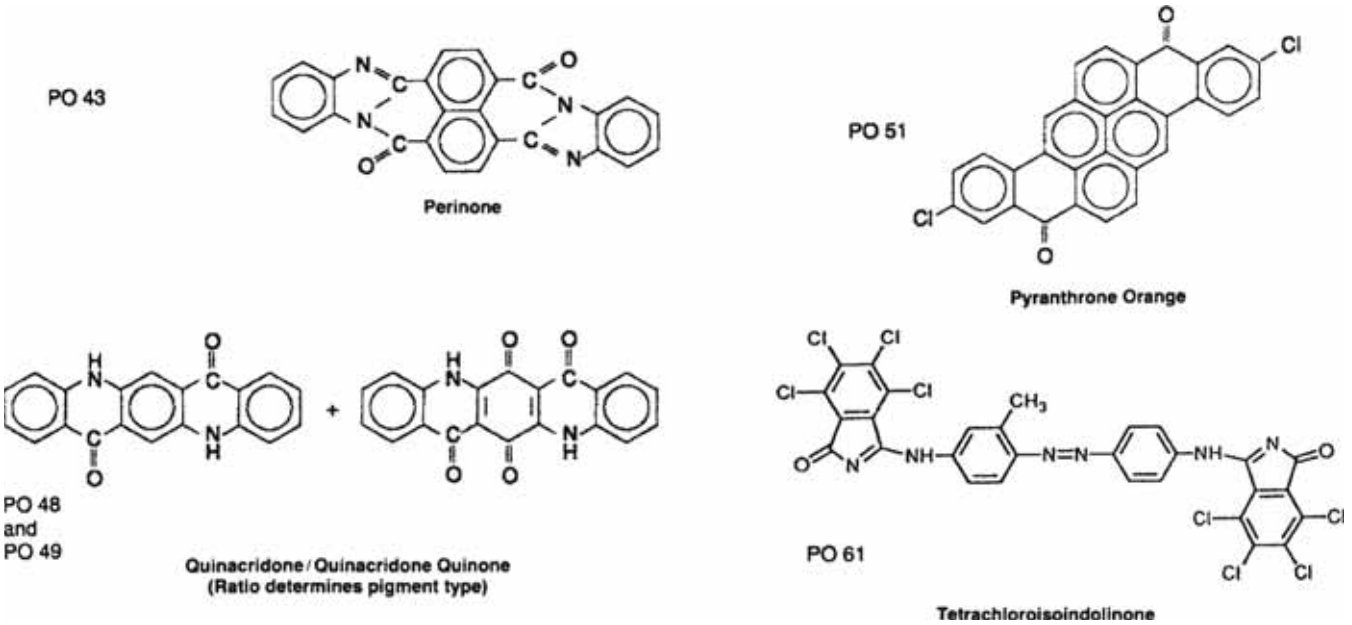


Fig. 24—Structures of the miscellaneous oranges.

TABLE 7—Properties of the miscellaneous orange pigments

Colour Index Name	Properties
PO 43	Perinone. Red shade. Strong clean vat pigment with excellent fastness properties. Used in metallized finishes and high-grade paints. Shows slight solvent bleed.
PO 48	Quinacridone gold. Yellow shade. Excellent light fastness. Lacks rightness in masstone. Used in metallics.
PO 49	Quinacridone deep gold. Red shade. Dull masstone. Excellent durability. Used in metallics.
PO 51	Pyranthrone orange. Medium shade. Excellent solvent, light, and heat fastness. Dull in tint. Exhibits slight solvent bleed. Used in air-dry and baked enamels.
PO 52	Pyranthrone orange. Red shade. Vat pigment with excellent solvent, light and heat fastness. Dull in tins. Slight solvent bleed. Used in air-dry and baked enamels.
PO 61	Tetrachloroisoindolinone orange. Medium shade. Exhibits some solvent bleed. Used in metallic automotive finishes.
PO 64	Bright red shade. Excellent solvent and light fastness. Used in industrial coatings.
PO 67	Yellow shade. Excellent brilliance in full shade. Good gloss retention. Very good weather and light fastness in full shade. Used in industrial and automotive coatings.

the pigment in question and which need to be known in spite of the end use application.

COLOR AND TINT STRENGTH [3]

The most obvious property of a pigment is its hue, that is, its color as being distinctly red, orange, yellow, green, blue, violet, etc., and the finer detail that distinguishes a green shade blue from a red shade blue. The other properties may be taken as those that are significant when the pigment is used in full tone and those of significance when the pigment is used in reduced shades after diluting the full shade with an opaque white, such as titanium dioxide (PW 7).

Evaluation of any pigment must include a test of full color or masstone that requires inspection of the pigment, undiluted with white, but fully dispersed in a medium that has relevance to the coating's formulation. Inspection of this full color shows the hue, intensity, transparency, cleanness, and jetness of the pigment. Comparison of these factors by making side-by-side evaluations with a standard or specification full color will illustrate just how close the pigment being used comes to the standard. The full color can then be tinted with a white base such as one made from titanium dioxide to enable the pigment's tinting strength to be assessed against a previously approved standard or control. Such a tint is known as a bleached, tinted, or reduced drawdown or display.

OIL ABSORPTION [4]

A broad definition of oil absorption is the amount of oil or vehicle that produces a uniform, cohesive paste when thoroughly incorporated with the test pigment. For standard purposes, it is the amount of refined linseed oil, by either weight or volume, necessary to produce a cohesive paste from 100 g of dry pigment. Since the transition point of going from a partially wetted powder to a cohesive paste is not a clearly defined measure, this test will always be

subject to differences between laboratories and technicians as to when the test's end point is reached. The figure for oil consumption is used by many coating formulators to give an indication of the effect different pigments will have on the flow properties of the system and to calculate the pigment loading limits.

BLEED TEST [5]

This test gives an indication of the extent to which the pigment will dissolve, however minutely, in the solvents the pigment is likely to be exposed to during its use. Additionally, an over-stripe test can be incorporated where the coating containing the pigment under test is over-striped with a white paint and allowed to dry. The extent of the discoloration of the white is an indication of the pigment's over-stripe bleed.

An attempt can be made to quantify this bleed by use of the "Grey Scale for Assessing Change in Color" (B.S. 2662) where the bleed is rated from 5, representing no visible bleed, to 1, corresponding to considerable bleed.

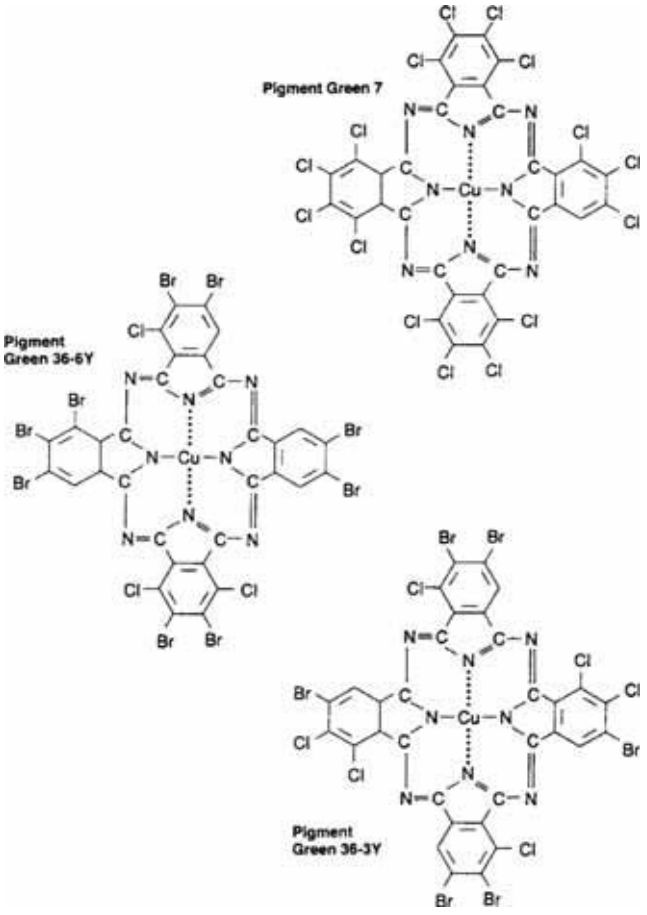


Fig. 25—Proposed structures for phthalocyanine greens (PG 7 and PG 36).

FASTNESS TESTS

The term "fastness" is used in this context to relate to how susceptible or durable a pigment is to the parameter under test. As such, the pigment's fastness to light, heat, solvent, etc., can be measured and rated using a "Fastness Scale." These scales rate a pigment from 1 (poor fastness) to 5, the highest number (excellent fastness), in all cases except light fastness, which is subdivided into 1 through 8, 1 being total failure while the highest number, 8, carries an outstanding rating corresponding to "no visible change" over the period of exposure.

Among those properties important to the formulator are fastness to solvents, where bleeding is observed by allowing a quantity of the dry pigment to stand for 24 h in contact with a solvent and observing any discoloration of the solvent that occurs; fastness to heat, where the effect of stoving temperatures on the pigment formulated into a finished coating is observed; fastness to acidic or alkaline environments; and fastness to light, where several tint levels of a formulation are exposed in such artificial sources as the Xenon or carbon arc fade-ometer [6]. To assess a pigment's behavior in accelerated exposure, the "Blue Wool Scale" is used to calibrate the measuring equipment (B.S. 1006).

EXPOSURE TESTING

It is now generally accepted within the coatings industry on a worldwide basis that the true test of a high-performance pigment is through prolonged outdoor exposure at specifically chosen sites throughout the United States and the world. To this end, many commercial establishments exist that provide a controlled service to expose sprayed panels of pigmented coatings angled in a predetermined manner toward the sun for periods extending as long as five years with assessments at predetermined intervals during this five-year period. Typically, many duplicate coated panels

TABLE 8—Properties of the miscellaneous commercial green pigments

Colour Index Name	Chemical Name	Properties
PG 1	Brilliant Green (Tri-phenylmethane PTMA)	Brilliant blue shade. Poor alkali, soap resistance, solvent bleed and light fastness. May be used in interior finishes.
PG 2	Permanent Green (Tri-phenylmethane PTMA)	Blend of Pigment Green 1 and Pigment Yellow 18. Bright yellow shade. Poor fastness properties overall.
PG 4	Malachite Green (Tri-phenylmethane PTMA)	Bright, blue shade. Poor fastness properties overall.
PG 8	Pigment Green B (Nitroso)	Yellow shade. Dull hue. Poor fastness properties. May be used in interior emulsions.
PG 10	Green Gold (Nickel azo complex)	Yellow shade. Loses metal in strong acid or alkali. Good light fastness. Moderate solvent fastness. Used in automotive and exterior paints.

will be exposed per test with a panel being returned to the formulator every six months, such that a measure of the system's weatherability as a function of time is maintained on record for each pigment and each system used in the outdoor situation.

SPECIFIC GRAVITY [7]

Defined as the mass of a given volume of a substance as compared to the mass of an equal volume of water at a previously specified temperature, the specific gravity of a pigment is used to obtain a bulk density or "bulking volume" of the pigment. This is a subjective test that cannot be easily compared between technicians and between laboratories.

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Inorganic Colored Pigments

Peter A. Lewis[1]

CLASSIFICATION OF INORGANIC PIGMENTS BY CHEMISTRY

BROADLY SPEAKING, COLORED INORGANIC PIGments all fall into one of four groups: lead chromates, metal oxides, sulfides, or sulfoselenides with a few miscellaneous pigments that do not fit into one of these classes such as cobalt blue, ultramarine blue, iron blue, and bismuth vanadate yellow. This chapter describes the chemistry, manufacture, and properties of each of these classes of inorganic pigments. Inorganic whites such as zinc oxide, titanium dioxide, lithopone, and zinc sulfide, while pigmentary in nature and most definitely a part of the coatings industry, fall outside of the scope of this chapter and are discussed elsewhere in this manual.

By chemistry, inorganic pigments can be subdivided as shown in Table 1. In addition to the inorganic pigments listed in Table 1, there also exist a series of pigments classed as mixed metal oxides (MMOs); for example, zinc iron chromite brown (PBr 33), cobalt chromite green (PG 26), cobalt titanate green (PG 50), and cobalt aluminate blue (PB 28 and PB 36). Currently, these mixtures are also referred to as complex inorganic colored pigments (CICP). Often CICP and MMO terminology are used interchangeably, but CICP indicates the pigment is colored. These types of inorganic pigments are sometimes also called ceramic colors because of their widespread use in the ceramics industry. Since they are covered in the next chapter of this book, no additional consideration will be given to these colors in this chapter. Before going further into this chapter, the reader is directed to Chapter 21 for an explanation of the "Colour Index" and the description of pigments, both inorganic and organic, that has become part of a global understanding with respect to pigment nomenclature.

Transparent iron oxide pigments are finding increasing importance for automotive [1] and wood [2] coatings as well as other coating end use areas. These nano-size (average size less than 0.1 μm) [3] pigments are available in various colors, such as yellow, red, green, blue, black, and brown. They provide color with transparency, durability, ultraviolet radiation protection, heat resistance, and improved transparency that accentuates particular coating effects. These interesting pigments are solid materials that achieve their transparency through their extremely small size and shape. They will be mentioned in some, but not in all, of the color classifications given below.

CLASSIFICATION OF PIGMENTS BY COLOR

Most often, when searching for a color to fulfill a particular specification, the coatings formulator is likely to begin the search on the basis of color rather than chemistry. Accordingly, the remainder of this section will concentrate on the classification of inorganic pigments based on their color rather than their chemistry.

Reds

IRON OXIDE REDS

Pigment Red 101, C. I. Number 77491: Fe_2O_3: Available as both natural and synthetic products, these pigments also carry such historic names as haematite (hematite), mars red, ferrite red, rouge, turkey red, bauxite red, chinese red, and Persian Gulf oxide. Transparent red iron oxide pigments are also available. Synthetic iron oxide makes up the largest volume of manufactured iron oxides and is produced by one of five major syntheses:

1. By calcining iron sulfates.

$$12FeSO_4 \cdot H_2O + 3O_2 \rightarrow 2Fe_2O_3 + Fe(SO_4)_3 + 12H_2O$$

2. From synthetic black oxide by calcining the material in a controlled atmosphere containing oxygen.

$$4FeO \cdot Fe_2O_3 + O_2 \rightarrow 6Fe_2O_3$$

3. Precipitated red oxide can be prepared in an aqueous medium by growing seed nuclei in the presence of a ferrous salt and scrap steel, the lightness/darkness of the resulting pigment being determined by the crystal size distribution of the precipitate.
4. By calcining synthetic yellow iron oxide to give the dehydrated product, Fe_2O_3.
5. Reaction of iron pentacarbonyl oxidized in oxygen and water to produce very pure compounds that are mainly used in semi-transparent applications.

Techniques used to prepare transparent iron oxides can be found in the literature [3]. The wide range of red iron oxide shades available, in addition to their acid and alkali resistance and their economy, accounts for the large volume of these pigments used in today's coatings marketplace.

MOLYBDATE ORANGE

Pigment Red 104, C. I. Number 77605: This pigment is a very yellow shade of red that has the common name

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TABLE 1—Summary of colored inorganic pigments

Lead Chromates	
Pigment Yellow 34 $PbCrO_4 \cdot xPbSO_4$	Primrose, medium and dark chrome yellow
Pigment Red 104 $PbCrO_4 \cdot xPbSO_4 \cdot yPbMoO4$	Molybdate orange
Pigment Orange 21 $PbO \cdot xPbCrO_4$	Light and dark chrome orange
Pigment Green 15 $PbCrO_4 \cdot xPbSO_4 \cdot yFeNH_4Fe(CN)_6$	Chrome green (mixture of lead chrome and iron blue)
Metal Oxides	
Pigment Yellow 42 Pigment Yellow 43 $Fe_2O_3 \cdot xH_2O$	Yellow iron oxide—synthetic Yellow iron oxide—natural
Pigment Red 101 Pigment Red 102 Fe_2O_3	Red iron oxide—synthetic Red iron oxide—natural
Pigment Brown 6 Pigment Brown 7 Fe_2O_3	Brown iron oxide—synthetic Brown iron oxide—natural
Pigment Green 17 Cr_2O_3	Chromium oxide green
Pigment Green 18 $Cr_2O_3 \cdot 2H_2O$	Chromium oxide green, hydrated
Sulfides and Sulfoselenides	
Pigment Yellow 35 $CdS \cdot xZnS \cdot yBaSO_4$	Lithopone, cadmium yellow
Pigment Yellow 37 CdS	Cadmium Yellow
Pigment Orange 20 $CdS \cdot xCdSe \cdot yBaSO_4$	Cadmium lithopone orange
Pigment Red 108 $CdS \cdot xCdSe$	Cadmium red
Miscellaneous Types	
Pigment Blue 27 $Fe(NH_4)_2Fe(CN)_6 \cdot xH_2O$	Iron or Milori blue
Pigment Blue 28 $CoAl_2O_4$	Cobalt blue
Pigment Blue 29 $Na_{6-8}Al_6Si_6O_{24}S_{2-4}$	Ultramarine blue
Pigment Violet 16 $MnNH_4P_2O_7$	Manganese violet
Pigment Yellow 184 $4BiVO_4 \cdot 3Bi_2MoO_6$	Bismuth vanadate/molybdate yellow

of molybdate orange, a pigment based on oxides of lead, chromium, and molybdenum with the empirical formula of $PbCrO_4 \cdot xPbMoO_4 \cdot yPbSO_4$, a solid solution of lead chromate, lead molybdate, and lead sulfate.

Molybdate orange is produced by the addition of a solution of sodium chromate, sodium molybdate, and sodium sulfate under carefully controlled conditions into a solution of lead nitrate at a temperature between zero and 40°C to precipitate the mixed crystal. Control of particle size, particle-size distribution, and crystalline shape combine to determine the actual hue of the pigment, from a red shade of yellow to a red shade of orange with specialty hues such as "chili red."

An opaque pigment with high solvent fastness, moderate heat fastness, and good economy, molybdate orange finds its major outlet in the coatings industry, particularly industrial finishes. On the negative side, the pigment has poor alkali and acid resistance; nontreated grades also tend to darken markedly on prolonged exposure to the environment. Additionally, the pigment is based on lead, which has been under an "environmental cloud" for some years. As a result, molybdate orange has been replaced in most paint and coating applications by more expensive, but less toxic, organic pigments such as benzimidazolone orange (PO 36) in architectural, industrial maintenance, and almost all original equipment manufacturer (OEM) paints made in the United States.

CADMIUM RED

Pigment Red 108, C. I. Number 77202 and 77196, $CdS \cdot xCdSe$: Cadmium sulfoselenide red, Pigment Red 108, is a solid solution of cadmium sulfide and cadmium sulfoselenide produced by calcining co-precipitated cadmium sulfides and sulfoselenides. The pigment's hue is determined by the amount of cadmium sulfoselenide incorporated into the solid solution and, to a lesser extent, the temperature of processing. Pigment Red 108:1 (C. I. Number 77202:1), cadmium red lithopone, is a co-precipitate with barium sulfate having the empirical formula:

$$CdS \cdot xCdSe \cdot yBaSO_4$$

Cadmium red features excellent stability to heat, alkali, solvents, and light when used at high tint and masstone levels. The pigment offers the formulator a clean bright red with high chroma. Use of the pigment in an extended formulation with an opaque white as a light tint is not recommended since the durability will suffer at weak tint levels.

MERCURY CADMIUM RED

Pigment Red 113, C. I. Number 77201, $CdS \cdot xHgS$: Mercadium red is yet another calcined co-precipitate. It is mercuric sulfide co-precipitated with cadmium sulfide to give a pigment with the empirical formula CdS-xHgS, offering good hiding properties and good solvent resistance with excellent brightness. The pigment's inferior heat and acid resistance when compared to Pigment Red 108 has limited its use in coatings applications.

Violets

Pigment Violet 15, C. I. Number 77007, $Na5HAl_4Si_6S_4O_{24} \cdot H_2O$ and Pigment Violet 16, C. I. Number 77742, $Mn(NH_4)P_2O_7$: Technically these are blue-shade reds, and the two most important inorganic violet pigments are Pigment Violet 15, ultramarine violet, prepared by the oxidation of ultramarine blue, Pigment Blue 29, and Pigment Violet 16, manganese violet, prepared when manganese dioxide and diammonium phosphate are slurried together at high temperature in phosphoric acid.

Ultramarine violet has good heat and light fastness and a brilliant red shade. The pigment will react with metals to form sulfides, and it finds use in cosmetic applications, specialty acrylic poster paint and artists' colors.

Manganese violet does not possess the same brightness of hue as Pigment Violet 15 and has only moderate opacity and poor alkali resistance. On the plus side, the pigment has improved light fastness and superior resistance to solvents and over-stripe bleed. Major uses are in the plastics and cosmetics industry with some minor uses in artists' colors.

Blues

IRON BLUE

Pigment Blue 27, C. I. Number 77510, $Fe_4[Fe(CN)_6]_3 \cdot xH_2O$: Also known as Chinese blue, Prussian blue and Milori blue, this pigment is manufactured by reacting ferrous sulfate and sodium ferrocyanide in the presence of ammonium sulfite to yield a leucoferricyanide, Berlin white, which is then isolated and dissolved in sulfuric acid and oxidized with sodium chlorate to yield iron blue.

$$Na_4Fe(CN)_6 + FeSO_4 + (NH_4)SO_4 \rightarrow Fe(NH_4)Fe(CN)_6 + 2Na_2SO_4$$

Berlin white

$$6Fe(NH_4)_2Fe(CN)_6 + 3H_2SO_4 + NaClO_3 \rightarrow 6FeNH_4Fe(CN)_6 + NaCl + 3(NH_4)_2SO_4 + 3H_2O$$

Differing grades of iron blue that offer varying depth of hue, strength, oil absorption, and dispersion characteristics exist. Chinese blue, for example, offers a greener undertone, whereas bronze blue features a surface "bronziness" effect that varies with a dependence on the viewing angle and film thickness.

Iron blue offers good resistance to weak acids but markedly poor resistance to even mild alkali; furthermore, the pigment has a tendency to "bleach out" on storage, losing almost all its color when incorporated into a paint formulation that contains oxidizable vehicles such as linseed oil. The pigment has only acceptable light fastness properties when used at masstone levels; extension of the paint with a white, such as titanium dioxide, gives a weak blue tint that will rapidly fade on exposure to the environment.

ULTRAMARINE BLUE

Pigment Blue 29, C. I. Number 77007, is a polysulfide of sodium alumino silicate of unknown constitution. Going by such varied common names as laundry blue, dolly blue, and lapis lazuli, this pigment, which is made by the controlled grinding of a mixture of calcined kaolin, soda ash, sulfur, coal, and sodium sulfate, is Pigment Blue 29. Empirically the product is $Na_6Al_6Si_6O_{24}S_4$, and its major use is as a component of laundry powders and detergent soaps. Metals such as potassium, lithium, or silver may also be incorporated into the structure. Less than 5 % of the production is used in the coatings industry for interior emulsion paints that require high alkali resistance and moderate light fastness.

Yellows

STRONTIUM YELLOW

Pigment Yellow 32, C. I. Number 77839, $SrCrO_4$: Strontium chromate is prepared by precipitating a suitably soluble chromate with an appropriate strontium salt. Finding a primary use in corrosion-inhibiting coatings, this pigment has poor tint strength, low opacity, and unsatisfactory alkali and acid resistance, which limits its more widespread use in the coatings industry. Little of this pigment is now manufactured in the United States.

CHROME YELLOW

Pigment Yellow 34, C. I. Number 77600 and 77603, $PbCrO_4 \cdot xPbSO_4$: A co-precipitate of lead sulfate and lead chromate, Pigment Yellow 34 has the empirical formula $PbCrO_4x$-$PbSO_4$. Various types exist that differ in the ratio of the lead sulfate to lead chromate and as such are described as medium chrome, primrose, and lemon chrome yellows. Typically primrose chrome will contain 23 %–30 % lead sulfate in the solid solution of the co-precipitate, whereas a medium chrome will contain 0 %–6 % lead sulfate. During manufacture, proprietary techniques are employed such that the orthorhombic crystal form is produced almost exclusively in preference to the unstable monoclinic form.

Many different grades of this type of pigment are available and they offer such improvements in properties as better chemical resistance, decreased tendency to darken on exposure, improved weathering, and as a silica-encapsulated product to minimize solubility of the lead contained within the pigment.

Primrose chrome exhibits a very green shade and offers good light fastness, high opacity, and low rheology coupled with economy of use. The coatings industry, closely followed by the ink and plastics industry, is the largest consumer of primrose chrome. Medium chrome is used widely in road-marking paints in the United States where the law requires a yellow marking line as opposed to white. Grades that have been pre-darkened by the use of antimony during the precipitation stage offer much increased stability to weathering since these grades will not darken further on exposure to sulfur in the atmosphere. Due to the concerns regarding the toxicity of lead-based pigments and their persistence in the environment, there has been a very significant move to replace such pigments with organic equivalents that do not contain lead [4]. The use of lead-based pigments, both yellows and white, in architectural and decorative paints was discontinued in the United States over 25 years ago.

ZINC CHROMATE

Pigment Yellow 36, C. I. Number 77955, $4ZnO \cdot K_2O \cdot 4CrO_3 \cdot 3H_2O$: Also called zinc yellow, this pigment is identified as Pigment Yellow 36, as opposed to the lithopone version incorporating barium sulfate, which is Pigment Yellow 36:1 (C. I. No. 77956). It is a bright, green shade of yellow made by the precipitation of hydrated zinc potassium chromate from the reaction of sodium bichromate with zinc oxide and potassium chloride. Used primarily in corrosion-inhibiting coatings, its poor tinctorial strength and poor resistance to acid and alkali severely limits this pigment's use elsewhere.

CADMIUM ZINC YELLOW

Pigment Yellow 35, C. I. Number 77205, $CdS \cdot xZnS$: Yet another solid solution, cadmium zinc yellow is prepared from a cadmium salt co-precipitated with zinc sulfide. Calcination of this product gives pure cadmium zinc sulfide. The hue of the pigment is readily altered by varying the

ratio of the two components of this solid solution. Levels of zinc sulfide of 14 % to 21 % yield a green or primrose shade, while 1 % to 7 % results in a redder shade that achieves a golden hue. Incorporation of barium sulfate during manufacture produces a lithopone version, Pigment Yellow 35:1.

Cadmium zinc yellows offer bright, clean, opaque pigments with excellent resistance to heat, light, and strong solvents. Their poor fastness to mineral acids and marked tendency to fade when used at low tint levels limits their use within the coatings industry.

CADMIUM SULFIDE YELLOW

Pigment Yellow 37, C. I. Number 77199, CdS: Also known as cadmium lemon yellow, this pigment is obtained by the calcination of calcium sulfide. This color can be produced with hues ranging from a green shade to a very red shade by simply varying the calcination conditions. Offering excellent stability to heat, light, acids, and alkali, this pigment's only major drawback is its tendency to fade in the presence of moisture. A lithopone version exists, $CdS{\cdot}xBaSO_4$. (C. I. No. 77199.1), which is a "primrose yellow" shade.

IRON OXIDE YELLOWS

Pigment Yellow 42, C. I. Number 77492, $FeO(OH) \cdot nH_2O$: As with most of the commercially available iron oxides, this pigment can also be obtained as the natural grade, Pigment Yellow 43, also known as Mars yellow, or the synthetic variant, Pigment Yellow 42, originally obtained from the mineral goethite (hydrated iron oxide). Both opaque and transparent grades are marketed.

The natural yellow oxides, $FeO{\cdot}xH_2O$, will also contain clay and various other minor minerals. Available under several names, often related to the country of origin or the pigment's history, the natural yellow oxide is also called Indian ochre, ocher, sienna, and limonite.

The synthetic oxide is produced by direct precipitation using ammonium hydroxide and ferrous sulfate, via the Penniman-Zoph process from scrap steel and a ferrous salt to grow seed particles, or by the aniline process where nitrobenzene is reacted with metallic iron to produce iron oxide and aniline. The synthetic product has the empirical formula $Fe_2O_3{\cdot}xH_2O$, irrespective of the manufacturing process.

Iron oxide yellows are economical pigments with excellent light fastness, weatherability, opacity, and flow properties. On the downside, they are dull in masstone and exhibit only fair tinctorial strength and moderate baking stability at best. It is their value in use that has resulted in their widespread acceptance throughout the coatings industry.

BISMUTH VANADATE/MOLYBDATE YELLOW

Pigment Yellow 184, C. I. Number 771740, $4BiVO_4{\cdot}3Bi_2MoO_6$: The most modern of the inorganic pigments discussed in this section, Pigment Yellow 184, was introduced into the marketplace in 1985. It is also know as bismuth vanadate yellow and is manufactured by dissolving bismuth nitrate, sodium vanadate, and sodium molybdate in nitric acid followed by precipitation of a complex mixture of the metals. The precipitate is calcined to give a poly crystalline product, $4BiVO_4{\cdot}3Bi_2MoO_6$. The product is a green shade of yellow.

The pigment is used principally for brilliant solid shades in both automotive and industrial coatings. It is recommended for use in alkyd and acrylic paints, water-based paints, nitrocellulose lacquers, and baking enamels. The pigment has excellent weather fastness coupled with good hiding power and gloss retention (light fastness). Thermal stability is also good. The pigment has found use in replacing lead-based pigments in such traditional colors as "school bus yellow" as well as chrome and cadmium pigments. Earlier grades suffered from the unusual phenomenon where the color under shadows would darken only to lighten again once the shadow was removed. This photochromic effect has been investigated [5] and CIE chromaticity diagrams were developed for changes of bismuth vanadate pigments under the influence of sunlight or incandescent light. More stable grades of the pigment have been introduced and these do not suffer this drawback.

Oranges

CHROME ORANGE

Pigment Orange 21, C. I. Number 77601, $x\text{PbCrO}_4{\cdot}y\text{PbO}$: A basic lead chromate also known as chrome orange, this color is formed under alkaline conditions to give a product of empirical formula $x\text{PbCrO}_4{\cdot}y$ PbO, shades varying from a yellow to red shade dependant on the alkalinity maintained during the reaction sequence [6].

As with all lead-containing pigments, the product will darken on exposure to the atmosphere with the rate of darkening dependant on the sulfur content of the air. The pigment offers low cost, moderate light fastness, and finds use in the protective coatings marketplace with some use as a shading pigment for road traffic paints. Grades encapsulated within an amorphous silica structure that offer a product that is environmentally safer due to the occlusion of the lead within the silica shell [7].

CADMIUM ORANGE

Pigment Orange 20, C. I. Number 77202, $CdS{\cdot}x\text{CdSe}$: Cadmium orange, cadmium sulfoselenide orange, is a solid solution produced by calcining cadmium selenide with cadmium sulfide at approximately 1000°C (1800°F). A change in the ratio of the solid solution components gives pigments that vary from bright yellow (PY 35) to bright red (PR 108). Barium sulfate added or produced during the processing will form the lithopone grade, Pigment Orange 20:1.

This pigment is used in industrial coatings, for color-coding applications, in ceramics and where chemical and heat resistance are principal end use requirements.

CADMIUM MERCURY ORANGE

Pigment Orange 23, C. I. Number 77201, $CdS{\cdot}x\text{HgS}$: This pigment is a solid solution of mercury sulfide in cadmium sulfide. Various hues can be obtained by controlling the formation of the mixed crystal manufactured by precipitating the sulfides of cadmium and mercury from a solution of their soluble salts. The final stage is calcination in an inert atmosphere to give an extremely heat-stable pigment with excellent chemical and weather resistance as well as solvent fastness. Little of this pigment is manufactured in the United States, and its use in paint and coatings is minimal due to environmental concerns [8].

Greens

CHROME GREEN

Pigment Green 15, C. I. Number 77520, 77601, 77603: This pigment, also known as Brunswick green, is merely a mix-

ture of a green shade chrome yellow (PY 34) and iron blue (PB 27). As such, Pigment Green 15 offers a range of hues with a light yellow shade to a deep dark shade, providing good hiding, high tint strength, and moderate chemical resistance at an economical price. It can be used for bake enamels where the bake temperature does not exceed 148°C (300°F), but is restricted to exterior and industrial coatings applications as opposed to decorative finishes because of its lead content.

CHROMIUM OXIDE GREEN

Pigment Green 17, C. I. Number 77288, Cr_2O_3: Chrome oxide green is a pure, calcined chromium oxide, Cr_2O_3, manufactured by reduction of sodium bichromate with carbon or sulfur:

$$Na_2Cr_2O_7 + 2C \rightarrow CO + Na_2CO_3 + Cr_2O_3$$

This pigment has a unique use in camouflage paints because of its ability to reflect infrared light. Otherwise, the product finds a use where its price can be justified by the resultant excellent light and chemical resistance properties the pigment features. Minor applications also exist in the cosmetics industry and as a colorant for cement.

HYDRATED CHROMIUM OXIDE GREEN

Pigment Green 18, C. I. Number 77289, $Cr_2O(OH)_4$: Also known as Viridian green or Guignets green, Pigment Green 18 is a hydrated chromic oxide of formula $Cr_2O_3 \cdot 2H_2O$ from the hydrolysis of the product produced by calcining sodium bichromate with boric acid. The pigment is an intense, bright, blue shade of green with outstanding fastness properties in both masstone and deep tints.

Browns

NATURAL IRON OXIDES

A natural product obtained from either iron oxide mines operating principally to supply ore as feedstock for blast furnaces with a small off-take directed to the pigment industry or pigment mines, which operate solely to supply pigment grade ore. Typically the mined ore is slurried in an aqueous suspension and washed through a series of stages to remove sand and clay after which the slurry passes into a separator tank, then through a Dorr bowl rake where the iron oxide ore is separated and dried as a thin layer on a rotary drum drier. The dried natural ore is pulverized and classified to produce pigmentary iron oxide. Pigment Brown 7 is an iron oxide brown that is available in shades ranging from light red to deep purple brown. Empirically the product is Fe_2O_3. Metallic brown is produced from calcined hematite (PR 102) and burnt sienna from calcined limonite (PY 43).

Pigment Brown 7:x is a ferrosoferric oxide derived from ores containing 25 % manganese dioxide with a distinct composition as $Fe_2O_3 \cdot x$MnO with varying proportions of clay. Classical names include such as raw umber, burnt umber, raw sienna, burnt sienna, and Turkish umber.

SYNTHETIC BROWN OXIDES

Pigment Brown 6, C. I. Number 77491, 77492, 77499: Also known as brown magnetite iron oxide, Pigment Brown 6 is produced by controlled oxidation of Pigment Black 11. Chemically the product may be represented as $Fe_2O_3 \cdot x$FeO$\cdot y H_2O$.

Pigment Brown 11 (C. I. No.77495) is magnesium ferrite from the calcination of a blend of ferric and magnesium oxides, $MgO \cdot Fe_2O_3$.

The volume of all types of brown oxides used in coatings is generally low, since most browns are achieved by mixing yellow, red, and black pigments. As a class, these pigments have good chemical resistance and high tint strength and as such find some use in wood stains and furniture finishes. Minor applications also exist in the field of colorants for cosmetics and for the coloration of cement.

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Ceramic Pigments

Richard A. Eppler[1]

CERAMIC PIGMENTS ARE COMPLEX MIXTURES of oxygen-containing materials that have been calcined at high temperatures to form specific crystalline phases [1]. In most cases, oxide raw materials are carefully mixed and then calcined in either batch kilns or continuous calciners [2]. After calcination, they are ground to the necessary fineness in mills. Micronizers and/or jet mills are used to break agglomerates. The final production step involves careful control of the color tone.

Because these pigments are formed at high temperatures, they generally offer superb thermal stability and are relatively inert. This results in excellent weathering and light fastness properties. Most of these pigments have superior acid and alkali resistance. They are nonmigrating and nonbleeding in nature and do not interact with polymer systems [3].

The principal disadvantage of ceramic pigments is their low tinting strength. In addition, some are relatively high in cost. This is particularly true with cobalt-containing pigments. Some of these pigments are difficult to disperse. However, the recent development of easily dispersed ceramic pigments should eliminate this problem. A final concern is the inherent hardness of these pigments. Their hardness can lead to processing system damage through abrasion. When using ceramic pigments, processing system components designed for use with abrasive materials should be considered.

The major use of ceramic pigments is for applications such as vinyl siding, automotive paints, coil coating, and high-temperature systems where the product is thermally cured and then placed in an outdoor setting.

CERAMIC PIGMENTS USED IN ORGANIC PAINTS

The major criterion used in selecting ceramic pigments for organic paints is hardness. The pigments listed in Table 1 and discussed below are those that can be used in paint processing equipment without causing excessive wear. Property attributes of the pigments are given in Table 2. All are compatible with most polymer systems, with manganese-doped rutile especially useful when it is necessary to avoid iron.

Nickel-doped rutile, which is often called sun yellow, is produced from a mixture of various amounts of titanium (IV) oxide, nickel (II) oxide, and antimony (V) oxide by high-temperature calcination [1]. The result is formation of a crystalline matrix of rutile that has the basic chemical formula $(Ti,Ni,Sb)O_2$. The pigment is used for coloring high-performance industrial coatings, wire coatings, vinyl sidings, automotive and other exterior paints, as well as for roofing, granules, porcelain enamels, and ceramic bodies.

Chrome-doped rutile is prepared from a mixture of varying amounts of titanium (IV) oxide, chrome (III) oxide, and antimony (V) oxide by high-temperature calcination [1]. The resultant crystalline rutile matrix has the basic chemical formula $(Ti,Cr,Sb)O_2$. The orange-yellow pigment is used for coloring the same systems as nickel-doped rutile.

Manganese-doped rutile is prepared from a mixture of various amounts of titanium (IV) oxide, manganese (II) oxide, and antimony (V) oxide by high-temperature calcination [1]. The resulting crystalline rutile matrix has the basic chemical formula $(Ti,Mn,Sb)O_2$. The brown pigment is used for coloring the same systems as nickel-doped rutile.

Spinel brown pigments are an example of the 2-4 inverse spinels [4]. The basic pigment is prepared by a high-temperature calcination of titanium (IV) oxide and iron (II) oxide [1]. The resulting crystalline matrix of spinel is brown in color and has the basic chemical formula Fe_2TiO_4. The spinel phase permits extensive substitution, within defined limits, with other compounds to provide a variety of shades of brown. Modifiers used for substitution include Al_2O_3, CoO, Cr_2O_3, Fe_2O_3, MnO, and ZnO. The pigments are used for coloring high-performance industrial coatings, wire coatings, vinyl sidings, and automotive and other high-quality exterior paints.

Titanate green and blue-green pigments are also produced by high-temperature calcination of mixtures of titanium (IV) oxide, cobalt (II) oxide, nickel (II) oxide, and zinc (II) oxide to form a crystalline matrix of inverse spinel [1]. The pigments have the basic chemical formula $(Co, Ni, Zn)_2TiO_4$. The pigments are used for coloring the same systems as the spinel brown pigments.

Cobalt blue pigments are crystalline spinels formed by high-temperature calcination of cobalt (II) oxide and aluminum (III) oxide in varying amounts [1]. The basic cobalt blue pigment (CAS 68186-86-7) has the chemical structure $CoAl_2O_4$. The lighter-colored cobalt blue is prepared by addition of zinc (II) oxide to the ingredients used for the basic pigment. The chemical structure of the resultant material (CAS 68186-87-8) is $(Co,Zn)Al_2O_4$. Blue-green shades are produced by introduction of chromium (III) oxide, partially replacing aluminum (III) oxide in the basic cobalt blue system. It has the chemical formula $Co(Al, Cr)_2O_4$. In addition to being used to color the same systems as the rutiles, the cobalt blues are used in ceramic glazes.

Cobalt phosphate violet is prepared by high-temperature calcination of cobalt (II) oxide and phosphorus (V) oxide

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TABLE 1—Recommended ceramic pigments for use in organic paints

Ceramic Pigment	Pigment Powder Color	Color Index/Name	CAS Number
Nickel-doped rutile	Yellow	77788/Pigment Yellow 53	71077-18-4
Chrome-doped rutile	Orange-yellow or maple	77310/Pigment Brown 24	68186-90-3
Manganese-doped rutile	Brown	77899/Pigment Yellow 164	68412-38-4
Spinel brown	Brown	77543/Pigment Black 12	68187-02-0
Titanate greens and bluegreens	Green	77377/Pigment Green 50	68186-85-6
Cobalt blue	Blue (basic)	77346/Pigment Blue 28	68186-86-7
Cobalt-zinc blue	Blue (lighter than basic)	77347/Pigment Blue 72	68186-87-8
Cobalt chromite blue	Blue-green	77343/Pigment Blue 36	68187-11-1
Cobalt phosphate violet	Purple	77360/Pigment Violet 14134	13455-36-2
Manganophosphate violet	Purple	. . .	10101-66-3
Ceramic black	Jet black	77428/Pigment Black 28	68186-91-4
Ceramic black	Jet black	66502/Pigment Black 27	68186-97-0

to form a crystalline phosphate [1]. It has the formula $Co_3(PO_4)2$. It is used for coloring the same systems as the spinels and in printing inks. Manganophosphate violet is produced by a precipitation process from ammonium salts of manganese (III) and phosphorus (V) [3]. This pigment has the chemical formula $NH_4MnP_2O_4$. It is used for inks and other applications where heat stability is of less importance.

One ceramic black is a jet black powder produced by calcination of mixtures of copper (II) oxide and chromium (III) oxide to form a crystalline spinel [1]. The basic jet black has the formula $CuCr_2O_4$. A marginally stronger black is produced by a high-temperature calcination of cobalt (II) oxide, iron (III) oxide, and chromium (III) oxide in varying amounts, also to form a spinel. The product has the chemical formula (Co, Fe)(Fe, $Cr)_2O_4$. The ceramic blacks are used in the same systems as the above-described rutiles.

Like most pigments, ceramic pigments are manufactured to have a suitable particle size for incorporation into the coating, but when a paint manufacturer receives them in bags of dry material, the particles generally have agglomerated or have absorbed moisture [5]. They are stuck together in groups by this layer of water or absorbed air. Hence, in the dispersing process, these layers must be destroyed and the primary particles dispersed in the paint.

There are a number of wetting and dispersing agents that can be added to a paint [5]. Discussion of this topic will

TABLE 2—Properties of recommended ceramic pigments (see Table 1 for color and pigment reference numbers)

Ceramic Pigment	Heat Stability	Weathering Properties	Light Fastness	Acid/Alkali Resistance	Hydrolytically Stable	Nonmigrating/ Bleed
Nickel-doped rutile	High	Excellent	Excellent	Excellent	Yes	Yes
Chrome-doped rutile	High	*Excellent	Excellent	Excellent	Yes	Yes
Manganese-doped rutile	High	Excellent	Excellent	Excellent	Yes	Yes
Spinel brown	High	Excellent	Excellent	Good	Yes	Yes
Titanate greens and bluegreens	High	Excellent	Excellent	Excellent	Yes	Yes
Cobalt blue-basic	High	Excellent	Excellent	Excellent	Yes	Yes
Cobalt zinc blue	High	Excellent	Excellent	Excellent	Yes	Yes
Cobalt chromite blue	High	Excellent	Excellent	Excellent	Yes	Yes
Cobalt phosphate violet	High	Excellent	Excellent	Excellent	No	Yes
Manganophosphate violet	High	Excellent	Excellent	. . .[a]	No	Yes
Ceramic jet black	High	Excellent	Excellent	Excellent	Yes	Yes
Ceramic Jet black-stronger	High	Excellent	Excellent	Excellent	Yes	Yes

[a]Manganophosphate violet has good acid resistance, but poor alkali resistance.

be found elsewhere in this manual. However, one important additional factor should be noted. Most ceramic pigment manufacturers today offer a line of easily dispersed pigments. These products are formulated with a proprietary dispersant. Adding the dispersant to the pigment itself promotes optimum contact between the dispersant and the pigment.

TESTING OF CERAMIC PIGMENTS

Ceramic pigments are usually tested for two important properties: particle size and tinting strength. Hardness is essentially a property of the pigment crystal produced and is insensitive to production details. Hence, handbook values for the crystal are usually adequate for most purposes.

There are three aspects of particle size to be considered: (1) the particle-size distribution, (2) the concentration of coarse particles, and (3) the particle shape as it affects the formulation of the paint. The measurement and reporting of particle-size distribution of pigments in paints is contained in ASTM Practice for Reporting Particle Size Characteristics of Pigments (D1366) [6]. The practice covers measurements by microscopic techniques, sedimentation methods, turbidimetric methods, absorption, and permeability methods.

The recent laser dispersion and electric sensing zone techniques are not yet dealt with in this standard. The procedures described in ASTM Test Method for Particle Size Distribution of Alumina or Quartz by Electric Sensing Zone Techniques (C690) and ASTM Test Method for Determining Particle Size Distribution of Alumina or Quartz by Laser Light Scattering (C1070) should be applicable to ceramic pigments [7].

Determination of the concentration of coarse particles that may cause defects in a coating is covered by ASTM Test Methods for Coarse Particles in Pigments (Dl85) [6].

The amount of pigment that may be added to a paint formulation is a strong function of the shape of the pigment particles. Higher loadings are possible for pseudo-spherical particles than is possible with plate-like particles. This property of a pigment is measured by determining the oil absorption characteristics of the pigment as described in ASTM Test Method for Oil Absorption of Pigments by Spatula Rub-out (D281) [8].

Tinting strength is the other important characteristic that needs to be evaluated. The determination of the color of a pigment requires that it be dispersed into a medium similar to that in which it is to be used. It is never acceptable to imply application color from the color of a dry pigment. The techniques for dispersing a pigment in a suitable vehicle and then measuring the color in both masstone and letdown are detailed in ASTM Test Method for Color and Strength of Color Pigments with a Mechanical Muller (D387) [8].

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Extender Pigments

Richard A. Eppler[1]

PREFACE

IN PREPARATION OF THIS CHAPTER, THE CONTENTS of the 14th edition were drawn upon. The author acknowledges the author of the 14th edition, Henry P. Ralston. The current edition will review and update the topics addressed by the previous author, introduce new technology that has been developed, and include up-to-date references.

INTRODUCTION

Coating formulators use extender pigments to reduce the raw material cost of a coating formulation and to improve coating performance. Extender pigments are relatively inexpensive compared to titanium dioxide or color pigments and are easily incorporated into a coating. Most are white or near-white inorganic minerals, beneficiated to varying degrees, with a coarser particle size and lower oil absorption (binder demand) than primary pigments.

Extender pigments include inexpensive fillers, such as coarse calcium carbonate, which are used to reduce cost by filling coating volume with minimal impact on performance. Very fine particle size silicates, particularly certain kaolins and ultrafine talcs, can enhance coating performance and provide very favorable economics by effectively separating the individual pigment particles, optimizing the opacifying effect.

The industrial mineral extenders—wollastonite, talc, mica, kaolin, feldspar, and nepheline syenite—are used as functional fillers, chosen for specific features that improve coating performance, such as better durability, coating stability, rheology, and dry film properties. These effects of the silicates on coatings are a consequence of (a) the mineral's structure, which influences the particle shape, (b) the volume fraction of the mineral in the coating film, which is affected by the particle shape and size, and (c) the mineral's compatibility with the binder matrix, which depends on the particle physical and surface chemical properties.

Some of these properties are derived from the unique platy particle shape of talc, kaolin, or mica, or the acicular particle shape of wollastonite. Platy extenders tend to enhance the mechanical properties of the film by lateral reinforcement. They also minimize internal stress by allowing better stress dissipation along the plane of the pigment. When oriented parallel to the substrate, they reduce the porosity of the film, sealing it. Acicular particles reinforce the film, by preventing cracking and increasing tensile strength.

While extender pigments can vary in form and use, the added value delivered to the coatings formulator remains [1–3].

CALCIUM CARBONATE

Description

Calcium carbonate, also known as calcite, whiting, or limestone, has the chemical formula $CaCO_3$. It is produced by dry or wet grinding of marble or calcite ores, or by precipitation via carbonization of slaked lime. Product from ground limestone is dependent upon both the initial crude mineral and the subsequent degree of processing or beneficiation. The ore is crushed and milled; the dry ground product is air classified to different particle-size fractions. Wet ground product is milled as a slurry, undergoes flotation to remove impurities, and is then filtered and dried. The proximity of the supplier to the customer is a major consideration, as transportation is a significant portion of the cost of the material.

Precipitated calcium carbonate is produced by heating natural limestone to form calcium oxide, which is then slaked in water and reacted with carbon dioxide to form a low-solids slurry. The precipitate is vacuum filtered, dried, and ground. Both particle shape and size of precipitated grades can be carefully controlled by altering reaction conditions to yield effective extender pigments.

Calcium carbonate is used primarily as an inexpensive filler material. However, fine-particle-size precipitated grades and fine-ground limestones may have some value as an extender pigment to lower titania or color pigment concentration [1,4,5].

Physical Properties

Calcium carbonate products are differentiated by physical properties, such as particle size, brightness, residue, and, for precipitated grades, oil absorption. Fine-particle-size products have an average particle size of from less than 1 to about 4 μm with coarse-particle-size grades ranging up to about 15 μm. Most calcium carbonates are high in brightness, ranging from 90 to 98, with a *p*H of 9–10. Ground carbonates have low oil absorption, which correlates with low resin demand in coatings. The finer grades may be modestly higher.

Coatings Performance

Calcium carbonate is widely used in water-based trade sales architectural coatings since it is less expensive than titanium dioxide, a primary pigment in paints and coatings, and significantly lowers raw material cost. Fine-particle-size calcium carbonate functions as an extender by spacing titanium dioxide and maintaining or improving optical properties of the dry coating film at lower titanium dioxide levels. Higher-oil-absorption (binder demand) precipitated grades may contribute to opacity.

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Finer-particle-size grades tend to develop high gloss and high brightness, which can have a positive effect on the color of the coating.

Coarser grades of calcium carbonate are primarily used as fillers to reduce cost but also contribute to flatting and enhance low sheen control. Some grades may cause frosting and chalking in exterior applications.

KAOLIN

Description

Kaolin, also known as china clay, is an aluminum silicate with the chemical formula $Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$, which is commercially available in both hydrous and calcined (anhydrous) forms. Domestic deposits occur primarily along the fall line in South Carolina and Georgia. It has a platy particle shape with finer particles present as individual platelets and coarse particles present as stacks of platelets or booklets.

The hydrous form is produced by air flotation or water washing. Air-floated grades are crushed and ground to a specific particle size and air-classified. This process is very dependent on the initial ore deposit.

Water washing involves processing the mineral in an aqueous slurry and separating particles of different size, which can then be recombined to yield products with controlled particle-size distribution. These products can also be further beneficiated by bleaching, ozonation, high-intensity magnetic separation, or chemical flotation to remove impurities and improve color. Some grades are subjected to a delaminating process that physically separates coarse platelets from one another.

Water washing offers a more carefully controlled product available in either slurry or dried form. Predispersed spray-dried beads offer ease of handling and are suitable for water-based coating systems. Pulverized acid grades are recommended for solvent-based coatings.

Calcined (anhydrous) forms are produced by subjecting water washed and bleached kaolin to thermal treatment. Low temperature calcination (650–700°C) removes structural hydroxyl, forming amorphous metakaolin. Specific gravity is decreased, while hardness and porosity are increased. When added to a coating, they promote trapping of air pockets, improving the opacity of the coating, probably by lowering the refractive index of the matrix. Fully calcined clays (1000–1150°C) are transformed into mullite, with increased hardness and specific gravity.

Physical Properties

Kaolins are also differentiated by properties such as particle size, brightness, residue, and oil absorption. Because of kaolin's effect upon the optical properties of coatings, they are offered in more varieties than are other functional fillers. Hydrous kaolins have an average particle size ranging from an extremely fine 0.2 up to 5 μm depending on the product. Dry brightness ranges from 85 % to 90 %, and most water-washed grades are very low in residue. Acid grades have a *p*H of 4–5, while predispersed grades are 6–7. Kaolins are chemically inert. Water-washed grades are lower in impurities such as soluble salts than are air-float grades.

Calcined grades range from below 1 to 2.5 μm in average particle size and are usually higher in brightness and hardness than hydrous grades. These grades have a more irregular particle shape and higher oil absorption than the hydrous grades.

Coatings Performance

Fine particle-size hydrous kaolins are commonly used in latex and alkyd trade sales paint. Finer particle size improves opacity and allows for cost reduction by extending/reducing the amount of titanium dioxide. Finer particle-size products also develop higher gloss and are particularly useful in enamels and semigloss formulations. Chemically modified hydrous kaolins are effective in high-solids and water-reducible industrial coatings.

Delaminated grades also develop good opacity, and the platy particle shape improves barrier resistance and film integrity. Delaminated grades or coarser hydrous grades are more suitable for interior wall paints and exterior trade sales formulations and exhibit more controlled chalking and better overall durability. Air-floated grades are not used significantly in coatings because the higher water-soluble salt content can cause viscosity instability.

Calcined kaolins are widely used in interior latex and alkyd trade sales flats to develop dry hiding and reduce cost at lower titanium dioxide levels. Dry hiding is due to the higher oil absorption (binder demand) of the calcined grades, resulting in more air/pigment and air/binder interfaces in the dry paint film. These grades develop good flatting, and the harder calcined particles also improve scrub resistance in interior latex coatings [1,6,7].

TALC

Description

Talc (also known as soapstone) is a hydrated magnesium aluminum silicate with the chemical formula $3MgO \cdot 4SiO_2 \cdot H_2O$. Deposits are found domestically in New York, Vermont, Montana, Texas, and California. Talc varies widely in purity depending on its source and may also contain dolomite, limestone, and silica, among others. Western talcs are highly platy, while eastern talcs have an acicular particle shape, and often contain substantial quantity of tremolite and other serpentine minerals. Both dry and wet grinding techniques are used in its beneficiation. Ore flotation processes are used to produce high-quality products. Dry processing includes use of jaw crushers, Raymond mills, and cyclones. Advanced milling technologies eliminate oversized particles.

Physical Properties

Key properties for talc include composition, color, particle size, water solubility, and oil absorption. Some grades are available with an average particle size of 1–3 μm, but most are around 5–15 μm. It is unique in its softness (Moh hardness 1–2) and lubricity. Brightness ranges from 70 to 85 for inexpensive grades and 87 to 92 for premium grades. Oil absorption depends on particle shape and size but in general fits in between calcium carbonate and kaolin. Slurry pH is basic at 9–10. Talcs are hydrophobic and organophilic.

Coatings Performance

Talcs are used in many different types of coatings including interior and exterior trade sales paints, primers, traffic paints, and industrial coatings. Western platy talcs develop good flatting and provide good chemical and water resistance due to high-purity and low-soluble calcium. These are best for sanding primers because of softness and good sealing properties, while coarse grades help develop surface roughness ("tooth"). Platy talcs have good flow

properties and improve barrier resistance and durability in exterior trade sales paints and enamel hold-out in interior applications. Talcs also enhance durability of traffic paints. Eastern acicular talcs have better color and develop lower viscosity at high loadings due to lower oil absorption [1,5,8].

SILICA

Description

Silica is a general term describing products with the chemical formula SiO_2 of which both natural and synthetic types are available. Those most widely used in paint and coatings are crystalline, microcrystalline, diatomaceous, precipitated, and fumed. They differ in method of production, physical properties, and function.

Crystalline silica is produced by crushing, grinding, and classifying quartz. Microcrystalline differs from crystalline in that its deposits, found principally in Arkansas, have a higher concentration of fine particles. It is produced in a similar manner as crystalline, but the ore is finer in particle size. Both are decreasing in usage because of reported health and safety issues related to crystalline silica.

Diatomaceous silica, also known as diatomaceous earth or simply diatomite, consists of the skeletal remains of single-celled aquatic plants called diatoms. Domestic deposits are located in California, Nevada, and Washington. The ore is crushed, milled, dried, and air-classified. Calcined grades are processed in high-temperature rotary kilns to remove organics and separated into selected particle size ranges by air classification. These products have superior color and are preferred for coatings applications.

Synthetic silicas are produced by a number of differing chemical and thermal processes. Precipitated silica is produced by acidification of sodium silicate in water solution, to form aggregates of ultra-fine particles. Aggregate size and degree of structuring are controlled by reaction conditions. Fumed silica, produced via high temperature hydrolysis of silicon tetrachloride with hydrogen, also exists in aggregates of ultra-fine particles, and particle size and surface area are also dependent on reaction conditions. It is more expensive than precipitated silica to produce.

Physical Properties

The several silica products are the optimum solution for chemical resistance in service. Since processing of crystalline silica is essentially a size reduction operation, particle size and particle-size distribution are the primary means of differentiating products. Crystalline silicas range from 2 to 10 μm average particle size. They are low in oil absorption, providing inertness and durability. Microcrystalline grades are easier to disperse and are less abrasive than crystalline grades. Brightness is from 85 % to 90 % and *p*H from 6 to 7. Oil absorption is intermediate between calcium carbonate and hydrous kaolins. These extenders are translucent and do not contribute to hiding as do some calcium carbonates and kaolin. Crystalline silica (quartz) has been identified as a carcinogen, limiting its use in some applications.

Diatomaceous silica is a very high oil absorption material found in aggregates ranging in mean particle size of 2 to 20 μm. They often contain up to 30 % organic material. Calcined grades are more porous and have a brightness of 87 % to 90 %.

The synthetic silicas are differentiated by surface area and particle size. Surface area of precipitated types is about 60–300 m^2/g, while fumed silica ranges from 50 to 400 m^2/g. Ultimate particle size of the individual particles are less than 0.1 μm for both; however, precipitated grades may develop larger aggregates. Fumed silica has a *p*H of 3–4, and precipitated silica has a *p*H of 6–8. These grades are often made hydrophobic by reaction with organofunctional silanes to improve performance in coatings. They are essentially amorphous so they will not cause silicosis.

Coatings Performance

Crystalline silica is used in trade sales, industrial coatings, and primers. It is an inexpensive extender that contributes to low sheen control, burnish resistance, and durability with minimal impact on rheology in latex trade sales paints. It is also used in powder coatings where its low binder demand does not affect flow properties.

Diatomaceous silica is primarily used as an inexpensive flatting agent in latex trade sales paints because of its high binder demand. Precipitated silicas are used as flatting agents in solvent-based industrial coatings. Fumed grades, more expensive than precipitated because of high-energy requirements during production, are used as rheology modifiers and flatting agents in industrial coatings [1,3,5,9].

MICA

Description

Mica is a family of hydrous aluminum potassium silicates of which one, muscovite, has the chemical formula $K_2O \cdot 3Al_2O_3 \cdot 6SiO_2 \cdot 2H_2O$. Micas are best known for a very platy particle shape and high aspect ratio. These are coarser in particle size than most extenders. Higher-aspect-ratio micas are produced by frictional wet grinding. Dry processing in high-pressure air jets to both delaminate and reduce the particles results in lower-aspect-ratio mica.

Physical Properties

Most coating grades of mica have an average particle size of 5 to 50 μm. Residue of 325 mesh varies from less than 1 to as high as 50 %, depending on the particle size of the product. Brightness ranges from 65 % to 80 %, low compared to other extenders, while *p*H is 7–8. Oil absorption is higher than other hydrous minerals and is closer to coarse-calcined kaolins.

Coatings Performance

Mica is best known for its very platy particle shape, which forms layers parallel to the paint film. Mica reinforcement increases durability and resistance to moisture penetration, corrosion, checking, heat, and chemicals. It helps prevent cracking in exterior architectural coatings and traffic paint. It prevents cracking and sagging in textured coatings. Mica provides good barrier resistance in primers and roof coatings. Its platy particle shape, however, limits loading levels due to rheology constraints [10].

WOLLASTONITE

Description

Wollastonite is a calcium metasilicate with the chemical formula $CaO \cdot SiO_2$ of which the primary domestic source is New York. It has an acicular particle shape, is white in

color, and is alkaline in pH. It is beneficiated by wet processing and/or high-intensity magnetic separation. Powder grades are milled in inpact mills to a low aspect ratio (3:1 to 5:1) and top particle sizes 325 mesh to 10 μm. High aspect ratio (HAR) grades are carefully attrition milled to yield aspect ratios of 12:1 to 20:1. Needle lengths range from 200 to 20 μm micrometers.

Both powder and HAR grades of wollastonite are available with organosilane treatments for compatibility with organic coatings. They are blended wet, and then dried.

Properties

Typical coating grades range from 2 to 10 μm in mean particle size. More important is the aspect ratio, as discussed in the last paragraph. Brightness ranges from 80 % to 95 %, and *p*H is 9–10. Wollastonite exhibits moderate hardness for scrub resistance, and moderate oil absorption relative to its non-spherical shape. Its acicular particle shape provides some reinforcement in coatings; and the high *p*H is effective in buffering latex systems. Surface-modified grades improve performance in industrial coatings by reducing resin demand and improving bonding between the mineral and resin.

Coatings Performance

In addition to their use for corrosion control, high whiteness powder grades of wollastonite are used in architectural, industrial, and marine coatings to ensure film integrity in service. HAR wollastonite grades are used in asphalt coatings, coal tar coatings, texture coatings, and block fillers for mechanical strength and durability. Wollastonite is used in epoxy powder coatings due to its low binder demand and water resistance. Adhesion, chip resistance, and thermal stability are benefits of using wollastonite. Coarser acicular grades are used in primers for a micro-textured surface [11].

FELDSPAR AND NEPHELINE SYENITE

Description

Feldspars are the most widespread mineral group, comprising about 60 % of the Earth's crust. They are commonly differentiated according to the dominant alkali, although most contain both soda and potash. Commercial feldspars are produced by flotation and magnetic separation followed by milling. Air classification is used for the finest grades.

Nepheline syenite is a rock composed of sodium and potassium feldspars and nepheline. It can form only in a geologic environment deficient in silica. In Canada, typical nepheline syenite is approximately 25 % nepheline, 55 % sodium feldspar, and 20 % potash feldspar, yielding a nominal chemical formula $K_2O{\cdot}3Na_2O{\cdot}4.5Al_2O_3{\cdot}20SiO_2$. It is produced by crushing, dry magnetic separation, and milling.

Properties

Milled feldspars and nepheline syenite crystalize as angular nodular particles, leading to low surface area, easy dispersion, and low vehicle demand. High loadings are possible. The particles interlock to improve the durability of the coating film, conferring crack resistance, high hardness, abrasion, and scrub resistance. They have high brightness (95 %–98 %) and are relatively coarse in particle size (2 to 16 μm).

Coatings Performance

The low binder demand of these materials make them particularly effective in exterior trade sales and architectural coatings. Their very low tint strength make them useful for deep-tone and pastel colors with minimum colorant. They provide good tint retention and prevent checking and cracking in exterior paints and also develop good scrub resistance in interior latex paints. They are the closest replacement for crystalline silica when toxicity concerns are raised.

Nepheline syenite is often favored over feldspar because it is silica-free. However, in acidic environments, such as acid rain, the durability of coatings using feldspar is superior [12].

BARIUM SULFATE

Description

Barium sulfate ($BaSO_4$) is available as barytes, its naturally occurring form, or as blanc fixe, a synthetic precipitate. Barytes has a nodular particle shape with deposits found predominantly in Nevada, Georgia, Missouri, Montana, Tennessee, Illinois, and Washington. The ore is beneficiated by flotation techniques and then wet ground to obtain the required particle size and bleached to improve color. Some higher quality ores are dry ground and air classified. Blanc fixe is a very white, fine-particle-size extender not as widely used in paints and coatings as barytes. It is precipitated to a specific particle size from solutions of barium salts and sodium sulfate. Blanc fixe is also used to make lithopone (extended) grades of pigments. Multistage washing and filtration removes soluble impurities, and the products are then dried and ground.

Physical Properties

Barytes is best known for its high density and very low oil absorption relative to other extenders. Particle size ranges from about 1 to more than 10 μm depending on the grade. Brightness also varies from below 70 % to greater than 90 % depending on the source and degree of beneficiation. Slurry *p*H runs from 4 to 10. Blanc fixe is a more uniform product with a 1–2 μm average particle size and high brightness (95 %–98 %).

Coatings Performance

Barytes is used in industrial and automotive primers and undercoats. Its low oil absorption allows for high loadings with less impact on rheology compared to higher binder demand extenders. It helps develop a smooth surface with minimal impact on the gloss of subsequent coats. Because extenders are sold by weight, high density can be a disadvantage in trade sales coatings where more weight is needed to fill a given volume. Higher density relative to other pigments can increase settling and cause stability problems. Blanc fixe has been used to develop dry hiding as a partial replacement for titanium dioxide in trade sales and industrial coatings [13].

OTHER

Sodium Aluminosilicates

Synthetic sodium aluminosilicates are produced by reacting aluminum sulfate with sodium silicate to produce a structured extender. These have high brightness (92 %–98 %) and relatively coarse particle size of 5–6 μm. Sodium

TABLE 1—Physical properties of pigment extenders						
	Ground Calcium Carbonate	**Precipitated Calcium Carbonate**	**Hydrous Kaolin**	**Calcined Kaolin**	**Talc**	**Crystalline Silica**
Free moisture	0.5	0.5	1.0	0.5	0.2–0.5	0.3
Specific gravity	2.71	2.71	2.58	2.63	2.80	2.65
Brightness, %						
Fine	90–95	97–98	88–90	90–95	75–92	85–90
Coarse	85–90	. . .	85–88	. . .	70–92	85–90
Average particle size						
Fine, μm	1–3	0.5–1.5	0.2–5	0.8–2.5	1–3	2–3
Coarse, μm	5–12	. . .	. . .	. . .	5–15	5–10
pH	9.5	9–10	4–7	4–5	9–10	6–7
+325 residue, %	0.01–1	<0.05	0.01–0.1	0.01	0.01–1	<1–4
Oil absorption, g/100 g	10–20	30–60	30–50	50–100	25–55	20–30
Refractive index	1.66	1.66	1.56	1.62	1.60	1.54
Wollastonite	**Diatomaceous Silica**	**Precipitated Silica**	**Fumed Silica**	**Mica**	**Powder Wollastonite**	**HAR**
Free moisture	<1	<1.5	5	0.10	<1	<1
Specific gravity	2.30	2.20	2.20	2.82	2.90	2.90
Brightness, %	87–90	96	white	65–80	80–95	85–95
Average particle size						
Fine, μm	3–4	0.01–0.05	0.01–0.05	0.2 × 5	2–4	1 × 20
Coarse, μm	5–10	. . .	. . .	2 × 50	7–10	16 × 200
pH	9–10	6–8	3–4	7–8	10–11	10–11
+325 residue, %	<1–3	0.01	0.01	<1–50	<0.1	<1–50
Oil absorption, g/100 g	90–130	100–300	100–400	56–74	20–30	20–30
Refractive index	1.46	1.46	1.46	1.60	1.63	1.63
	Feldspar	**Nepheline Synite**	**Barytes**	**Sodium Alumino–Silicate**	**Alumino Hydrate**	
Free Moisture	<1	<1	<1	<1	<1	
Specific gravity	2.62	2.61	4.40	2.1–2.3	2.42	
Brightness, %	80–84	88–98	80–95	95–98	86–99	
Average particle size						
Fine, μm	. . .	. . .	1–4	2–4	0.05–3	
Coarse, μm	3–10	2–10	8–12	7–16	0.3–60	
pH	5–9	10	4–10	7–10	10	
+325 residue, %	<0.5–6	<0.5–6	<1	<0.5	<0.5+50	
Oil absorption, g/100 *g*	10–20	21–30	10–15	75–115	41–53	
Refractive index	1.53	1.53	1.64	1.53	1.57	

aluminosilicates are used as partial replacements for titanium dioxide in latex trade sales paints similar to calcined kaolin but at higher cost; some of the highly structured grades are used as flatting agents in latex paint [14].

Calcium Borosilicate

Synthetic calcium borosilicate is produced by melting complex mixtures of alkaline earth silicates and borates, followed by fritting and milling to produce a structured extender with particle size 1–10 μm microns and oil absorption 25–45 [15].

Alumina Trihydrate

Alumina trihydrate (ATH) has the chemical structure $Al(OH)_3$ and is produced from bauxite ore as an intermediate in aluminum production. It is most commonly used as a flame retardant and smoke suppressant in thermoplastic and thermoset polymer applications. ATH has a brightness ranging from 85 % to 98 % depending on the grade. Some very fine particle size grades, less than 1 μm, may be effective in spacing titanium dioxide in trade sales paints [14].

COMPARISON OF DIFFERENT EXTENDER PIGMENTS

Physical Properties

Physical properties of the pigment extenders described above are compared in Table 1. Calcium carbonates are available in different particle size grades and are very white in color and high in brightness. Low oil absorption enables high loading levels with minimal influence on rheology.

TABLE 2—Comparative properties of extender pigments in coatings

	Calcium Carbonate 5 μm	**Hydrous Kaolin 0.5 μm**	**Hydrous Kaolin 4.8 μm**	**Calcined Kaolin 1.8 μm**	**Talc 8 μm**	**Silica 5 and 10 μm**
Hiding power	Very low	Very high	Moderate	Very high	Moderate	Moderate
Gloss	Low	Moderate	Low	Low	Low	Low
Enamel holdout	Poor	Excellent	Very good	Poor	Fair	Poor
Stain removal	Poor	Excellent	Very good	Poor	Fair	Fair
Abrasion resistance	Fair	Poor	Poor	Excellent	Good	Good
Adhesion	Poor	Very good	Very good	Fair	Good	Very good
Water spot resistance	Poor	Excellent	Excellent	Excellent	Good	Excellent
Chemical resistance	Very poor	Very good	Very good	Good	Good	Excellent
Viscosity	Very low	High	Low	High	High-mod.	Low
Stability	Poor-v.good	Excellent	Excellent	Very good	Poor-v.good	Excellent
Suspension	Poor	Excellent	Very good	Very good	Very good	Poor
Ease of brushing	Fair	Excellent	Excellent	Good	Fair-Poor	Good
Leveling	Excellent	Very good	Very good	Good	Fair	Very good
	Wollastonite	**Feldspar**	**Nepheline Syenite**			
Hiding Power	Low	Low	Low			
Gloss	Low	Low	Low			
Enamel Holdout	Poor	Poor	Poor			
Stain Removal	Good	Very good	Very good			
Abrasion Resistance	Excellent	Very good	Very good			
Adhesion	Good	Good	Good			
Water Spot Resistance	Good	Very good	Very good			
Chemical resistance	Fair	Excellent	Excellent			
Viscosity	Low	Low	Low			
Stability	Excellent	Excellent	Excellent			
Suspension	Good	Very good	Very good			
Ease of Brushing	Fair	Good	Good			
Leveling	Fair	Very good	Very good			

TABLE 3—ASTM standards for extender pigments

Standard	Title
Specifications	
D602	Specification for Barium Sulfate Pigments
D603[a]	Specification for Aluminum Silicate Pigments (Hydrous)
D604[a]	Specification for Diatomaceous Pigment
D605	Specification for Magnesium Silicate Pigment (Talc)
D607	Specification for Wet Ground Mica Pigments
D1199	Specification for Calcium Carbonate Pigments (Anhydrous)
D3619[a]	Specification for Aluminum Silicate Pigments (Anhydrous)
D4288	Specification for Calcium Borosilicate Pigments
Analytical	
D34	Guide for Chemical Analysis of White Pigments
D715	Test Methods for Analysis of Barium Sulfate Pigment
D716	Test Methods for Evaluating Mica Pigment
D717	Test Methods for Analysis of Magnesium Silicate Pigment
D718	Test Methods for Analysis of Aluminum Silicate Pigment
D719[a]	Test Methods for Analysis of Diatomaceous Silica Pigment
D4487	Test Methods for Analysis of Calcium Borosilicate
D5381	Guide for X-ray Fluorescence (XRF) Spectroscopy of Pigments and Extenders
Physical Properties	
D153	Test Methods for Specific Gravity of Pigments
D185	Test Methods for Coarse Particles in Pigments, Pastes, and Paints
D281	Test Method for Oil Absorption of Pigments by Spatula Rub-out
D1208	Test Methods for Common Properties of Certain Pigments
D1210	Test Method for Fineness of Dispersion of Pigment-Vehicle Systems by Hegman-Type Gauge
D1366	Practice for Reporting Particle Size Characteristics of Pigments
D1483	Test Method for Oil Absorption of Pigments by Gardner-Coleman Method
D2448	Test Method for Water-soluble Salts in Pigments by Measuring the Specific Resistance of the Leachate of the Pigment
D3360[a]	Test Method for Particle Size Distribution by Hydrometer of the Common White Extender Pigments
D4139	Guide for Determining Volatile and Non-Volatile Content of Pigments
D5380	Test Method for Identification of Crystalline Pigments and Extenders in Paint by X-ray Diffraction
E70	Test Methods for pH of Aqueous Solutions with the Glass Electrode

[a] These ASTM Standards have been withdrawn; however, the designations and titles have been included for historical purposes.

High *p*H makes these products appropriate for latex paints. Surface-treated grades are available for solvent-based systems. Precipitated forms are higher in brightness, finer in particle size, and have higher oil absorption approaching that of calcined kaolins.

Hydrous kaolins are the finest particle size naturally occurring extenders. Neutral predispersed grades are available for latex systems, and acid grades are available for solvent-based systems. These products have very low residue, which improves gloss development. The calcined grades have slightly better color and higher oil absorption contributes to opacity.

Talcs are available in a wide variety of grades depending on the source. These are more similar to calcium carbonate in particle size, although brightness is somewhat deficient. Platy particle shape is a key parameter, improving durability.

Crystalline silica has lower binder demand than kaolin or talc. It improves coating stability and durability. There is concern about its toxicity. Coarser grades are effective flatting agents.

The high oil absorption of diatomaceous earth makes it an effective flatting agent. Precipitated and fumed silica, as more carefully controlled reaction products, are more appropriate for industrial coatings applications where high oil absorption is acceptable.

Mica is much coarser in particle size than most extenders. Its platy particle shape improves durability. It also has lower brightness and high residue, which limit the levels at which it may be used.

Wollastonite has a unique acicular particle shape, which provides superior stability and durability, with less increase in oil absorption than platy talc or mica.

Feldspar, nepheline syenite, and barytes are coarser-particle-size products. Feldspar and nepheline syenite find use as replacements for crystalline silica when there are toxicity concerns.

Comparative Performance in Coatings

Performance characteristics of the extenders previously discussed are compared in Table 2. Coarse calcium carbonate filler does not provide significant improvement in coatings performance and is primarily used to reduce

cost. Fine-particle-size hydrous kaolin helps develop hiding power and gloss. These extenders develop good film properties, help maintain stability, and aid in coating application. Calcined kaolin also contributes to opacity development and is fairly good in maintaining film properties, rheology, and application properties. Talc and mica are platy materials that improve durability and develop good film properties but may have a deleterious effect on rheology, particularly at higher loadings. Crystalline silica is an adequate filler, which improves durability, but it is toxic. Amorphous silicas improve durability without the toxic problem, but are limited in possible loading by very high oil absorption. Wollastonite is an acicular material that improves durability and film properties without the adverse effect on oil absorption of platy materials. Feldspar and nepheline syenite are fillers of low oil absorption, which improves durability. They act very similar to crystalline silica and can be used as replacements for it.

PERTINENT ASTM TEST STANDARDS

ASTM standards useful in evaluating extender pigments are shown in Table 3. Standard specifications are useful for categorizing extenders by mineral type and provide some general test guidelines. Analytical standards are useful for chemical analysis of extenders for identification purposes.

Standards for measurement of physical properties are very useful in categorizing extenders and for predicting suitability for a particular coatings application. Particle size, oil absorption, fineness of dispersion, *p*H, and water-soluble salt content are important parameters in determining the suitability of an extender for a particular coatings application. Actual product specifications should always be mutually agreed upon by supplier and user.

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Metallic Pigments

Russell L. Ferguson[1]

PREFACE

THIS CHAPTER IS BASED ON THE CONTENTS OF THE 14th edition. Careful consideration has been given to the addition of new information, test methods, and technology, thus providing the most up-to-date information available on metallic pigments.

Metallic pigments, including aluminum zinc, gold, bronze, nickel, and stainless steel, provide the paint and coatings industry with a variety of aesthetic and functional properties. These pigments, either in flake or powder form, contribute to the metallic effects associated with automotive topcoats; general industrial finishes; silver, gold, and copper finishes; metallic ink systems; and many of the high-performance primers for coatings systems. In addition to providing metallic and polychromatic effects, they provide functional anticorrosive benefits.

HISTORY AND MANUFACTURING METHODS

The origin of metallic coatings can be traced back to early civilizations, who utilized thin gold sheets to overlay wood, bone, or other materials. As the artisans molded these foil sheets, the thin edges would break off into flakes. It was soon discovered that by mixing these flakes in a resinous polymeric material, a similar effect could be achieved. This process was later continued, and by shredding the foil into flakes, artisans were able to produce gold and later silver and bronze metallic effects on ornamental objects. In the middle of the 19th century, a mechanical stamping process, along with newly developed smelting processes, made gold and silver substitutes more readily available. Aluminum, gold, bronze, and later stainless steel and nickel became readily accepted substitutes.

Today, with *only a few exceptions,* most metallic pigments utilize the hall wet-ball milling method [1]. This process carries out the particle-size reduction in the presence of a suitable lubricant and solvent, offering a safer production method. Eliminating the explosive hazards associated with mechanical stamping processes has allowed the production of finer metallic flakes that finds widespread use today. Stamping and dry-ball milling are still utilized in the manufacture of gold bronze flakes.

The post-milling manufacture processes for metallic flakes generally include a screening operation to remove undesirable particles, along with tight controls on aesthetic properties. Color adjustments, along with polishing and blending operations, are utilized in the final stages of the manufacturing process. The metallic flake pigments are available as a dry flake or in a wide range of solvents, including aliphatic and aromatic solvents, alcohols, plasticizers, water, and coalescing solvents.

Zinc powders have a similar but divergent history. Not being sought after for aesthetic properties, they were first used in the mid-1800s for anticorrosive functionality and were referred to as "blue powder." Zinc-gray coatings were used extensively for industrial and marine environments by the early 1900s. However, it was not until the late 1930s and 1940s that the industry gained a firm foothold. The manufacture of zinc dust is carried out by melting and vaporizing zinc metal followed by a controlled condensation of the vapor in an inert atmosphere. The product is collected, screened, classified, and packaged [2].

In addtion to zinc powders, there is one additional type of metallic pigment not manufactured by the Hall wet ball milling method. Physical vapor deposition (PVD) is a method used to produce aluminum pigments with very unique characteristics. High purity aluminum metal is vapor deposited, in a vacuum chamber, onto a flexible web that is surface treated with a release coating. The metal is deposited in a very thin layer and subsequently removed by solubilizing the release coating in a solvent bath. The metal is then collected, sized, and concentrated for sale.

PROPERTIES

Metallic pigments share similar properties; however, each is distinct enough to be considered separately.

Aluminum

Aluminum flakes should be differentiated based on their manufacturing method, i.e., milled using the Hall process and PVD using a vapor deposition process. All aluminum pigments, however, are manufactured from aluminum metal with a purity ranging from 99.3 % to 99.97 %, depending on the grade being manufactured. Although amphoteric in nature, the pigment exhibits a high degree of chemical resistance. Aluminum pigments owe their aesthetic and functional properties to the geometry of the particle, particle-size, and particle distribution. The pigment is a flake-like particle (lamellar) and has either a round or irregular perimeter. Once formulated into a coating, they orient parallel to the substrate and film surface. This orientation provides for exceptional barrier properties in the appropriate coating system. Metallic or polychromatic coatings containing aluminum flake pigments, either by themselves or in combination with transparent colors, offer a two-tone quality often sought after. The two-tone, or flop, feature is an important characteristic in many automotive top coats.

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There are two general types of *milled* aluminum pigments: leafing and nonleafing. Leafing grades are manufactured using a saturated fatty acid as the lubricant (typically stearic acid); which allows the flakes to float at, or near, the surface of a paint film. This continuous layer of flakes provides a solid silver color, unable to be tinted with other pigments. The nonleafing grades utilize an unsaturated fatty acid as the lubricant (typically oleic acid), which allows the flakes to orient throughout the paint film. Nonleafing pigmented coatings can be tinted with organic pigments to offer a polychromatic appearance.

Milled aluminum flakes range in size from 0.1 to 2.0 *μm* in thickness and 0.5 to 200 *μm* in diameter. Generally, aluminum flakes are supplied in a paste form with a typical composition of 64 % aluminum metal, 1 % lubricant, and 35 % hydrocarbon solvent [3].

PVD-generated flakes have dramatically different physical properties than milled flakes. The flakes have very regular, well-defined perimeters, exceptionally smooth surfaces, and are very thin. The thickness of these flakes is measured in angstroms with a typical mean thickness of 300 Å.

Gold Bronze

Gold bronze pigments are neither gold nor bronze, but are typically manufactured from a composition of copper and zinc alloy. By altering the copper-zinc ratios, four standard gold bronze colors can be produced. The standard alloy subdivisions are: (1) copper—100 % copper, 0 % zinc; (2) pale gold—90 % copper, 10 % zinc; (3) rich pale gold—85 % copper, 15 % zinc; and (4) rich gold—70 % copper, 30 % zinc. Further oxidative treatments can be utilized to produce special colored bronzes, varying from brown-golds to oranges and reds. Additionally, blending of any of the above-mentioned bronze powders will result in an almost unlimited pallet of gold-bronze colors.

Gold-bronze pigments are flake-like particles (lamellar) with an irregular perimeter. In a coating or ink application, they orient parallel to the substrate and film surface [4].

Zinc Pigment

Zinc dust is the only metallic pigment that is not found in a lamellar form. Produced through the condensation of zinc vapor in an inert atmosphere, the zinc dust is a spherical particle averaging about 8 μm in diameter. Zinc dust is predominantly zinc metal (96 %–97 %), with some zinc oxide (3 %–4 %), and traces of lead, cadmium, iron, and other elements.

Stainless Steel Flake

Stainless steel is a composition of iron, chromium, nickel, manganese, and molybdenum. There are three groups of stainless steel alloys available: (1) martensitic, (2) ferritic, and (3) austenitic, differentiated according to alloy composition. Of the three groups, austenitic is the most corrosion resistant and typically used to manufacture stainless steel flake. Austenitic alloys owe their corrosion resistance to higher levels of nickel and molybdenum. Stainless steel pigment has a lamellar geometry and will orient itself parallel in a coating system. Stainless steel flake has a high degree of durability and will resist tarnishing, abrasion, and chemical attack. Additionally, stainless steel flake is able to maintain stability in water-based systems.

Nickel

Nickel pigments can be found in either powder or flake-like form. They are typically composed of nickel metal, with traces of carbon, oxygen, sulfur, and iron. Nickel flake powders are available dry, as a paste in mineral spirits, or as a paste in mineral oil. Nickel powders have good electrical conductivity [5].

METALLIC PIGMENT GRADE CLASSIFICATION

Aluminum Pigments

Aluminum pigments are more widely used than any other metallic pigment and can be divided into a number of different categories. The grade classification is, in general, determined by the intended use. Most of the following categories contain a wide range of grades from very coarse large flakes to very fine small flakes.

LEAFING GRADES (MILLED)

The standard grade category is composed of a series of grades from very coarse flakes (having water coverage from) to very fine flakes (having water coverage in the area of 35,000 cm^2/g). These grades are used, primarily, in trade sales and maintenance coatings. Their leafing values are traditionally 50 % minimum.

The ultra-leafing grades are characterized by very high leafing values (in the area of 90 + %) and exceptional brightness. Their uses include aerosol coatings and ink applications.

NONLEAFING GRADES (MILLED)

The standard grades are represented by a full range of products from very coarse, low-opacity to very fine, high-opacity grades. They are used in diverse applications from maintenance coatings to general industrial applications and automotive refinish.

The automotive grades are distinguished from standard grades by possessing improved aesthetics, including brighter, more sparkling appearances, with tighter control on particle-size distribution. Many subcategories exist under this heading, including specialized grades for base coat/clear coat systems, circulation resistance, etc.

Plasticized and polymer-modified grades are represented by a full range of products designed for end-use systems that cannot tolerate solvents (mineral spirits). The primary end use is plastic and ink applications.

The dedusted grade category comprises dry aluminum flakes held loosely together by Teflon bonds, resulting in a nondusting product. These grades are used in some general industrial coatings; however, the primary application is to act as a sensitizer for slurry explosives.

The surface-treated grades include aluminum flakes whose surface chemistry has been altered to allow for improved aluminum flake performance. These grades are used in powder coatings and some solvent-borne coatings where improvements in flake orientation and performance are desired.

The aqueous grade category consists of aluminum pigments treated with various chemical components to stabilize the flake for use in waterborne systems. Various levels of inhibition and performance are available.

PHYSICAL VAPOR DEPOSITED (PVD)

The grade differentiation is based on percent solids, and the solvent in which the metal is dispersed. The typical com-

position is 10 % metal flake, 90 % solvent, although metal concentrations as high as 20 % are available. The types of solvents used are almost limitless; however, ethyl acetate is most common. The particle size of these flakes can also be controlled; however, most grades fall within the 12–17 μm median particle size range. Although most of these products are used in solvent-borne coatings and ink systems, appropriate inhibition permits use in waterborne applications.

Gold Bronze Pigments

These pigments are primarily used for coating and ink applications. They can be divided into four categories, based on alloy composition:

1. *Copper*—coppery-red color (100 % copper).
2. *Pale gold*—reddish gold color (90 % copper, 10 % zinc).
3. *Rich pale gold*—gold color (85 % copper, 15 % zinc).
4. *Rich gold*—greenish gold color (70 % copper, 30 % zinc).

Zinc Pigment

The zinc pigment, dust and flake, is used in coatings, primarily for corrosion-resistant properties. The categories available are:

1. *Regular zinc dust*—7–8 μm particle-size diameter.
2. *Fine zinc dust*—5–6 μm particle-size diameter.
3. *Ultra-fine zinc dust*—3–4 μm particle-size diameter.
4. *Zinc flake*—Available in several grades, based on particle-size.

Stainless Steel Flakes

These flakes are used in specialized coatings that require good resistance to severe environmental conditions.

Nickel Powder and Flake

The powder and flake are used in coating and plastic systems to provide electrical conductivity and corrosion-resistance characteristics.

FORMULATION AND APPLICATION GUIDELINES

Formulation Considerations

Metallic flake pigments, by the nature of their geometry and composition, are malleable and therefore somewhat fragile. The dispersion of these flakes into a coating system is critical in maintaining optimum aesthetic and functional performance. The preferred dispersion process involves the addition of vehicle or solvent to the metallic pigments, with slow-speed mixing, to gently separate the flakes. Once a thick, uniform slurry of metallic flakes, solvent, and vehicle is achieved, the formulator can continue to let down to final product composition. Severe dispersion techniques, such as Cowles high-speed mixers, sand mills, etc., will destroy the flake integrity, resulting in loss of aesthetic and perhaps functional properties. Zinc pigment, which is not a flake, can be dispersed using conventional paint dispersion techniques.

Appropriate selection of vehicle, solvents, and additives must also be considered when formulating with metallic pigments. The leafing properties of aluminum and bronze flakes can be detrimentally affected by such properties as acid value of the resin; polar solvents, or solvents with low-surface tension; moisture in the system; and additives, including driers that are good wetting agents. Since most *milled* metallic pigments contain mineral spirits, coating system compatibility must be considered.

The current trend toward waterborne coatings also poses problems in formulation. Dispersion of metallic pigments is assisted by the correct selection of an appropriate coalescing solvent. However, even good dispersion will not guarantee good coating performance. Metallic waterborne coatings have the potential for hydrogen gas generation. This potential has been addressed by many manufacturers through various inhibiting processes. While many inhibited grades are available on the market today, performance may vary in different aqueous systems. In addition to the potential for hydrogen gas generation, tarnishing and printability have been addressed by manufacturers of gold bronze flakes. Stainless steel flakes, because of the very nature of their composition, can be used in waterborne coating formulations without the possibility of gas generation.

The use of waterborne coatings is generally targeted toward resolution of environmental issues, most notably VOC reduction. There are other solutions to the VOC issue such as the use of powder coating sytems. Specialized grades of aluminum pigments have been developed to meet the needs of these 100 % solids systems. These grades have been surface-treated to allow for improved flake orientation, along with modified electrical conductivity. Applied electrostatically, the surface-treated aluminum flake will perform in a similar fashion to the powder coating resin.

PVD flakes, because of their high volatile contents, generally pose issues relating to their use in low VOC type systems. However, appropriate solvent carriers help limit this concern. PVD flakes, because of their exceptionally high aspect ratio (diameter:thickness), along with their very high opacity or coverage, require special attention when formulating. Typical inks and coating systems have very high pigment-to-binder ratios (from 2:1 up to as high as 8:1), thus very little resin is employed to assist in flake orientation. At the same time, the loading levels of the pigment are held at low levels because of the exceptional hiding or opacity.

The application of metallic pigmented coatings and inks will depend on the system being used. Traditional ink application methods will apply to both leafing and nonleafing metallic pigments. In the case of coating systems, leafing metallic pigments can be applied by brush, roller, or spray application. *PVD and milled* nonleafing grades, however, must be applied using appropriate spray application techniques. Improper application techniques can lead to poor flake orientation, which will result in reduced aesthetic and functional properties.

Market Applications

Metallic pigments are widely used in the coating, ink, plastic, and explosive markets. In the coating industry, metallic pigments offer both functional and aesthetic properties. Those pigments that are lamellar (aluminum, gold, bronze, stainless steel, and nickel) are opaque and orient parallel to substrate and coating film surface. Thus, they provide a barrier to ultraviolet and infrared light, along with moisture and oxygen penetration. Zinc pigment, while not a flake, possesses superior corrosion protective properties for steel or iron substrates. Because zinc is higher in the electromotive series, it acts as the anode of a corrosion cell. The iron or steel substrate is protected by the zinc because of the formation of insoluble compounds with lower oxidation states.

The aesthetic benefits of metallic pigments are widely known in the coatings industry. In the area of trade sales

and maintenance coatings, aluminum pigments provide very bright silvery finishes typically found in many roof coatings, aerosol applications, and bridges. In general industrial and automotive coatings, various polychromatic and metallescent appearances are produced utilizing nonleafing grades. *The PVD aluminum flakes can also generate a second surface image that is mirror like. These pigments are useful in applications that require high specular reflectance.*

In the ink and plastic industries, the primary benefits derived are from aesthetic properties. Gold bronze flakes, along with aluminum flakes, provide attractive polychromatic finishes.

The explosives industry utilizes aluminum flake pigment as a sensitizer in slurry explosives.

Economics of Use

The extensive market for metallic pigments has mandated their use in a wide range of systems for many years. Their properties, both functional and aesthetic, along with the traditional economic values associated with their properties, have established them as an important raw material in the coating, ink, and plastic markets. The economics of these pigments are dependent on a number of factors, including cost of the raw material, degree of sophistication of the pigment, and the end product for which it is intended.

TESTING

ASTM Test Methods

ASTM covers various specifications and test procedures for metallic pigments. Included are:

- D962—Specification for Aluminum Powder and Paste Pigments for Paint.
- D480—Test Method for Sampling and Testing of Flaked Aluminum Powders and Pastes (includes tests for volatile analysis; coarse particles; leafing properties; brushing, smoothness, lustre properties; and easily extracted fatty materials).
- D95—Test Method for Water in Petroleum Products and Bituminous Materials by Distillation.
- D185—Test Methods for Coarse Particles in Pigments.
- D235—Specifications for Mineral Spirits (Petroleum Spirits) (Hydrocarbon Dry-cleaning Solvent).
- D267—Specifications for Gold Bronze Powder.
- D520—Specification for Zinc Dust Pigment.
- D521—Test Methods for Chemical Analysis of Zinc Dust (Metallic Zinc Powder).
- D4017—Test Method for Water in Paints and Paint Materials by Karl Fischer Method.

Other Test Methods and Specifications

ASTM test methods cover many of the properties of metallic pigments; however, there are additional test methods and non-ASTM tests that further serve to characterize these pigments. Included are:

- *Federal Specification: TT-P-320D Pigment, Aluminum Powder and Paste for Paint*
- *DIN 55923: Pigments; Aluminum Pigments and Aluminum Pigment Pastes for Paints; Technical Delivery Specification*
- *ISO 1247: Aluminum Pigments*
- *BS 388: Specification for Aluminum Pigments*
- *GOST5494: Aluminum Pigments*

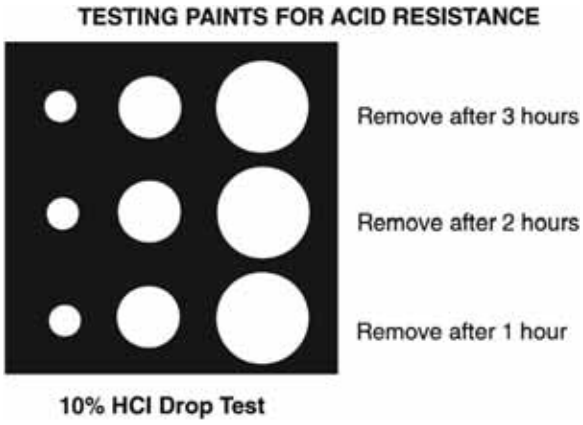

Fig. 1—Testing paints for acid resistance.

ACID SPOT TEST

This test is designed to determine the acid resistance of aluminum pigments in coating systems. A metallic pigmented coating is tested by placing drops of a 10 % solution of hydrochloric acid on the panel. Three rows of three drops are placed on the panel and each row is removed after 1 h intervals (Fig. 1). If the aluminum pigment is acid resistant, no spotting will be apparent after the first or second hour, with only slight spotting after 3 h. A nonacid-resistant aluminum will show definite spotting from the acid solution after the first hour.

PARTICLE-SIZE ANALYSIS

One of the key elements in any metallic pigment is the particle-size distribution. Instruments are available on the market today to characterize, or fingerprint, metallic pigments. Unfortunately, most of these instruments are incapable of characterizing lamellar-shaped pigments; however, their increased sophistication has allowed for a very close approximation. In addition to providing a distribution of the particles in a pigment, also provided are surface area, average particle size, and percentages at various levels.

WATER COVERAGE

This test can be used to determine the particle-size thickness and surface area of leafing and nonleafing metallic flake pigments. This test has been fully described by Edwards and Ray [6]. A dry metallic pigment is dusted onto a surface of clean distilled water, which is contained in a shallow rectangular pan. The accurately weighed flake metallic pigment is dusted onto the surface of the water and separated until it is one flake thick. The coverage of metallic flake on the water can then be measured, and total surface area can be calculated based on the weight of the metallic flake pigment used. The thickness of the metallic flake pigment can also be calculated using simple density and volume calculations.

DEGRADATION TEST

This test is designed to determine the level of flake deterioration in a coating system when subjected to severe stress. Automotive coating systems are often circulated through pumps, regulators, and long piping and tank systems to keep all the components of the coating in suspension. Circulation may have detrimental effects on the metallic flake integrity, causing bending, curling, and even breakage of the metallic flake. The loss in aesthetic properties due to

flake deformation results in a darkening of the coating, along with a change in the flop characteristic. This test is designed to evaluate the capability of the metallic flake to resist deformation under these stress conditions.

A metallic pigmented coating is placed into a water-jacketed Waring blender. Using a standard cutting blade, the blender is operated at high speeds for 5-15 min. The metallic coating is a sprayed pre- and post-blender operation, and visual and instrumental comparisons are made. The degree of flake deformation can be translated into numerical data based on the brightness of the metallic coating (face and flop).

GASSING TEST

Aluminum and other metallic pigments, by their very nature, will react with water to generate hydrogen gas. Today, due to VOC regulations, more and more coating and ink systems are moving toward waterborne technologies. Metallic pigment manufacturers have developed technologies to inhibit the aluminum flake pigments, and this test is designed to determine the gas generation potential and stability characteristics of metallic flake pigmented aqueous coating systems. Approximately 200 mL/s of a metallic pigmented coating is charged into an Erlenmeyer flask. Attached to the flask is a glass condenser with Tygon tubing coming out of the top and extending into an inverted buret filled with water. The Erlenmeyer flask is suspended in a hot oil bath, which accelerates the potential for hydrogen gas evolution. This test is operated for seven days (168 h) at a temperature of 52°C. The acceleration of the environmental conditions will allow for hydrogen gas generation, which will pass out of the Erlenmeyer flask, through the Tygon tubing, and into the inverted buret. The water in the inverted buret is displaced by the hydrogen gas and generation can be easily read through this displacement (Fig. 2). The specifications for gas generation should be designed around the metallic flake pigment and coating system tested. The specification for gas generation should not exceed the volume of the buret (typically 100 mL/s).

ELECTRICAL RESISTIVITY/CONDUCTIVITY

In waterborne coating systems, it is often useful to know the conductivity or resistivity of the components of the system. In order to measure metallic pigments, it is necessary to disperse the metallic pigment in an isopropyl alcohol/de-ionized water mixture. This mixture should be agitated using an air mixer for at least 5 min, after which the metallic pigment should be filtered out. The resultant filtrate can be tested for resistivity/conductivity using a conductivity meter (i.e., Jenway Conductivity Meter, Model 4010).

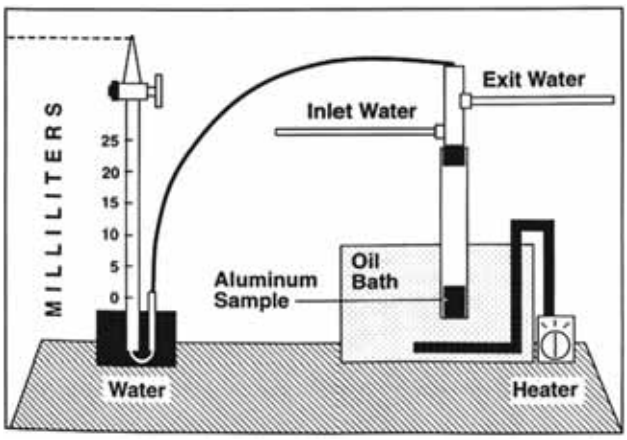

Fig. 2—Gas evolution test for metallic coatings.

pH MEASUREMENT

In waterborne coatings and ink systems, it is often necessary to know the *p*H of the components of the system. The *p*H of metallic pigments can be evaluated by adding the metallic pigment to a mixture of isopropyl alcohol/de-ionized water. The slurry should be mixed using an air mixer for at least 5 min. The metallic pigment should then be filtered out, and the *p*H of the resultant filtrate can then be evaluated.

AESTHETIC PROPERTIES

Metallic pigments are used for the aesthetic properties they lend to coating systems. Every metallic pigment grade offers its own unique appearance due to the properties of the individual pigment. Visual and quantitative data can be generated to provide numerical data describing aesthetic differences. It should be noted, however, that the appearance of a metallic film is significantly impacted by various application methods. Coating application plays a definitive role in flake orientation, which is critical to optimized metallic appearance. Many papers have been written describing the mechanism and challenges of flake orientation in paint films [7–10]

- The *face-color,* or *head-on-brightness,* attribute generally refers to the amount of reflected light from a metallic pigmented coating when viewed at approximately 20° to 25° off of specular [11].
- The *flop, flip/flop,* or *metallic travel angle* refers to the amount of reflected light when viewing a metallic pigmented coating at an angle that is 70° to 110° off of specular. Metallic travel is often referred to as the degree in change of brightness going from the face angle to the flop angle [12].
- *Seed level* refers to the degree of protrusion of the metallic flake through a coating film surface.
- *DOI (distinctness of image),* closely related to gloss, refers to the reflection of an image from a metallic pigmented coating back to the observer. The clearer, or more distinct, the reflected image, the higher the DOI value. Typically, the finer the pigment, the higher the level of DOI [13].
- *Patina* is the packing appearance of the metallic flakes in coating systems. A good patina is often described as having a smooth velvety appearance, lacking individual flake identity in the coating. If an observer sees only a continuous metallic film without breaks, protrusion, or individual flake identity, the metallic coating is considered to have a good patina. Many coating systems and pigment parameters affect the patina of a coating system. Typically, higher solids coatings, poor application methods, coarse pigments, and poor flake orientation contribute to poorer patina properties.
- The *color* attributes from the face and flop angles can be numerically measured. There are a number of instruments available today that are capable of measuring reflected light at different angles. All of them are goniospectrophotometers and are capable of measuring

reflected light on metallic pigmented coatings at angles from 10° off specular to 110° off specular. Measurement techniques are described in ASTM E2194, Standard Practice for Multiangle Color Measurement of Metallic Flake Pigmented Materials.

PHYSICAL PROPERTIES

- *The aspect ratio of metallic flakes, which is a ratio of flake thickness to median flake diameter, can be calculated using data generated by the water coverage test, and particle size analysis. A mathematical calculation can be made from the water coverage test to generate reliable information on flake thickness, which can then be compared to the median particle size, thus generating the aspect ratio.*
- *Another physical property relating to flake brightness is surface smoothness of the metal flake. Using Atomic Force Microscopy, relative differences in flake smoothness can be measured. This advanced technology offers analytical information, which, when combined with other physical information, can describe the aesthetic property of the flake.*

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Effect Pigments

Paul J. Nowak[1]

EFFECT PIGMENTS ARE "TYPICALLY" DEFINED as flake or platy structures that impart a directional light reflectance, scattering, absorption, or optically variable appearance to the substrate in or on which they are applied. It will be shown that effect pigments are no longer limited in composition to inorganic materials and in fact can have alternative geometries. The mechanisms, however, by which all effect materials manipulate light, and thus color, still revolve around three basic optical principles, "reflection," "interference," and "diffraction." It should be noted that while metallic flake pigments can also be considered effect materials, the article will focus on structures that manipulate light primarily through selective interference, and more recently diffraction, rather than "specular" reflection only. It should be emphasized, however, that reflection is still an integral parameter in the most recent technologies developed.

WHY EFFECT PIGMENTS?

What is the driving force that has led to the development of so many different types and complexities of effect materials? The answer to this question may be more closely related to our human condition versus commercial reasoning. For centuries, man has made colors symbolic of the events and materials found in nature. While solid colors have regional differences in terms of significance [1], a few colors and effects could arguably be considered universal. For example, the sparkle and luster of precious metals have always denoted value. Pearls and other precious stones denote wealth, and silk gives the impression in our mind's eye of a specific tactile feel and thus a sense of luxury. The natural forms of such materials have been pursued throughout history requiring men oftentimes to go beyond the boundaries of the known, risking their lives to acquire such materials. So is it the rarity of a substance that triggers the desire or is it a psychological drive that may be simply stated as perception? After all, color and effect are merely our individual interpretation of a small part of the vast electromagnetic spectrum that encompasses and connects all things. Color is not a tangible object. It is a vast and complex interactive biological process whose preference is not static but rather dynamic. So it is more likely that the development of effect materials is a result of our ability to relate, on a deep emotional level, to the symbolic representations that our culture and society has effected. They are tools used to appeal to our changing moods and emotions caused by our own physiological and psychological makeup at the moment, to create preferences and associations that we then link to the color-emotion response itself.

From a commercial standpoint, with the prominence of branding, color and effect are often the living embodiment of a brand's values and personality [2]. They are identifying factors that connect with the consumer, are recognizable, stand out from the competition, and trigger, on a subliminal level, the buying decision [1]. Color and design play a pivotal role in ensuring that the consumers' perception of the brand is mirrored in the package or product. Consumers make a brand purchase just as much as they make a product purchase. The study of the importance of color and effect on us as human beings is still largely not well understood.

HISTORY

Many excellent reviews on effect pigments have been written [3–5]. In contemporary terms, the most common effect pigments are referred to as pearlescent (nacreous) or iridescent pigments. Pearlescent pigments are high-refractive-index materials that are coated onto thin transparent flakes that usually are mica, but many other substrates have been investigated as, for example, silica flakes [6]. Various flake materials will be discussed in the ensuing text. The flakes reflect incident light but allow a portion of the light to be transmitted. Basically, they are an attempt to create the natural luster effect seen in pearls or seashells [7]. These types of materials hold by far the lion's share of this specialized, rapidly growing and changing market, and they were described in detail in the previous edition of this manual [8]. Pearlescent pigments, interference pigments, and special-effect pigments are all names used for effect pigments.

The origin of effect pigments has been customarily attributed to the French rosary maker Jaquin, who isolated the silvery substance (guanine/hypoxanthine) found inside fish scales around the 15th century [9]. The widespread commercial use of such material really had its start in the early 20th century where it was used to simulate mother of pearl by incorporation into early forms of plastic, cosmetics, and even applied to automobiles [10]. Due to the obvious difficulties of isolating large quantities of guanine, synthetic mono-crystalline alternatives were developed in the 1930s and included compounds such as mercurous chloride, lead hydrogen phosphate, lead hydrogen arsenate, and basic lead carbonate. Due to the obvious toxicity concerns, these materials have been replaced by bismuth oxychloride [11], which is still commercially produced.

Despite many efforts to create natural pearl essence synthetically, a method to create the necessary platelike structure has never been found even though the internal crystal structure has been duplicated. This inability to

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synthesize a true pearl essence led to the multi-layer "inorganic synthetics." Most notably was the work by Linton of E.I. DuPont and others that was carried out in the early 1960s. These efforts involved coating titanium dioxide, iron oxide, or combinations thereof onto mica platelets via a hydrothermal process [12]. In this instance, the failure of the obvious synthetic approach to produce natural pearl essence was responsible for the ultimately greater success of creating a new type of color unknown in previously existing pigments. It is this initial work by Linton that is credited as the foundation on which most, if not all, successive technologies have been based.

In the 40-plus years that have followed, numerous variations of the Linton method have been duplicated and improved upon. Additionally, postprocessing of standard oxide-coated mica-based pigments has provided a means to create new color variants. A couple of examples, which are historically important as well as commercially important, are the DynaColors® [13] introduced to the market by the Mearl/Engelhard Corporation of Iselin, NJ,[2] in 1988.

In this instance, standard high-performance organic pigments have been coated onto variants of oxide-coated micas to create interference colors at the specular angle and a dramatic highly saturated color at the diffuse or flop angle. There were few limitations with respect to the color combinations that could be created. With such technology, it is possible to create colors with very specific and dramatic color shifts. Outside of the cosmetics industry, these materials were the first attempt at creating what we now consider true optically variable color effects.

Alternatively, the Infinity Colors® [14] developed through a joint project between Shiseido of Japan and Merck GmbH/EMD Industries of Hawthorne, NY[3], and was introduced to the general industrial market in 1991. In this instance, the TiO_2 coated onto mica was subjected to a solid-state redox reaction using a rotary kiln in the presence of nitrogen, Fig. 1. The reduction of the TiO_2 allowed for the creation of a dark color base, which not only greatly improved opacity, but also when subsequent layers of TiO_2 or other oxides were deposited in varying thicknesses on this surface, unique, highly chromatic, optically variable colors were produced. By using such methods and variations of them, literally hundreds of colors based on metal oxide combinations coated onto mica have been produced, leading to an estimated global market of $600 million dollars per year.

Since the early 1960s, the implementation of computer-controlled manufacturing, improvements in particle size classification methods (primarily the ability to selectively remove large or fine particles), the availability of higher purity precursors, and more advanced mica beneficiation methods have pushed the envelope for this class of effect materials. The result of these advancements has been not only an improvement in the overall batch-to-batch consistency, but also a tremendous improvement in the purity and number of colors available. Some of the more recent product lines introduced to the market using these

[2] The Engelhard Corporation, 101 Wood Ave., Iselin, NJ 08830, www.engelhard.com

[3] EMD Chemicals, Inc., 5 Skyline Dr., Hawthorne, NY 10532, www.emdchemicals.com.

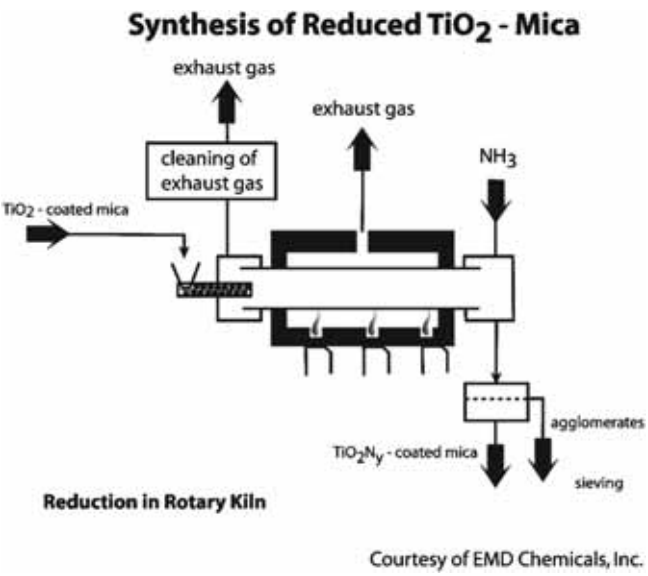

Fig. 1—Synthesis of reduced TiO_2-mica.

developments are the Ultra Colors® developed by Merck GmbH and the Lumina Colors® developed by the Engelhard Corporation in the mid- to late 1990s.

More recently, several new classes of materials have been developed that build off of the advancements in manufacturing and the development of alternative substrates to mica. Such advancements allow for the application of more complex optical principles, such as those used in the field of interferometry on a commercial scale. These newer materials are more precisely able to separate closely spaced spectral wavelength bands and impart goniochromaticity (change in color with viewing angle) through either interference or diffraction of the visible wavelengths of light.

REFLECTIVITY AND THIN FILM INTERFERENCE

To understand the recent developments in effect pigment technology, it is necessary to understand some basic laws of optics as well as a few more complex principles. For purposes of studying effect pigments, light is considered as a wave that follows Maxwell's theory [15].

Based on this wave nature of light, it is known that the speed of light in a vacuum is a constant. However, when light passes through matter its speed is altered and its direction is changed. The measure of these changes is called the index of refraction, **n**. Table 1 lists the index of refraction for several materials that are utilized in both traditional and non-traditional effect materials.

When light passes from a substance of low index of refraction to a substance of higher index of refraction, the speed of light is decreased and if the light enters at an angle, the refracted ray is bent toward the normal. If, however, light enters a substance from a medium of high index of refraction to a medium of low index of refraction, the opposite is true and the light is bent away from the normal. In Fig. 2, Snell's law is used to calculate the angle **e**" between the perpendicular (normal) and the light ray entering the medium:

$$\mathbf{n}_1 \sin \mathbf{e} = \mathbf{n}_2 \sin \mathbf{e}'' \quad (1)$$

The factors $\mathbf{n}_1$ and $\mathbf{n}_2$ are the refractive indices of the involved optical media. They can be considered as a relative measure of the optical density.

TABLE 1—Refractive index for materials used in effect materials

Medium	Refractive index, n
Vacuum, air	1.0
Water	1.33
Alumina	1.35
MgF_2	1.38
Plastics, paint	1.4–1.7
Mica	1.5–1.6
SiO_2	1.50
Synthetic mica	1.55
Guanine, hypoxanthine	1.85
Basic lead carbonate	2.09
Bismuth oxychloride	2.15
Fe_2O_3	2.4
TiO_2 (anatase)	2.5
TiO_2 (rutile)	2.7

Another important factor to consider in studying effect materials is the reflection of light. We generally speak of two kinds of reflection. One is specular and the other is diffuse. Specular reflection occurs when the angle of incidence equals the angle of reflection (**e** = **e**' of Fig. 2). It is dependent on the absorption coefficient (**k**) of the material. For example, metals have an extremely low absorption coefficient and for practical purposes reflect all of the light impinging on their surface. To get optimum specular reflection such as that with a mirror, the surface has to be extremely smooth. If the surfaces are not smooth, light is not reflected in a specular manner but is diffused resulting in a lower luminous flux being generated (θ_r), see Fig. 3.

Effect pigments follow the laws of reflection of smooth surfaces, and there have been a large number of developments in the past ten years that have resulted in the ability to create smoother surfaces. However, in many constructions of effect pigments the platelets besides being smooth are also transparent. This means that only a portion of the light is reflected. That portion that is not reflected is transmitted through the platelet to the next layer, where it can be further reflected, creating what we visually perceive as depth, Fig. 4.

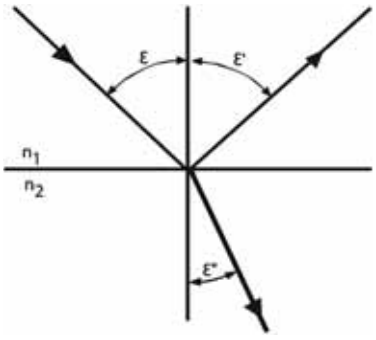

Fig. 2—Effect of increasing refractive index on light.

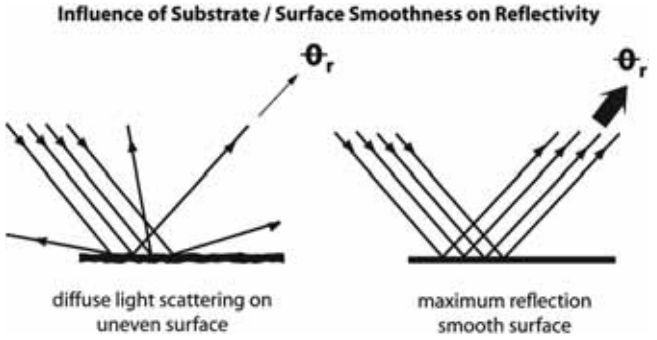

Fig. 3—Influence on substrate/surface smoothness on reflectivity.

The reflection and transmission of the light from the phase boundaries of multiple thin film structures is the basis for interference, thus the generation of color, and follows the superposition principle based on Maxwell's equations [16]. If as in Fig. 3, a parallel plane layer with the refractive index $\mathbf{n}_2$ lies in a medium with a different optical density, then $\mathbf{n}_1 = \mathbf{n}_3$. As mentioned, a light ray **L** reflected upon an interface to an optically denser medium (g_1) will be shifted in phase length by half a wavelength or 180°. At interfaces to substances with a lower refractive index, no phase shift occurs. The phase shift λ/2 for the former case is pictured in the shape of a sine wave, Fig. 5.

Both partial rays $\mathbf{L}_1$ and $\mathbf{L}_2$ can interact with each other. Interference effects can occur. The rays have an optical path difference resulting from the phase shift λ/2 of $\mathbf{L}_2$ and the geometrical and temporal detour of $\mathbf{L}_1$, Fig. 3. The detour of the $\mathbf{L}_1$ partial ray (at vertical incidence) is $2\mathbf{dn}_2$. The product $\mathbf{dn}_2$ is known as the "optical thickness" in the case where the pigment platelet thickness plays a roll [17].

During sinusoidal oscillation, the optical thickness can result in a wave crest of one partial ray meeting the wave trough of the other, Fig. 6. This situation in which the light intensity is weakened (destructive interference) occurs when in Eq (2) the following conditions are met (m = 1,2,3. . .); λ =wavelength of partial rays: m is an integer that allows the equation to describe reflections of successive orders.

$$\lambda_{\min} = \frac{2\mathbf{dn}_2}{m-1} \qquad (2)$$

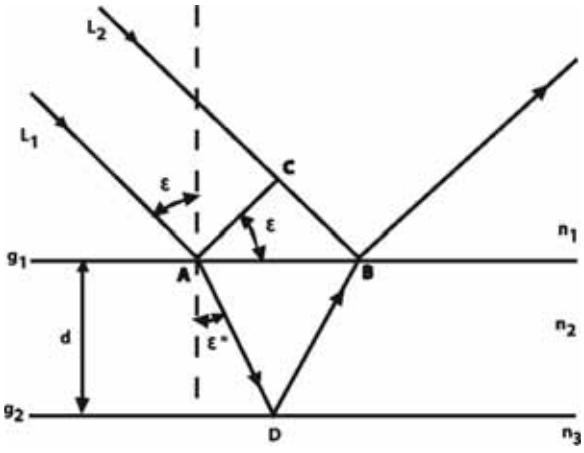

Fig. 4—Diagram to determine the phase relationship between interfering light rays.

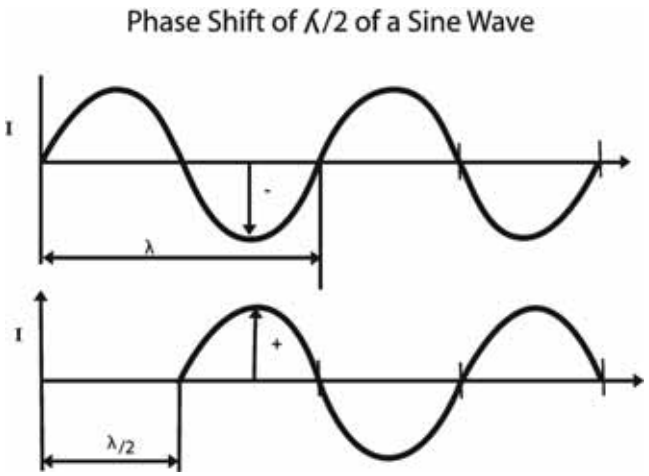

Fig. 5—Phase shift of λ/2 of a sine wave.

All colors in the achromatic spectrum whose wavelengths correspond to the equation will be cancelled out. If, however, a wave crest meets a wave crest, the intensity of light is amplified (constructive interference) and Eq (3) is valid (m = 0,1,2,3. . .):

$$\lambda_{max} = \frac{4\mathbf{n}_2\mathbf{d}}{2m-1} \tag{3}$$

All colors whose wavelengths correspond to this equation will be amplified. The relative intensity of the reflection maximum can be calculated using a simplified Fresnel equation [18]. Since Eqs (2) and (3) are only valid for one wavelength or its multitudes, a part of the visible spectrum will weaken or be deleted while another part will be reflected optimally. This is called selective reflection [19] and can be calculated by using Eq (4)

$$\mathbf{r}(0^0)_{max} = \left[\mathbf{n}_2^2 - \mathbf{n}_1^2/\mathbf{n}_2^2 + \mathbf{n}_1^2\right]^2 \tag{4}$$

The color of the reflection maximum depends upon the layer thickness of the material in which the light enters at the interface g_1, Fig. 3. The maximum shifts to larger wavelengths with increasing layer thickness. The numerator indicates that the greater the difference in refractive indices, the greater the reflectance. The effect of the difference is magnified by the exponents.

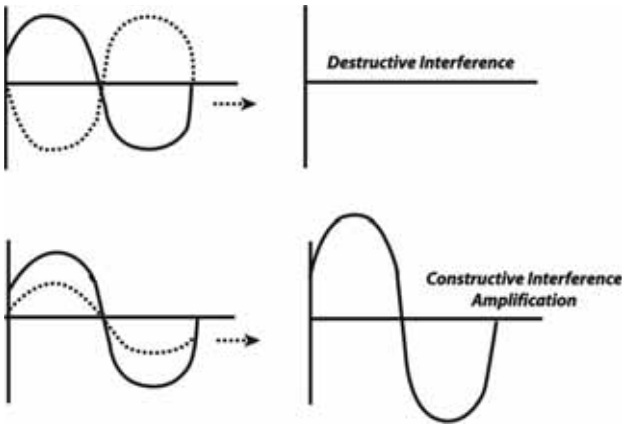

Fig. 6—Interaction of light rays with various phase lengths.

With increasing layer thickness a minimum is added to the reflection maximum in the visible range and clear color impressions on the order of the colors of the rainbow result. For example, if we increase the optical path length to 100 nm, the reflection maximum lies in the bluish-white range, and if the product $\mathbf{n}_2\mathbf{d}$, Fig. 3, is further increased to 140 nm, a reflection maximum of yellow-white results. By increasing the optical thickness further, reflection colors are produced that change continuously from white, yellow, red, violet, blue, and green, each reflection color accompanied by its complementary transmission color. This pattern of color is repeated with the colors of the second and higher orders. The color series of higher orders follow in the same manner by increasing optical path length. As the layer thicknesses increase, maxima and minima follow each other more quickly and become more difficult to resolve. The colors in the various higher orders are extremely desirable as they typically differ in shade, brilliance, and level of saturation [20], Fig. 7.

In interference, the reflection and transmission colors vary with angle of incidence. The reflection maximum and minimum shift to lower wavelengths as the angle of incidence increases. The color shift is governed by the expressions

$$\lambda_{max} = (4\mathbf{d}/2m-1)(\mathbf{n}_1^2 - \sin^2\mathbf{i}) \tag{5}$$

and

$$\lambda_{min} = (2\mathbf{d}/m-1)(\mathbf{n}_1^2 - \sin^2\mathbf{i}) \tag{6}$$

in which **i** is the angle of incidence at the initial phase boundary. Equations (5) and (6) reduce to Eqs (2) and (3) for perpendicular incidence where **i** = 0°. The radical in Eqs (5) and (6) change more rapidly with i for smaller values of $\mathbf{n}_1$. Thus a lower refractive index produces a greater color shift.

From the discussion above, it can be seen that through the manipulation of the variables within the optical equations it should be possible to maximize the levels of reflection at the phase boundaries by using semi-transparent metal layers. When light falls on a metal, we would expect that it should be totally absorbed. It is exactly because of this extremely strong absorption of metals that absorption does not have an opportunity to occur! To understand this apparent paradox, we need to examine the process of reflection.

In dealing with an insulating material, such as most inorganic and organic substances, the percent reflectivity **R** for a beam of light falling on the material at normal incidence, or on leaving the material, is given by the equation:

$$\mathbf{R} = 100(\mathbf{n}-1)^2/(\mathbf{n}+1)^2 \tag{7}$$

where **n** is the refractive index. A typical dielectric medium with **n** = 1.5 gives **R** = 4 %; thus most of the light is transmitted into the medium and only very little is reflected. When light falls onto a metal, it is so intensely absorbed that it can penetrate to a depth of only a few hundred atoms, typically less than a single wavelength. Since the metal is a conductor of electricity, this absorbed light, which after all is an electromagnetic wave, will induce alternating electrical currents on the metal surface. These currents immediately remit the light out of the metal, thus providing an extremely strong reflection.

Mathematically, in Maxwell's equations we need to replace the refractive index n by the complex refractive index

$$\mathbf{N} = \mathbf{n} + \mathbf{ik} \tag{8}$$

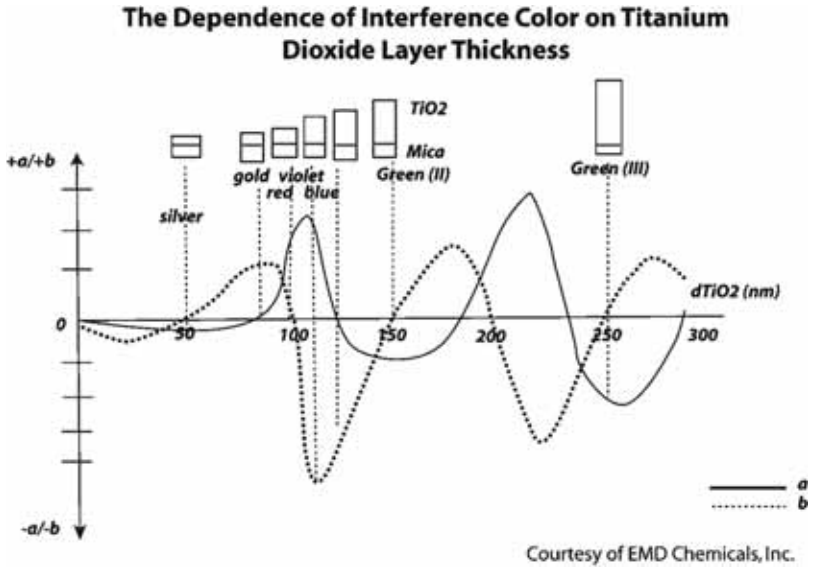

Fig. 7—The dependence of interference color on oxide layer thickness.

where **i** is the imaginary square root of negative one and **k** is the attenuation index, coefficient of absorption, or extinction coefficient. Equation (7) now becomes

$$\mathbf{R} = \left[100(\mathbf{n}-1)^2 + \mathbf{k}^2\right] / \left[(\mathbf{n}+1)^2 + \mathbf{k}^2\right] \qquad (9)$$

The percent reflectivity for silver, as an example, and sodium D light, the values **n** = 0.18 and **k** = 3.6 give a reflectivity of 95 %. The metallic luster thus turns out to be no more than a high reflectivity. To show its high reflectivity the surface of a metal alloy or semiconductor must, of course, be very smooth.

Multiple reflections between parallel surfaces of semitransparent metals are used in the Fabry–Pérot filter used in the study of interferometery [21]. Through modification of the geometric thickness or path length, the transmitted beams can be made to constructively and destructively interfere. With the usual air-dielectric interface, a reflectivity of 4 % is generated, the intensity of these reflected beams falls rapidly, and the resulting interference pattern is shown in the top curve of Fig. 8. If the reflecting surfaces are metallized, the multiple reflections become more effective and there is a drastic change in the transmission pattern as shown in the second and third spectral curves of Fig. 8. Therefore, using such a construction, it is possible to resolve very closely spaced colors and significantly improve the levels of saturation, especially at the higher orders of interference. In addition, the spectral bands are separated as well as magnified, resulting in extremely sharp color changes at various angles of viewing, which is essentially a change in the angle of incidence. Only until recently has it been possible to construct such a material on a commercial scale mainly due to the developments in manufacturing. It is this ability to magnify and resolve color using such a system that the Chromaflair® pigments produced by Flex Products, a JDS Uniphase Company,[4] are based. They provide not only very highly saturated interference colors but also have a very sharp angle-dependent multiple-color effect. Such materials are without a doubt the most intricate and highly sophisticated effect pigments on the market today (see Fig. 9).

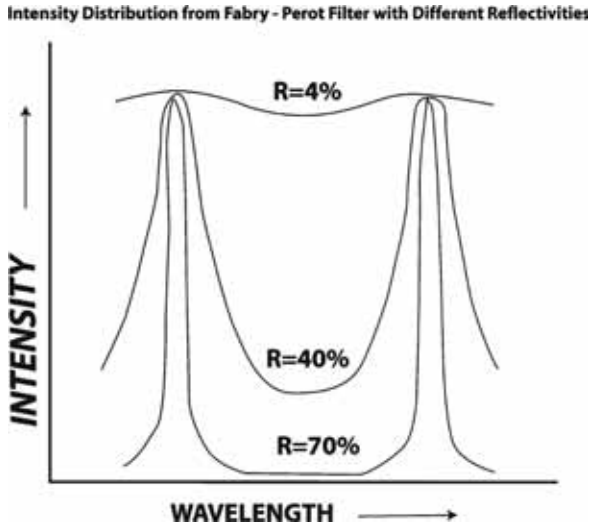

Fig. 8—Intensity distribution from Fabry-Pérot filter with different reflectivities.

Advances have been made recently with the more traditional interference effect materials as well. While they are not as precisely constructed as the Fabry–Pérot filters, they do share many of the same attributes, namely, the ability to produce optically variable colors with strong angle dependence and reasonably high saturation.

In these cases, multiple thin films of varying thickness of high refractive index such as the traditional metal oxides (optical stacks) are coated onto substrates or layers of low refractive index. By varying the thickness of the dielectric and the metal oxides, they also can produce relatively narrow transmission bands through constructive and destructive interference. One example is the structure of Fig. 10, using only dielectric (nonmetallic) layers as the substrate. Here, each layer contributes to the development of color. The TiO_2 layer being a higher refractive index material does not separate the light ray as far from the normal as the SiO_2 layer. Thus

[4] Flex Products, A JDS Uniphase Company, 1402 Mariner Way, Santa Rosa, CA 95407, www.flexprod.com.

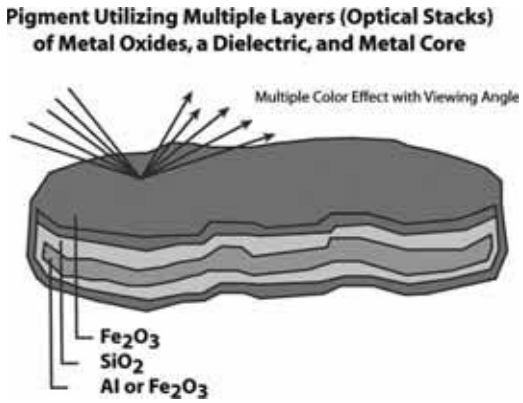

Fig. 9—Thin film interference pigment flake cross section (Fabry-Pérot filter type).

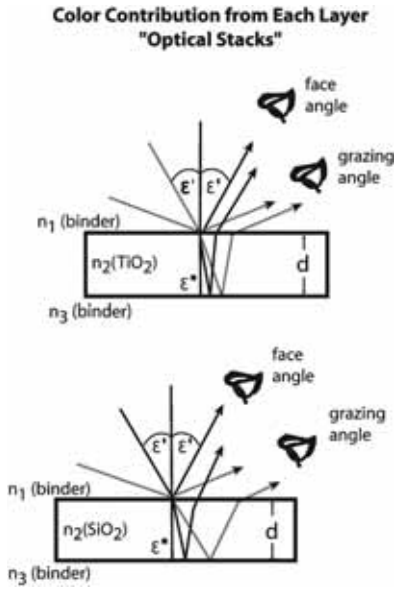

Fig. 10—Color contribution from each layer of an optical stack.

by varying the thickness of each layer, each can be tailored to a specific thickness to reflect selectively, specific wavelengths of light as previously discussed. Since there is very little absorption in such a construction, essentially all of the light not transmitted is reflected. Materials used for such dielectric interference filters include MgF_2, borosilicate glass, alumina, or SiO_2. The latter two materials are marketed under the trade name of Xirallic® and Colorstream™, respectively. They are manufactured by EMD Chemicals of Hawthorne, NY.

Another variation is to use a standard metallic flake as a core and then coat the metal with a dielectric material followed by a semi-transparent metal oxide. The optical principles of color generation in this case are more similar to the Fabry–Pérot filters. Here, the effect of the metal core is to enhance the amount of light available for constructive and destructive interference. BASF GmbH of Ludwigshafen, Germany,[5] is currently marketing such materials[4] under the trade name of Variacrom®.

Using these principles, the extent of extinction and enhancement of particular wavelengths is efficiently

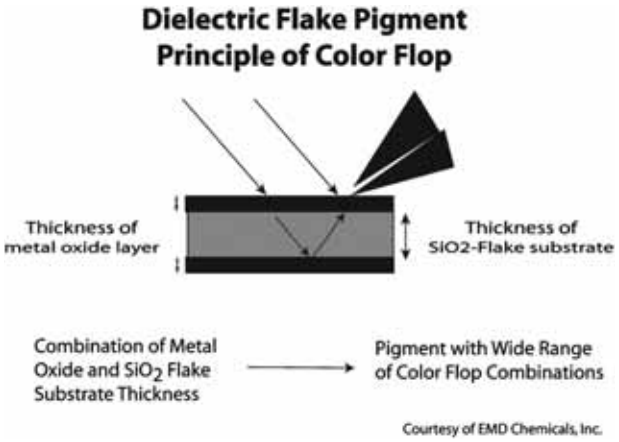

Fig. 11—Dielectric substrate pigments principle of color flop.

increased although less so than with the Fabry–Pérot filter types. Through the manipulation of the composition of materials and thicknesses of those materials "optical stacks," there has been created a totally new series of effect pigments that exhibit highly saturated interference colors, a high degree of reflectivity, with the potential for high color dependence on viewing angle (color flop), Fig. 11.

DIFFRACTION

An alternate method of separating light into its various components is by diffraction [22]. Diffraction is the bending of light waves around an object. The term diffraction is used to describe the behavior of light when it departs from rectilinear propagation. This happens when the edge of an object produces an interrupted wave front and the light then bends around the edge: The resulting color-producing phenomena involve interference. While diffraction necessarily involves interference, the reverse is not true [23].

Just as increasing the number of reflections in the Fabry–Pérot etalon increases the sharpness of the interference colors, so the same happens with a diffraction grating. The diffraction grating can be defined as an optical component made by a periodic assembly of reflecting or transmitting obstacles (grooves) separated by a distance comparable to the wavelength of light applied. Various shapes, such as triangular symmetrical, triangular blazed, square-wave with different top plateau sizes, and sinusoidal gratings can be produced. Additionally a variety of groove frequencies, blazed angles, and depth profiles can be produced. For a given grating frequency, the depth, shape, and orientation of the grooves determine the relative intensity of the various interference orders through the process as previously discussed, mainly constructive and destructive interference.

When light is incident on a grating, it is diffracted into discrete wavelengths. The incident beam is separated forming the zero order diffraction or specular reflection, that is a mirror effect color of the incident light. First order diffractions (negative first order and first order) surround the zero order. Eventually other higher orders surround the first orders depending on the groove frequency of the grating, Fig. 12.

The ability of a grating to diffract light is described by the grating equation:

$$m\lambda = \mathbf{d}(\sin\alpha + \sin\beta), \tag{10}$$

[5] BASFAG Ludwigschafen, Germany, www.basf.com.

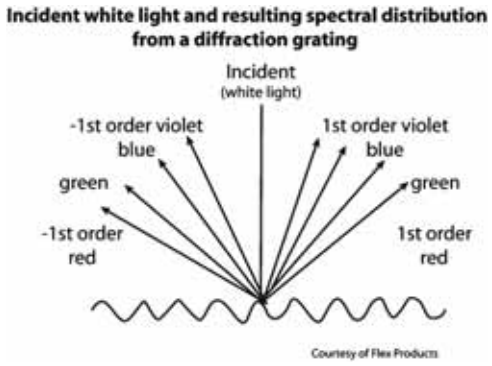

Fig. 12—Incident white light and resulting spectral distribution from a diffraction grating.

where α and β are the angles between incident light and normal, and the diffracted beam and the normal to the grating, respectively. The integer m is called the diffraction order. For $m = 0$, $\beta = -\alpha$ for all λ, where the wavelengths are not separated, this is the specular reflection or zero order.

The higher the groove frequency, the greater the angular separation between orders. The size of the grating will improve definition of the various orders (resolving power) as adjacent spectral lines are clearly separated. Finally, for a given grating frequency, the orientation of the grooves, the depth and shape, determine the relative intensity of the various orders.

In nature, color by diffraction is relatively rare. However, one of the most outstanding natural diffraction gratings is the gemstone opal, showing on a white or black background, flashes of varied colors can be observed. This was at one time thought to involve thin film interference, but electron microscope photographs taken of an opal reveal its secret, demonstrating a regular three-dimensional array of equal-size spheres, Fig. 13. The actual composition of the spheres is amorphous silica (SiO_2), containing a small amount of water. These spheres are cemented together with more amorphous silica containing a different amount of water so that a small refractive index difference exists between the spheres and the cement [24].

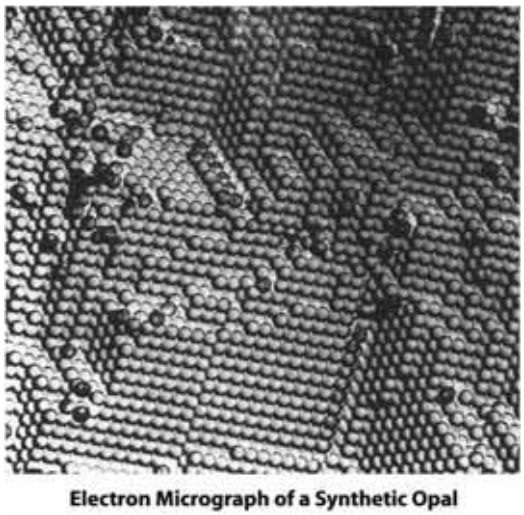

Fig. 13—Electron micrograph of a synthetic opal.

The theory of a three-dimensional diffraction grating consisting of stacks of identical layers is well known from the field of x-ray crystallography, Fig. 14, where Bragg's law applies, Eq (11). Reinforcement of diffracted waves occurs when the angle of incidence for diffraction from a layer equals the angle of reflection, and when the path difference between the reflections from adjacent layers with a spacing **d** is a whole number of wavelength. The condition for reinforcement becomes

$$\mathbf{n}\lambda = 2\mathbf{nd}(\sin\theta) \tag{11}$$

In natural opals, the uniformly packed spheres providing diffraction occur in patches ranging from less than a millimeter to more than a centimeter across. Within each patch the color will vary with the angle of viewing, with the longest wavelength appearing at normal incidence with $\mathbf{I} = 0$ as in

$$\mathbf{n}\lambda = 2\mathbf{d}(\mathbf{n}^2 - \sin^2\mathbf{I})^{1/2} \tag{12}$$

Films of certain types of liquid crystals, organic compounds with a structure intermediate between that of a crystal and that of a liquid, can show a left-handed or right-handed twisted structure resulting in layer gratings with a repeat distance in the range of visible light. Such substances are called cholesteric or chiral liquid crystals (not superimposable on their mirror images). When a beam of white light falls on a film of such a substance, a narrow wavelength region will be reflected by diffraction according to Bragg's law. This is expressed in the form of Eq (13), where **n** is the refractive index, **p** is the pitch distance in nm, and θ = angle of viewing.

$$\lambda_{ref} = \mathbf{np}\cos\theta \tag{13}$$

An interesting and unique phenomenon occurs with such substances. The light will be circularly polarized with the sense of the polarization related to the handedness of the twist of the structure. Both the opposite polarization and all other wavelengths are transmitted through the film. The diffracted light resembles that from an ordinary diffraction grating except for the polarization. It should be noted that the diffracted color does not depend on the total film or layer thickness as it does with interference pigments, but rather on the layer "repeat" distance within the film. Similar to a typical diffraction grating the colors vary

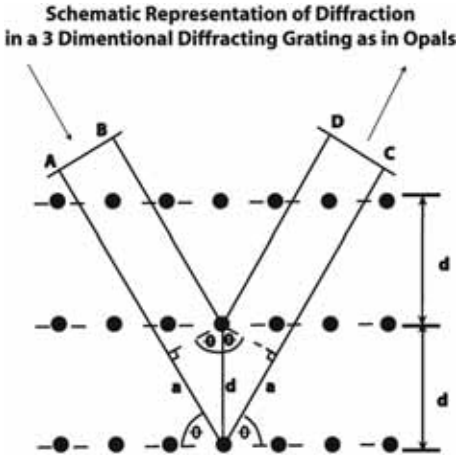

Fig. 14—Schematic representation of diffraction in a three-dimensional diffraction grating as in opals.

with viewing angle [25]. One difference, however, is that in diffuse light the interference phenomenon is still visible.

Closely related to the diffraction effect in opals is the ability of small particles to selectively scatter light [26]. This scattering of light will depend on whether the wavelength of the light is large or small compared to the diameter of the particle. In practice, two different theories are used to describe the scattering or diffraction of light from a particle [27]. They can be distinguished by a dimensionless size parameter, (**a**).

$$(\mathbf{a}) = 2\pi\mathbf{r}/\lambda \qquad (14)$$

For very small values of (**a**), the Rayleigh theory of light is valid. For larger values of (**a**), the Mie theory [28] of light scattering is necessary. For very large values of (**a**), diffraction, reflection, and refraction can be used to explain scattering. In practice, Raleigh theory is normally only employed to describe the interactions between gas molecules and light. However, it can be used up to an (**a**) value of 0.5 without incurring great error. Raleigh's theory can be simply expressed by Eq(15),

$$\mathbf{Is/Io} = \text{constant}/\lambda^4, \qquad (15)$$

where **Is** is the intensity of scattered light and **Io** is the initial light intensity. In general, the shorter wavelengths are more efficiently scattered by very small particles. The end result is that it is possible to create optically variable color effects with such small particles. Good blue scattering can be observed from particles as large as 300 nm (still smaller than the 400 nm wavelength of violet light) down to particles just a few atoms or molecules in size, say 1 nm in diameter. The exact shade of blue depends in a very complex way on the size of the scattering particles, the distribution of sizes, their arrangement, and even their shapes.

When the size of the particle approaches and then becomes larger than the wavelength of light λ, the Mie theory is used to explain the scattering. The scattering is no longer predominantly blue, but sometimes shows different colors, mostly red and green bands, but only at certain angles. The Raleigh scattering effect is the basis for the nanoparticle size TiO_2 type of effect pigments that produce a soft opalescent highlight with a blue undertone [28].

In more recent times (within the past ten years), novel approaches to using the physical principles behind generating color through interference and diffraction have resulted in what are now considered "state of the art" effect pigment chemistries. These developments have primarily revolved around the development of novel substrates and methods of manufacture building on the foundation of the original layer substrate technology.

DEVELOPMENT OF NEW SUBSTRATES

Apart from naturally occurring muscovite mica, naturally occurring phlogopite, sericite, and biotite have all been used to create various pearlescent and iridescent pigments. Each of these common materials has their various advantages and disadvantages when it comes to physical properties [29]. However, of these, the most widely used type of mica is muscovite, chemically defined as $KAl_2(AlSi_3O_{10})(OH)_2$. More specifically is a grade of muscovite mica that originates from mineral deposits in India. It differs from domestic sources in that it has improved optical clarity due to a lower level of iron and manganese contaminates. The bulk color is typically a pale pink, rather than beige or yellow. The improvement in the initial quality of the substrate bulk color allows for the ability to create brighter, and whiter, white pearlescent pigments and more chromatic iridescent pigments. The mica is ground as an aqueous paste in a Muller or friction mill to delaminate it into very thin platelets with smooth surfaces. As the mill rollers go over the mica, it becomes thinner and smaller in particle-size, increasing the aspect ratio (lateral diameter to thickness). These mica flakes are then dried, sieved, and classified into the desired starting particle-size distribution.

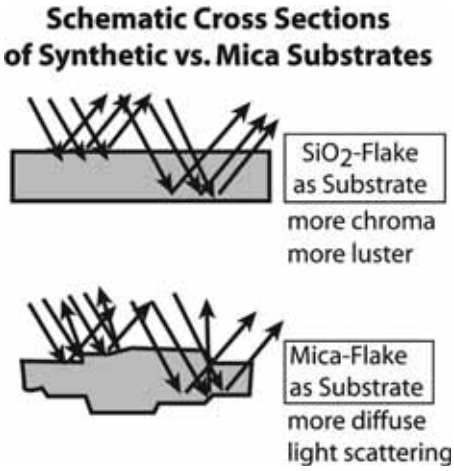

Fig. 15—Schematic cross section of synthetic versus mica substrates.

The optimum particle size distribution as measured by laser diffraction methods falls between 10–40 μm. This is the particle size at which maximum luster occurs. Smaller particles <5–10 μm act as light scatters due to insufficient coating or inefficient parallel orientation. Particles larger than 40 μm give a coarse effect and reduce opacity. It has been found that not only the particle size distribution but also the uniformity in thickness of each particle is important. The wet grinding process while fairly good with respect to delamination and creating smooth flat flakes is by no means optimum. There is some unavoidable uneven delamination of the mica layers resulting in a "stair step" type morphology on the surface. These "steps" scatter light similar to the platelet edges, which, in turn, reduces the direct light reflection from the coated pigment surface, Fig. 15. Furthermore, multiple domains of thicknesses reduce the intensity of the interference chroma and cause a desaturation of the reflected color. The fact that most mica in use today is a naturally occurring mineral, it inherently has variation in terms of purity, crystal structure, and surface smoothness. Therefore, nearly all of the newer substrate technologies that have been developed to date optimize the prerequisite properties of the substrate that are delineated in Table 2.

The importance of the initial substrate quality cannot be overstated. Of particular interest in this respect is the development of synthetic mica or fluoro-phlogopite, $KMg_3(AlSi_3O_{10})F_2$, by Topy Industries in conjunction with Nihon Koken Kogyo (NKK)[6] of Japan in 1992, and commercialized in

[6] Nihon Koken Kogyo Co., Ltd., 15-18 Kodenmacho, Nihonbashi Chuoku, Tokyo, Japan, Tel: 81-3-3663-6721.

TABLE 2—Prerequisite properties of effect pigment substrates

Number	Property
1	Refractive index
2	Optical clarity
3	Surface smoothness
4	Uniform particle thickness
5	Aspect ratio

1995 under the trade name Ultamica® [30] and distributed in North America by Itochu Specialty Chemicals Inc. The synthetic mica contained significantly fewer impurities and provided a means to significantly optimize the level of luster and chromaticity of interference and reflected light. Synthetic mica still, however, had to be ground and classified, leading to irregular surfaces and uneven thickness although it was greatly improved, see Fig. 16.

In the late 1990s the Engelhard Corporation of Iselin, NJ², introduced a series of interference pigments based on a synthetic borosilicate glass [31]. The glass had many of the prerequisites of an ideal substrate (e.g., low refractive index, optical clarity, smooth surface, fairly uniform thickness, and a high aspect ratio) and was introduced to the market under the Firemist® trade name.

The latest generation of effect pigments based on the layer substrate principle has been the development of synthetic substrates based on calcium-aluminum-borosilicate, and SiO_2 flakes [32] by Merck KGaA. These synthetic substrates are manufactured in a way similar to the web coating device used for synthetic mica [33], see Fig. 17. The thickness can be controlled so precisely as to impart an interference color of its own. This, when combined with a layer of metal oxide similar to other more common pearlescent pigments, allows for the development of a series of optically variable pigments (OVPs) in which the color is viewing angle dependent. They generate their colors through the optical principles of simple interference filters. The materials have been commercialized under the trade name Colorstream®, by Merck/EMD Chemicals of Hawthorne, NY.

From the above discussion with respect to the prerequisites of a substrate, these materials have a low refractive index (1.5, 1.3), respectively, an absolutely flat surface, optical clarity due to lack of impurities, and a thickness that can be very well controlled, allowing for a higher and more uniform aspect ratio. Due to the ability to artificially control the thickness during the manufacturing process, delamination of the flake is no longer required. Therefore, the issues with a step type surface and variations in thickness are eliminated. The resulting pigments can be made with soft, gradually changing color effects as well as monochromatically and dichromatically combined interference effects.

Another new substrate developed by Merck/EMD, which has recently become commercially important, is based on crystalline alumina flakes ($A1_2O_3$) [34]. This substrate is created through a crystal growth method similar to the early mono-crystalline materials such as bismuth oxychloride, in which two solutions of metal salts are added to an acidic medium at roughly the same time, leading to platelets with extremely flat surfaces, a sharp particle size distribution, high aspect ratio, excellent optical clarity, and good crystalline properties. These crystals also require no milling. The deposition of metal oxides onto this type of surface results in pearlescent and interference pigments with a significantly greater degree of luster, and interference colors of high color purity and saturation for its particle size than has previously been known. They are currently supplied under the trade name Xirallic®. These newly developed pigments are arguably the most commercially

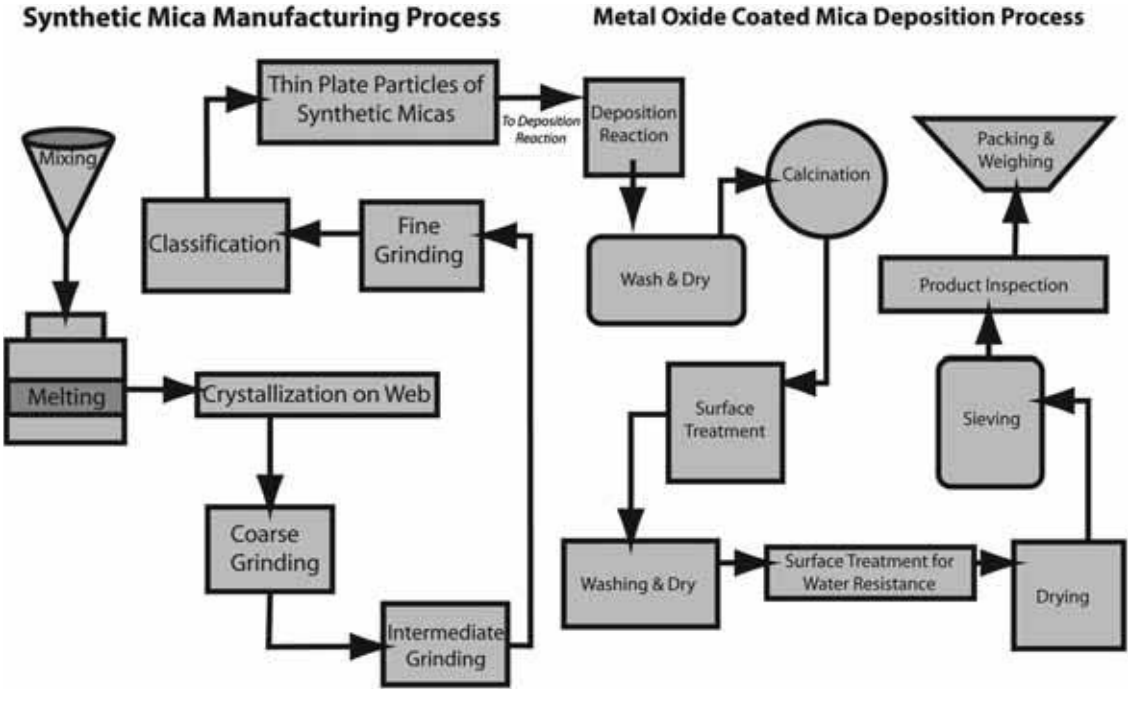

Fig. 16—Synthetic mica manufacturing process and metal oxidecoated mica deposition process.

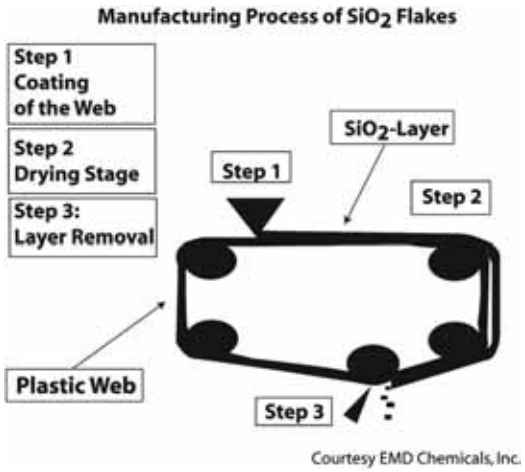

Fig. 17—Manufacturing process of SiO_2 flakes.

important effect pigments to be introduced to the market since the original metal oxide coated mica-based pigments.

DEVELOPMENTS IN MANUFACTURING

The standard hydrothermal process of depositing metal oxides on the surface of a substrate has drawbacks (see Fig. 18). While the improvement in surface smoothness of substrates allows for a smoother oxide coating, the crystallite growth is, from an optical standpoint, fairly rough, and the aqueous method cannot be used for all possible substrates or all metal oxide depositions. If we can gain anything from the evolution of effect materials to date, it is that where there have been limitations, there have been methods found to overcome those limitations. Two of the companies leading the way in this regard are Flex Products, a JDS Uniphase Company of Santa Rosa, CA, and BASF of Ludwigschafen, Germany.

The process by which these companies create lamellar pigments with optically variable interference effects is based on deposition of metal oxides on a platy substrate by either chemical or vacuum vapor deposition. The idea of creating effect pigments by vapor deposition was actually described in a patent by Greenstein in 1955 [35] but it was not until the process was actually developed for other applications by the Polaroid Corporation in 1979 [36] that it was actually proven to be feasible.

The two methods, while similar in theory, differ quite substantially in the means by which the deposition and the resulting pigments are constructed. In the BASF system

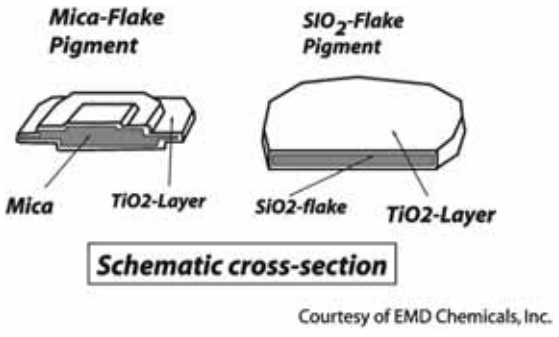

Fig. 18—Schematic cross section of mica versus synthetic flake.

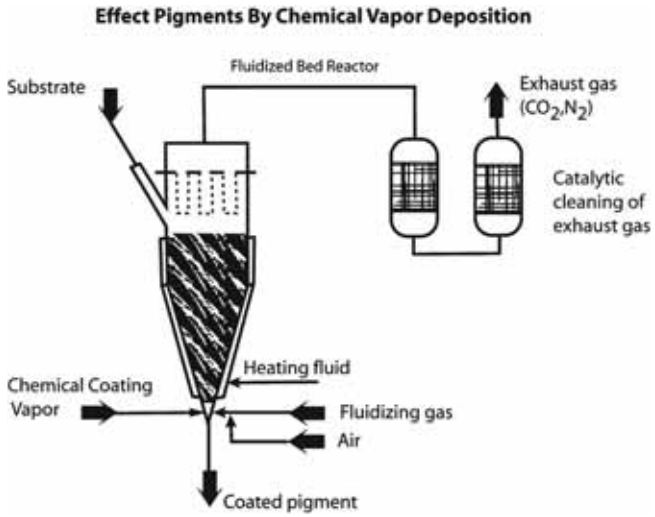

Fig. 19—Effect pigments by CVD.

first described in 1981 by Ostertag [37] (Fig. 19), a substrate is introduced into a cylindrical reaction chamber with a conical bottom and fluidized by the introduction of nitrogen. The fluidization results in a complete separation of the substrate particles, so that all surfaces of the pigments are free. Once the fluidization is complete, the various chemicals are introduced in a vaporized form. If the reaction conditions are properly adjusted, the formed nano-crystalline oxide particles are packed close together on the surface of the substrate building a smooth and optically homogenic film. The coating time determines the thickness of the oxide layer. Once the appropriate thickness has been reached, the reactor is cooled and the particles sieved to remove any agglomerates. In principle, a variety of different substrates and coatings are possible using the chemical vacuum deposition process. It especially allows materials that cannot be handled in acidic aqueous media to be coated, i.e., aluminum or organic pigments. Due to this feature, completely new species of pigments can be manufactured. They are currently supplied to the marketplace under the trade names of Paliocrom® and Variacrom®, respectively.

The second method is based on vacuum vapor deposition, see Fig. 20, and it was first described by Optical Coatings Laboratories, Inc., [38] and commercialized by Flex Products. This class of effect pigments creates Color by

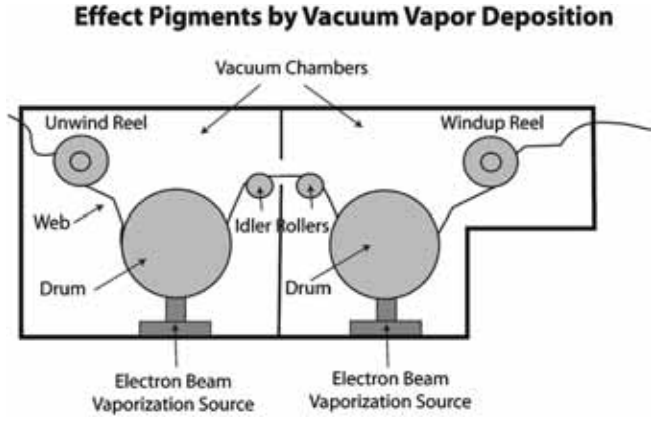

Fig. 20—Effect pigments by VVD.

Physics™. The optical principles on which they create the sharp, dramatic, optically variable interference colors are based on Fabry–Pérot type light filters [39] and thin film interference, which was previously discussed.

The pigment is comprised of three to five layers of precisely controlled thickness that are deposited on a polymeric film. Large rolls of the polymer film, either soluble or non-soluble, are passed through a vacuum chamber containing an electron beam that vaporizes the deposition material from a crucible. Running the film at a specific speed through the chamber controls the thickness of the various layers deposited. This method is, to date, the most precise in terms of controlling thickness of the various layers deposited. The film is then brought in contact with a chill roller and subsequently passed back and forth multiple times in order to build the various layers. These layers are comprised of an opaque reflective core (aluminum oxide) followed by a layer of MgF_2 which has a low refractive index, at quarter wave thickness, on top of which is deposited a thin glass-like layer (SiO_2), followed by a semi-transparent layer of absorber metal oxide. The pigments can be made in either a symmetrical or nonsymmetrical fashion. In addition, many color combinations can be constructed by varying the thickness of the various layers or composition of those layers. The thin film is stripped from the web by passing it through a solvent bath where the pigment particles are "released," and due to their specific gravity (2.0–4.0 gm/cm^3), fall to the bottom of the tank, where they are subsequently recovered, washed, and dried. The particle size is adjusted by dispersing the material in a solvent and ultrasonically agitating. Again the flakes are filtered, dried, and if an even smaller particle size is required they can be subjected to an air grind using an impact pulverizer without readily destroying the color characteristics of the flakes. The result is a pigment with high reflectivity, opacity (due to the metallic core), and outstanding sharp color changes, in a very narrow particle size distribution and a thickness of 1 μm (see Fig. 21).

The color is computer controlled to provide a running color profile at a specific angle across the width and length of the web. An average can be ascertained for the roll that then makes it possible to modify the color at a later step in the event that the color is slightly off by essentially adding a lower or higher color. For example, if the average dominant wavelength of a roll is 495 nm and the desired wavelength is 490 nm, the desired wavelength can be obtained by adding some lower-wavelength material having an average value of 485 nm to achieve the 490 nm target. In addition, it is also possible to blend batches after final sizing to get an even more precise and consistent color match to standard [40].

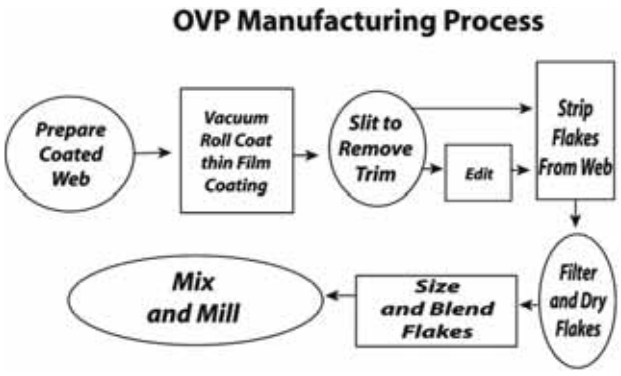

Fig. 21—OVP manufacturing process.

DIFFRACTION

Another exciting development in effect pigment technology arises from the development of color through diffraction rather than thin film interference. There are many demonstrations of diffractive optical effects in non-flake form, notably linear diffractive gratings on plastic or metal foils and holograms [41]. The major characteristic of colors by diffraction is that they are only visible in direct light and disappear when light is diffused. There is a strong color change with viewing angle and the color reflection is iridescent in nature (see Fig. 22).

Three companies have introduced variants of such technology to the marketplace. They are Flex Products of Santa Rosa, CA[4] [42], Spectratek Technologies, Inc., of Los Angeles, CA,[7] and Eckart GmbH[8] (Prismatic Metalure®). Of particular commercial interest are the developments by Flex Products, in which several limitations with respect to particle size, color development, and aspect ratio have been optimized or overcome.

The process by which these pigments are constructed utilizes the vacuum vapor deposition (VVD) process as mentioned above for the Chromaflair® line of colorants. The pigments are produced under tolerances similar to semiconductor chip technology. The particles are comprised of an embossed reflective core layer (usually aluminum) that provides the optical interference pattern of a diffraction grating. This reflective optical layer is then encapsulated by a dielectric layer (MgF_2) that provides the necessary rigidity and durability to the diffractive pigment flakes. The line frequency of the diffractive structure on the flakes is between 1400 and 2000 ln/mm such that light corresponding to the range of visible wavelengths in the first or higher order diffracted beams is substantially

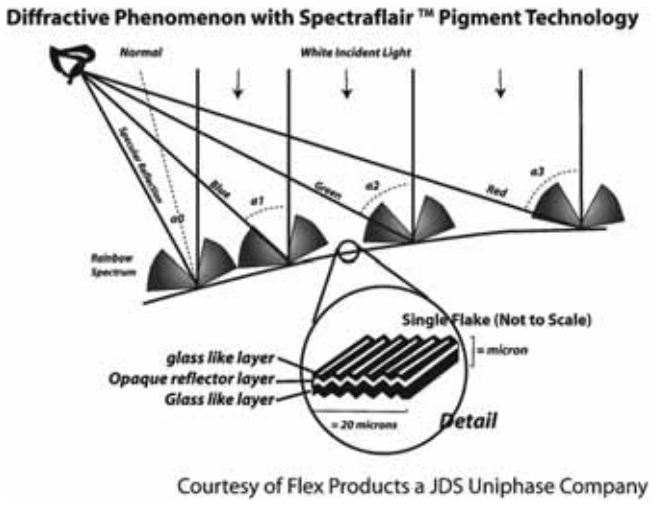

Fig. 22—Diffractive phenomenon with Spectraflair™ pigment technology.

[7] Spectratek Technologies, Inc., 5405 Jandy Place, Los Angeles, CA 90066, www.spectratek.net.

[8] Eckart America L.P., 830 East Erie St., Painesville, OH 44077, www.eckartamerica.com.

angularly separated from the same range of wavelengths in higher order diffracted beams when illuminated at normal incidence up to about 60° from normal incidence. Additionally, the diffractive structure amplitude, which in a grating is the depth of the grooves (160 nm or greater), is such that the zero order diffracted beam is substantially suppressed in intensity so that the intensity of the higher order beams are enhanced over the desired range of wavelengths and/or angles of incidence. The diffractive structure is a linear sinusoidal grating that is constructed by depositing thin films (two to three atoms in thickness) on a structured surface substrate having a releasable intermediate coating layer such that the appropriately sized flakes defoliate from the substrate, replicating its shape. The "recovery" process of the flakes is then similar to the Fabry–Pérot OVPs discussed previously. The result is a very smooth, optically variable diffractive pigment with an average particle size of 25 μm and an overall thickness of 1–1.4 μm, resulting in an aspect ratio of approximately 25:1. The effect achieved with direct illumination is that of the rainbow and in diffuse light gives a liquid metal look. They are currently sold under the trade name of Spectraflair® and manufactured by Flex Products, a JDS Uniphase Company in Santa Rosa, CA.

UNSUPPORTED (NON-SUBSTRATE) EFFECT MATERIALS

It has been shown that many developments in the substrate layer principle have occurred since 1963 and have led to several "state of the art" effect pigments being commercialized. Another area of relatively recent commercial interest is the development of effect pigments that provide color by interference, diffraction, absorption, or a combination thereof, without the use of a supporting material. Several efforts in this regard have been concurrently developed over the last several years along with the advances in novel substrates and manufacturing. It has long been known that various mono-crystalline platy materials could be used as effect materials (e.g., bismuth oxychloride). Some relatively recent developments of particular commercial interest are synthetic platy micaceous iron oxide (BASF Corporation GmbH), platy graphite (Ciba-Geigy of Hawthorne, NY[9]), platy TiO_2 (EMD Industries, Hawthorne, NY, and Engelhard, Iselin, NJ), and nano-particle size TiO_2 (Dainichiseika Color and Chemicals America, Inc., Clifton, NJ[10]).

An area of special interest is the development of effect materials based on purely organic components rather than inorganic materials. Iridescent film technology developed and commercialized by the Engelhard Corporation uses thin film interference principles to manipulate light through the use of alternating layers of polymers differing in their respective refractive indices. The material is manufactured using a co-extrusion process whereby a specialized dye at the extruder head is used to create the 172-plus alternating polymer layers into a film that is then stretched, slit, and chopped using cryogenic techniques to create a flake that can be and is used as an effect material. Such polymers or more commonly called "glitters" have been commercialized for some time and have been developed in a variety of colors. To date, it has not been made robust or thin enough in its flake form for most industrial and high-performance decorative applications. They are, however, prevalent in the hobby, craft, graphic arts, and cosmetics industries.

Liquid crystal polymeric effect pigments (LCPs) have been introduced to create yet another class of unique effect materials. Through developments in the late 1990s by Wacker-Chemie GmbH [43], these materials are quickly becoming commercially important as a means to provide optically variable color effects with a high degree of metallic luster, through the use of a cholesteric or "twisted nematic" helical structure. They are in the chemical class of modified polyacrylates. They are manufactured, Fig. 23, by applying a solution comprised of nematic liquid crystal monomers, or oligomers, a chiral additive that acts as the template for the helical superstructure, and an appropriate cross-linking agent to form a polymer web. A sheer stress is applied to the resulting film to control the thickness and also orient the molecules into offset layers of parallel rows, each row having a slightly different molecular orientation. It is then exposed to ultraviolet radiation to complete cross-linking and to fix optical properties. Subsequently the cured film is mechanically removed from the web and subjected to an air impact pulverizer, wherein it is made to a specific particle size distribution, air classified, and packaged.

The color is controlled by spectrophotometrically monitoring various points across the web during the manufacturing process, and the process parameters are adjusted automatically as required to provide a uniform, consistent color. If required, additional blending of the flakes can be done to further adjust color to standard.

The resulting cigar-shaped polymer platelets are approximately 3–5 μm in thickness and can have a longitudinal diameter of between 40 and 200 μm and a specific gravity of 1.3 g/cm^3. Light falling upon the cholesteric nematic liquid crystal helix is split into two parts. Most of the light is transmitted but a small amount of light is reflected. The wavelength of the reflected light corresponds to the "pitch" (the distance between two layers of the same molecular orientation) of the cholesteric helix, Fig. 24. This determines the wavelength of light being reflected. If one thinks of the molecule as a spring and by either increasing or decreasing the ratio of the chiral additive to liquid crystal, it is possible to arbitrarily tune the wavelength of reflection by compressing or expanding the length of the spring. The wavelength of reflected light changes continuously with the

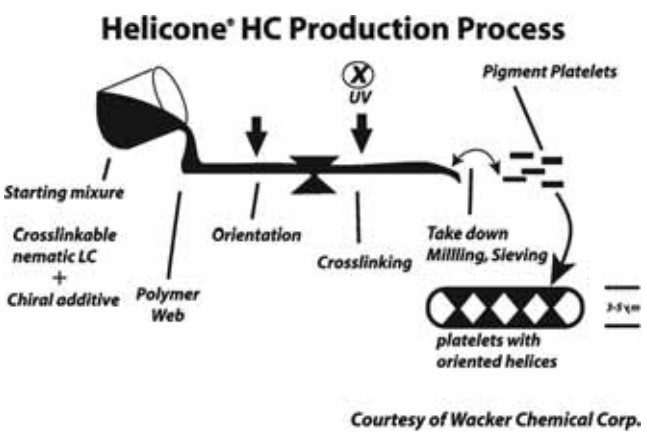

Fig. 23—Helicone liquid crystal production process.

[9] Ciba-Geigy Corporation, Pigment Division, 7 Skyline Dr., Hawthorne, NY 10532, www.cibasc.com.

[10] Dainichiseika Color and Chemicals America, Inc., 40 Webro Rd., Clifton, NJ 07012, Tel: 201-777-0200.

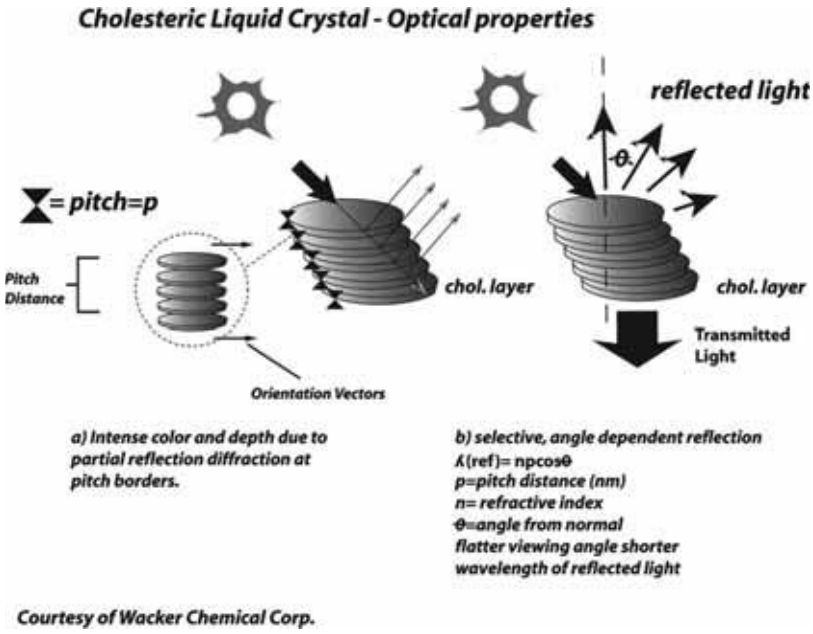

Fig. 24—Cholesteric liquid crystal-optical properties.

viewing angle due to the reflective diffraction of light by the edges of the rigid molecules comprising the helix. The color transition effect is significantly softer and less sharp than corresponding multi-layer inorganic materials based on Fabry–Pérot interference filters, or diffraction gratings, as discussed previously. Due to the sharp spectral reflection bands, however, the mixing of various colors results in each particle retaining its own individual color characteristics since there is little overlap of the spectral bands and thus little destructive interference. Such polymer flakes are also not as dependent upon orientation, as there are no edges to scatter the light, resulting in superior levels of chroma at the diffuse angle. In addition, such chiral molecules can reflect and transmit circularly polarized light based on the handedness of the helix. This property also allows color and effect to be seen in diffuse light. They are supplied to the marketplace by Wacker-Chemie GmbH of Munich, Germany, under the trade name of HELICONE® HC, which describes the helical-conical molecular structure.

FUNCTIONALITY

The ability of flake type materials to impart barrier properties to coatings is well established [44,45]. Over the course of the past 15 years numerous examples of functional effect pigments based on the layer substrate principle have been developed. In automotive and coil coatings, for example, patented surface treatments have been applied to improve humidity resistance for such high-performance applications [46–48]. They have also been modified to provide better adhesion, improved dispersion [49], and even handling characteristics during the coating and plastics master batch-manufacturing process (e.g., pre-wetted). Treatments have also been applied to enhance the performance of the matrix in which they are used. In cosmetics, for example, where smoothness and feel when applied to the skin are important, effect pigments have been developed that not only improve these properties but also improve press and payoff of the powders in which they are formulated. In sunscreens, where ultraviolet radiation protection is paramount, effect pigments have been developed to enhance ultraviolet-radiation-screening capabilities [50–52] while providing a soft lustrous glow to the skin and thus an enhancing cosmetic effect.

Traditionally, for use in powder coatings, effect materials needed to undergo a proprietary postproduction step called "bonding," whereby the pigment was essentially encapsulated in the powder resin. This process improved the transfer efficiency, facilitated the use of overspray as reclaim, and improved flake orientation. Surface treatment technologies have now been developed that can help eliminate the need for this extra step in the process [53]. Such materials are marketed under the trade names of Af flair® PC DB by EMD Chemical and Cyclo™ by the Engelhard Corporation.

In agricultural applications such as seed coatings, effect materials have provided not only an easy means of identification, but also a way to prevent premature germination and retain moisture during storage through decreases in diffusion. By incorporation into plastic horticultural film, it is possible to modify, through transmission and reflection, certain wavelengths of the electromagnetic spectrum which are beneficial to plants while blocking others enhancing the speed, and quality of growth [54].

The laser marking of plastics has become a rapidly expanding process used by end-product manufacturers due to its speed, permanence, and quality versus standard printing methods. Metal oxide-coated effect pigments have been found to enhance and broaden the types of polymers that can be used in this regard [55]. They provide a means to improve the contrast within the surface of the plastic by acting as a heat sink and allow the oxide on the surface of the pigment to be partially reduced to the black sub-oxides of titanium and can both amplify as well as enhance the dark coloring.

An area of significant commercial importance, especially with the newer generations of effect materials, is security. This functional application can be described to have differing levels of importance. For example, credit

cards and high-end luxury packaging may have a number of effect materials combined in specific ratios to create a brand color that is difficult to copy. The needs for brand identification, and protection, is a rapidly expanding area in which effect pigments are being used either in or on the products they are protecting. It has been known for some time that standard interference colors when printed onto documents cannot be photocopied due to the angle dependence of the color. Many of the newer technologies such as Chromaflair®, Spectraflair®, Variochrom®, Helicone®, and Color Stream®, which travel in multiple quadrants of color space, have been used in this respect for higher levels of security such as printing on currency, stock certificates, bearer bonds, and the like.

To a lesser extent in commercial importance are effect pigments that have been developed that provide conductivity for coating of plastics, magnetic, and anti-static properties.

TESTING

In the development and manufacture of effect pigments, investigators use several standard-testing procedures. These tests are both standard and in-house in nature, and most will not be listed herein. However, some ASTM tests that are of interest are tabulated in Table 3.

FUTURE

The future developments in effect pigment technology will undoubtedly be influenced by several factors. If history is any indication, the ability to create more varied and precise multi-layer films on a substrate in a cost-effective manner are expected to push the limits of physics as well as optics. Improvements in the ability to handle and create small particles of various compositions (nanoparticle technology), developments in geometries apart from platelets (spheres, prisms, rods, etc.), improvements and alternatives to hydrothermal, chemical vapor deposition (CVD), and VVD manufacturing technologies (e.g., sputtering [54] and biotechnology), and the development of alternative raw materials, or combinations of materials (hybrids) [56–58], can also be expected to play a role. Electrochemical, electromechanical, thermal, and laser-induced color may also be possible.

Changes currently under way, however, in areas such as application and processing technology are expected to have a more immediate impact on developments where in-mold coatings, pre-colored films, ultraviolet radiation-cured coatings, expanded use of powder, advances in printing type technologies, and the trend toward thinner decorative films will create the need for more advances in performance and functionality. In the cosmetics and pharmaceutical industries, where the need to deliver "active" ingredients is important, it may be feasible to see effect pigments playing a dual role in terms of not only providing color but also carrying and then delivering actives when applied to the skin.

The result of offshore manufactures entering the market will drive current producers to design and incorporate additional functionality into effect materials to add value. Whether it is to improve the performance of the pigments themselves, or the properties of the matrix in which they are used, the necessity to add value above and beyond color can be expected to become more important in order to defend against emerging competition.

Developments in color preference by young consumers influenced by the "age of electronics" or changing demographics, like the number of aging citizens and a more diverse ethnic population, will drive changes in color preferences and will require development of novel color shades and color combinations. A true red, or red to black combination, blue to orange, a true black pearl, brushed nickel, or gun-metal effect are just a few examples. Optically variable color effects are expected be more widespread as the general public becomes more comfortable with such dramatic effects.

In areas of brand identification, protection, and security, it is plausible to see effect pigments containing microscopic tags or possibly company logos, which could be applied to a particle through the use of lasers. It may even be possible to create radio frequency identification tags directly into multilayer effect materials.

While it is expected that many of the new technologies will be even more complex, there is some evidence to suggest that environmental considerations could create a trend toward utilizing materials from existing waste streams as effect pigments [59,60]. For example, the use of recycled

TABLE 3—Tests related to effect pigment investigations

ASTM Designation	Title
D1729	Standard Practice for Visual Appraisal of Colors and Color Differences of Diffusely-Illuminated Opaque Materials
D4086	Standard Practice for Visual Evaluation of Metamerism
D5497	Standard Terminology Relating to Buttons
E284	Standard Terminology of Appearance
E805	Standard Practice for Identification Instrumental Methods of Color or Color Difference Measurement of Materials
E1610	Standard Guide for Forensic Paint Analysis and Comparison
E1808	Standard Guide for Designing and Conducting Visual Experiments
E2175	Standard Practice for Specifying the Geometry of Multiangle Spectrophotometers
E2194	Standard Practice for Multiangle Color Measurement of Metal Flake Pigmented Materials
E2539	Standard Practice for Multiangle Color Measurement of Interference Pigments

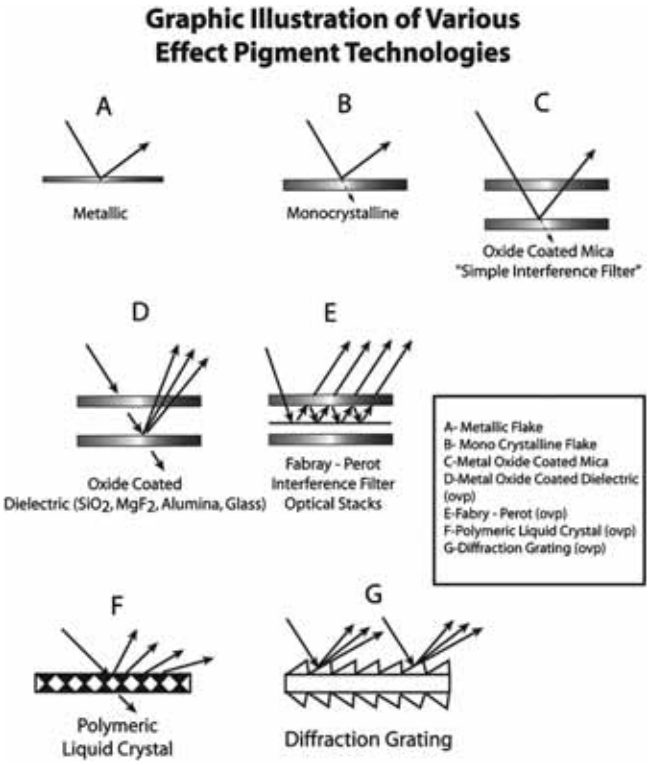

Fig. 25—Graphic illustration of various effect pigment technologies.

mirrored or colored glass (spheres, chips), metals, and rubber may become either an alternative or supplement to more conventional effect materials. Bead-Brite Research[11] and Rubber-Tech Research of Boca Raton, FL, have supplied such material to the markets.

SUMMARY

The past 40 years have witnessed an era of phenomenal growth and development in the area of effect pigment technology. Due to the advances and the complexity of such materials, it becomes important for both the designer and formulator alike to be aware of why these materials do what they do, allowing each to fully capitalize on their optical and appearance properties. The most significant constructions of commercial importance are graphically illustrated in Fig. 25. These developments have been fueled primarily by the advances in the methods of manufacture, the methods of application, the creation of new substrates, the availability of higher purity precursors, and utilization of alternative raw materials outside of the realm of the inorganic. Such advancements, applied to the original layer substrate principles and first described by Linton in the early 1960s, have led to the creation of totally new species of effect materials. They have expanded from simple thin film interference filters, to optical stacks of the Fabry–Pérot filter type, and even diffraction. The latest developments comprised of more optically precise constructions have subsequently created more dynamic and varied optical effects. Another very important factor that cannot be overlooked is society's voracious appetite for the new and different, which relates on the deepest level to the human condition of emotion.

It is expected that as further advancements are made, effect materials will play an even more prominent role in providing functionality to the products on or in which they are used. While effect materials may become even more complex in both their constructions and optical properties, the desire to use materials from current waste streams may also lead to further developments in this highly dynamic and emotional area of special effect pigment technology.

[11] Bead Brite Research/Rubber Tech Research, Inc., 4811 Lyons Parkway, Suite 4, Coconut Creek, FL 33073, BeadBrite@aol.com.

ACKNOWLEDGMENTS

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Measurement of Gonioapparent Colors

Allan B. J. Rodrigues[1]

TECHNICAL TERMS

THESE TERMS ARE SPECIFIC TO GONIOAPPARENT phenomena. The definitions below are from ASTM Standard E284 [1]. They are italicized when they first appear in this chapter.

annular, *adj* – descriptor for directional illuminating (or viewing) geometry in which the illuminator provides radiation (or the receiver possesses responsivity) that is distributed continuously and uniformly throughout the 360° of azimuth of the measurement. (See also *circumferential.)*

anormal, *adj* – of angles, measured with reference to the normal to the surface. (2008)

anormal angle, *n* – the angle subtended at a point on the specimen by a given ray and the normal. (2009)

Discussion – Use the inward normal with transmitted rays; use the outward normal for other rays. In uniplanar instruments, the "point" is the point of incidence and the anormal angle is understood to have a sign. The anormal angle of an illumination axis is positive or zero. The anormal angle of a detection axis is negative if the illumination and detection axes are on opposite sides of the line of the normal and positive or zero otherwise.

aspecular, *adj* – away from the specular direction.

aspecular angle, *n* – the angle subtended at the point of incidence by a given ray and the specular direction.

Discussion – In instruments, the "given ray" is understood to be a detection direction. In uniplanar instruments, the aspecular angle is to be understood to have a sign: negative when the specular direction lies properly between the detection direction and the illuminator axis and positive otherwise.

circumferential, *adj* – descriptor for directional illuminating (or viewing) geometry in which the illuminator provides radiation (or the receiver possesses responsivity) in many beams (or directions), normally distributed at uniform intervals and uniformly throughout the 360° of azimuth of the measurement. (See also *annular.*)

color angle, *n – in measurement of gonioapparent phenomena,* half the angle between the illumination and detection axes of the measurement geometry.

Discussion – The color of an interference pigment is determined by the angle of incidence of the light relative to the normal of the interference pigment flake. Flakes in a coating have an angular distribution, and the interference effect will be exhibited in a given measurement geometry only by the flakes that are oriented so that they behave as specular reflectors. Since the refractive index of the specimen is often unknown, color angle is defined here as if the flakes were in air. Color angle provides a relative indication of the angle between the flake normal and the illuminator axis.

color tolerance, *n* – the permissible color difference between sample and specified color.

far-aspecular, *adj* – pertaining to the appearance of a material when viewed from a direction far from the specular angle, typically 70° or more. (2006a). Note: The *adjective* **flop,** formerly used, is now deprecated.

far-aspecular angle, *n* – the aspecular angle when a material is viewed from a direction.

flake angle, *n – in gonioapparent coatings,* the angle subtended at a point on a pigment flake by the pigment flake normal and the specimen normal line through that point.

Discussion – A flake angle is understood to be the smaller of the two supplementary angles defined by the pigment flake normal and the specimen normal line.

flop, *n* – a difference of appearance of a material viewed over two widely different aspecular angles.

gonioapparent, *adj* – pertaining to change in appearance with change in illuminating or viewing angle.

gonioappearance, *n* – the phenomenon in which the appearance of a specimen changes with change in illumination or viewing angle.

Discussion – Examples of gonioappearance are specimens of coatings containing flake pigments.

goniochromatic match, *n* – match between a pair of specimens that holds under all sets of angular illuminating-viewing conditions.

Discussion – The specimens may or may not exhibit goniochromatism and may or may not exhibit metamerism.

goniochromatism, *n* – change in any or all attributes of color of a specimen on change in angular illuminating-viewing conditions but without change in light source or observer.

Discussion – Changes associated with first-surface specular reflection are not understood to lead to goniochromatism.

goniospectrophotometer, *n* – a spectrophotometer having the capability of measuring with a variety of illuminating and viewing angles using bidirectional geometry; also known as multi-angle spectrophotometer.

metallic, *adj* – pertaining to the appearance of a gonioapparent material containing metal flakes.

mid-aspecular, *adj* – pertaining to viewing a specimen between the near-aspecular and far-aspecular angles at an

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aspecular angle close to 45°. (2006a). Note: The term **face,** formerly used, is now deprecated.

mid-aspecular angle, *n* – the aspecular angle where a specimen is viewed between the near-aspecular and far-aspecular angles, typically at the mid-aspecular angle.

Discussion – This term also applies when the illuminating and viewing angles are interchanged.

near-aspecular, *adj* – pertaining to the appearance of a material when viewed from a direction close to the specular angle, typically within 25°. Note: The *adjective* **near-specular,** formerly used, is now deprecated.

near-aspecular angle, *n* – the aspecular angle when a material is viewed close to the specular direction, typically within 25°.

pearlescent, *adj* – exhibiting various colors depending on the angles of illumination and viewing, as observed in mother-of-pearl.

side-tone, *n* – appearance at the far-aspecular angle.

side-tone scattering, *n* – scattering of light in a material resulting in a milky appearance only when the specimen is viewed at the far-aspecular angle.

solid color, *n* – not containing flake or gonioapparent pigments.

sparkle, *n* – the visual contrast between the appearance of highlights on the particles of a gonioapparent pigment and their immediate surround.

specular, *adj* – pertaining to flux reflected from the surface of an object, without diffusion, at the specular angle.

specular angle, *n* – the angle of reflection equal and opposite to the angle of incidence.

Discussion – In gonioapparent phenomena, this definition assumes an illuminator subtending a small angle.

venetian-blind effect, *n – in surface coatings,* uniform change in an appearance attribute such as lightness as a directionally illuminated specimen is rotated in its own plane.

Discussion – The venetian-blind effect is thought to result from preferential orientation of flakes within a specimen, as may occur in the process of spraying paint on a vertical surface in the earth's gravitational field.

WHAT IS GONIOAPPARENT COLOR?

The painted ping-pong balls shown in Fig. 1 illustrate the phenomenon of gonioapparent color. They are illuminated by a single directional light and viewed against a dark background. The uppermost ball appears the largest. The entire ball is visible with about the same lightness across its surface except for a small *specular* highlight. The ball on the lower left appears smaller. Its lightness decreases as its surface is viewed away from the specular highlight, causing it to appear more rounded. The only clue to its true diameter comes from reflections off the other balls on its periphery. The ball to the right appears the smallest of all. Its lightness diminishes to near zero so rapidly that its outermost surface is not seen and it seems to have the smallest diameter of the three. These balls illustrate the phenomenon of *gonioappearance.* The ping-pong balls were all coated with glossy paints, the first with a gray paint containing a lot of white, light-scattering pigment. Paints used to coat the other two balls contained only transparent, nonscattering pigments and aluminum flakes. These flakes act like little mirrors within the coating, aligned roughly parallel to the coated surface. Most of the light illuminating the surface is reflected in the specular direction. Thus the lightness decreases as the viewing angle moves away from the specular direction, i.e., at larger *aspecular angles.* The coating on the third ball contained a coarser, shinier aluminum flake, resulting in a more rapid decrease in lightness, further accentuating the curvature of the ball. The third ball exhibits a greater *flop* than the second ball. Larger flakes with more polished surfaces are more effective in reflecting in the specular direction, resulting in a greater flop. Colors not containing flakes are generally referred to as solid colors; those containing flakes are gonioapparent colors.

A schematic of a paint film containing flake pigments is shown in Fig. 2. The flakes are distributed uniformly through the film, more or less oriented parallel to the substrate. Each flake acts like a mirror, reflecting incident light in a specular direction. If the flakes were perfect mirrors and perfectly oriented, all the light would be reflected in the specular direction. In practice, orientation is not perfect and the flake surface is not mirror smooth, so that there is dispersion of the reflected light. Additionally, some light scattering occurs off the edges of the flake. Fig. 3 shows photomicrographs of two different types of aluminum flakes. The flake on the left is shaped somewhat like cornflakes. The surface is a little rough and the edge of each flake is irregular, allowing for more light scattering. The flake on the right is often referred to as "silver dollar" flake. It is much more rounded with more polished surfaces. It allows for much better specular reflection, little edge scattering, and greater *sparkle.* The paint film itself generally contains some absorbing pigments to impart color. All pigments will also scatter light. Pigments of a larger particle size or a higher refractive index will scatter more light. Titanium dioxide is a good example of a high scattering

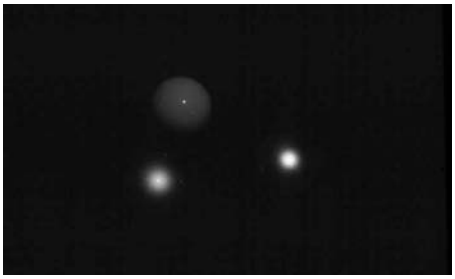


Fig. 1—Ping-pong balls coated with solid and metallic color paints.

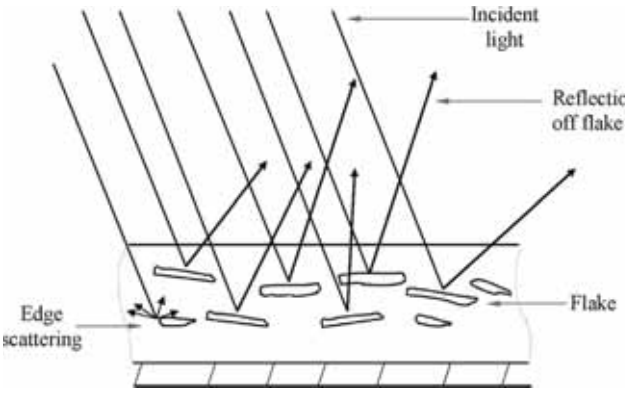


Fig. 2—Schematic of a flake-containing paint film.

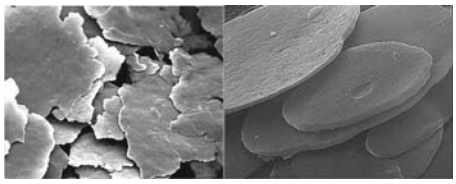


Fig. 3—Photomicrographs of two different types of aluminum flakes. Courtesy of Eckert America Corp.

pigment. The result of any light scattering within the paint film is that there is a decrease in light reflected back from the paint in the specular direction, and an increase in light reflected at larger aspecular directions, i.e., a decrease in flop. It also results in decreased sparkle.

Automotive stylists design car bodies, contouring them to make them more appealing to customers. Gonioapparent coatings accentuate these contours, just as they enhance the curvature of the ping-pong balls. Their sparkle further contributes to customer appeal. These enhancements to appearance account for their popularity with about 70 % of today's automotive colors being gonioapparent. Simple flakes, first introduced in a 1935 automotive paint, were made of aluminum. They have evolved over the years to include color-coated aluminum and flakes coated with thin metal-oxide layers exhibiting light interference effects. Coatings containing these flakes exhibit not only a lightness flop but also chroma and hue flop. This change in any or all attributes of color of a specimen on change in angular illuminating-viewing conditions but without change in light source or observer is called *goniochromatism*. It should be noted that goniochromatism, while prevalent in automotive finishes, is also observed in other finishes as well as products such as cosmetics. The discussion in this article is generally applicable to all such products. However, the experimental work was done with automotive paints. Some of the work described was done by a manufacturer of interference flakes, supplied to several coatings and noncoatings industries. The previous chapter of this book [2] provides an excellent review of goniochromatic pigments.

International standards for measuring color and appearance of finishes have been well established. ASTM has several Standard Practices for both visual (e.g., D1535, "Standard Practice for Specifying Color by the Munsell System," and D1729, "Standard Practice for Visual Appraisal of Colors and Color Differences of Diffusely-Illuminated Opaque Materials") and instrumental (e.g., E308, "Standard Practice for Computing the Colors of Objects by Using the CIE System," and E1164, "Standard Practice for Obtaining Spectrometric Data for Object-Color Evaluation") evaluation and specification of color as well as appearance (e.g., D523, "Standard Practice for Specular Gloss"). Yet none of these international standards addresses the gonioapparent characteristics of these finishes. ASTM subcommittee E12.12 was formed in 1989 to address standardization specific to gonioapparent color. It led to addition of a section in ASTM E284 [1] on specialized terminology on gonioapparent phenomena. Unlike solid colors, which can be measured diffusely or at one angle, measurement of gonioapparent color requires several angles of illumination and view. Practicality demands use of the minimum number of angles, sufficient to characterize the overall color.

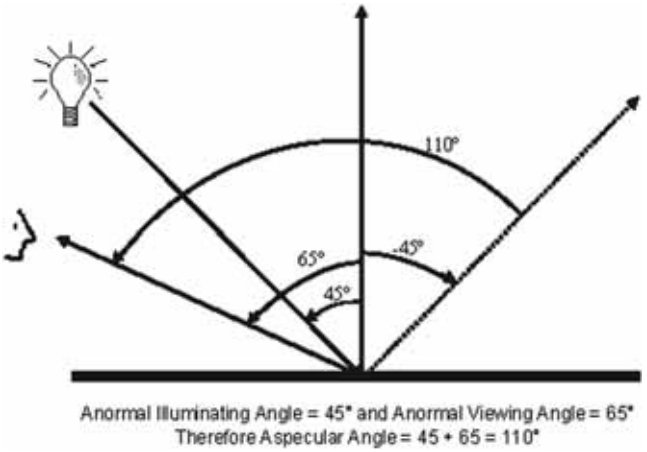


Fig. 4—Example of illuminating and sensing geometry.

CONVENTIONS FOR DESIGNATING MEASUREMENT GEOMETRY

Fig. 4 illustrates the traditional convention for designating measurement geometry. This convention has been to indicate the anormal angle, i.e., the angle away from the normal or perpendicular to the surface being measured. The illuminating beam is shown in Fig. 4 at 45° from the surface normal. Viewing angles on the same side of the normal are shown as positive, e.g., the viewing angle at 65° in the figure. Angles on the opposite side of normal are assigned a negative sign. Thus the specular reflection is at minus 45°.

Discussions in the early days of E12.12 led the subcommittee to recognize that gonioapparent colors were observed with attention to change in color as a specimen is viewed at increasing aspecular angles for a given direction of illumination. E12.12 introduced a modified convention, designating the illuminating angle with the anormal angle convention, while designating the viewing angle by its *aspecular* direction. ASTM E2175 [3], "Standard Practice for Specifying the Geometry of Multiangle Spectrophotometers," details this convention. Positive values of the aspecular angle are in the direction towards the illuminator axis. This aspecular convention is intuitive for those who have worked with gonioapparent colors. It is also an easy adaptation from the anormal convention because the aspecular angle is simply the sum of the anormal convention illuminating and viewing angles. Thus in Fig. 4, the 110° aspecular angle is the sum of the anormal illuminating angle (45°) and the anormal viewing angle (65°).

Longtime users of the anormal convention expressed discomfort with having to calculate the anormal viewing angle. Hence the convention finally agreed upon includes the illumination anormal angle, the viewing anormal angle and the aspecular angle. Under this convention, the 110° angle in Fig. 4 is expressed as 45°:65° (as 110°).

MEASUREMENT OF METALLIC COLOR AND COLOR DIFFERENCE

Gonioapparent colors may be viewed in three different modes. Object modulation utilizes a fixed angle of observation relative to the illuminating direction, and the specimen is rotated about an axis to change both viewing and illumination angles. This method is commonly used in viewing a panel coated with a metallic paint, where the light source

is usually fixed and the observer rotates the panel to view it at different aspecular angles. When viewing a car, it is generally stationary under sunlight, whose direction is fixed at any given time, while the observer moves around to view it from different angles. This is detector modulation. The third mode is source modulation, where the object and viewer are fixed, while the direction of illumination is varied. Alman [4] and Schmelzer [5] in independent studies reported that measured color of *metallic* specimens is independent of the method of changing aspecular angle. They showed that measured color is simply a function of aspecular angle itself. The objective then in measuring metallic color is to determine the minimum number of aspecular angles of measurement, optimizing these angles to best characterize color and color differences measured at all possible measurement angles. Three independent studies using different approaches arrived at very similar recommendations.

Venable [6] reasoned that light reflected from a metallic finish has a diffuse component (from multiple interactions with flake and other pigments) and a flake component (from a single reflection from a flake). The diffuse component dominates measurements far from the specular direction and can be characterized by a single measurement at an aspecular angle greater than 60°. The flake component is manifested at angles closer to specular and has an angular distribution dominated by the flake orientation, thus requiring two measurements to quantify. He recommended that one of these measurements be at an angle as close to specular as possible, while excluding first surface reflection (gloss). The other measurement angle for the flake component should be at a point where the flake component is still significant but its measurement is significantly different from that close to specular. He also suggests a model which, using measurements at 20°, 40°, and 70°, correlated well with goniocolorimetric data.

Saris et al. [7] correlated visual assessments of color differences with measurements at different geometries. They had 22 clusters of five metallic color panels, each providing ten color difference pairs, for a total of 220 observations by each of six observers. For uniformity of lighting conditions, observations were done in an "artificial window," simulating lighting at a natural window commonly used by color shaders in their laboratory. This "window" provided a color-corrected diffuse light about the size of a window behind the observer. The specimens to be viewed were placed on a table in front of the observer. This table could be tilted to provide three different viewing angles. Color differences were judged at these angles against a gray scale with six lightness difference pairs. An overall match rating was also recorded. Several instrumental measurements were taken, ranging from aspecular angles of 25°–115° and they also included a $d/8^{\circ}$ measurement. These were correlated to observations using a logistic regression model. Measurements at $d/8°$, 45°, and 95° correlated well with visual observations. Inclusion of the $d/8°$ measurement in the optimized combination is not surprising considering the "diffuse-directional" lighting used in the observations. Interestingly, statistically equivalent results were obtained with 25°, 45°, and 110° measurements.

Alman [4] measured lightness, hue and chroma of 36 metallic colors as a function of aspecular angle. The

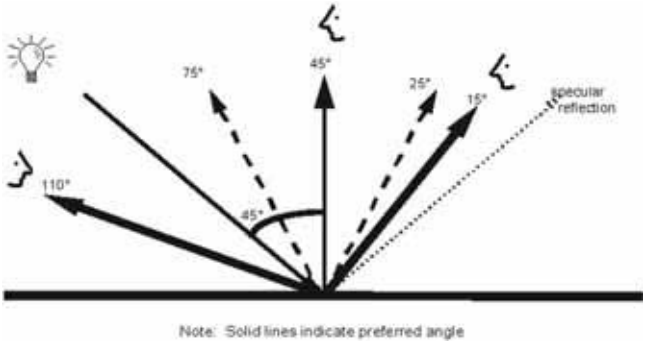


Fig. 5—Diagram of aspecular angles.

experiment was done in 1980. Metallics of those days exhibited a strong lightness flop, while chroma flop was small and hue flop almost nonexistent. Using polynomial modeling of lightness as a function of aspecular angle, he determined the residual error for each model. Large residual errors resulted from linear models, obviously unable to fit the curvature of the lightness response. Quadratic models with three appropriately chosen measurement angles dramatically reduced the average residual variance. Three angles of measurement requires attention to color data (e.g., L, a, b) at each of these angles, making colorimetric analysis a nine-dimensional problem. Further reduction in residual variance with four angles was insufficient to justify the increased complexity posed by twelve dimensions. Based on this work, he recommended measurement of metallics at aspecular angles of 15°, 45°, and 110°. Rodrigues [8] repeated this experiment with base coat/clear coat colors, including 18 metallics and 16 interference pearl colors used in automotive finishes of the late 1980s. The interference pearl colors exhibited strong lightness and chroma flop and some hue flop. These experiments confirmed 15°, 45°, and 110° as the optimum angles of measurement. ASTM E2194 [9], "Standard Practice for Multiangle Color Measurement of Metal Flake Pigmented Materials," standardized this geometry for measurement of metallic colors, as shown schematically in Fig. 5. The 15° angle is referred to as the *near-aspecular angle,* 45° as the *mid-aspecular angle*, and 110° as the *far-aspecular angle.*

Visual assessments of gonioapparent matches typically cover a wide range of aspecular angles, from very near specular (e.g., aspecular angle of 15°), all the way to far from specular (e.g., aspecular angle of 110°). Occasionally specimens are an acceptable match at angles between 25° and 75°, but visual and instrumental assessments find the match unacceptable outside this angular range. An example (Fig. 6) shows lightness as a function of aspecular angle for a standard (dark curve) and a batch (lighter curve) paint sprayed on aluminum panels. The curves are a reasonably good match at angles between 20° and 75° and were judged visually acceptable when judged at these angles. However, they deviate below 20° and above 75° and the panels were judged as an unacceptable overall match. Both paints contained the same absorbing and flake pigments. However, the standard was a low solids paint, while the batch was a medium solids paint. Higher solids allowed for less film shrinkage as the sprayed batch paint dried, resulting in poorer flake orientation. *Side-tone scattering* of light caused by poorer flake orientation was visually quite apparent

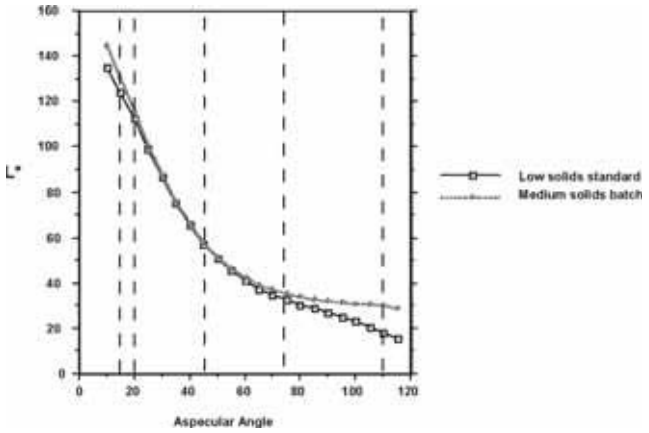
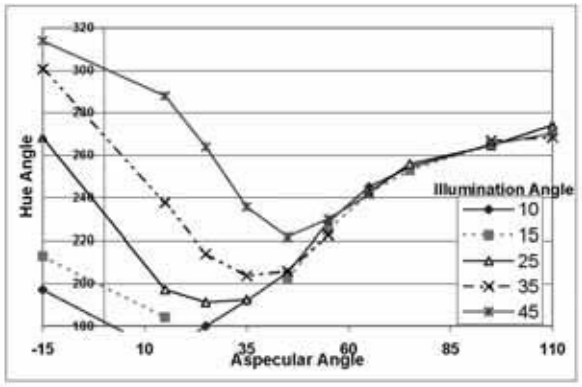


Fig. 6—L* gonio-curves on real metallic paints showing relative effectiveness of different geometries.



Note: Some data points are missing because of the physical limitation of the goniospectrophotometer to measure at angles requiring close proximity of the light source and the detector

Fig. 7—Hue shifts observed in strong interference colors.

with the batch being judged unacceptably lighter and bluer at the far-aspecular angle and slightly lighter at the near-aspecular angle.

Commercially available spectrophotometers often provide 25° and 75° aspecular measurements in addition to the angles standardized by E2194. The German standard DIN 6175-2 [10] recommends use of 25°, 45°, 75°, and 110°. E2194 allows for this variation in angles as shown in Table 1. Angles other than the preferred angles but within the acceptable range may be used for less critical color matches. For example, surface imperfections (e.g., orange peel) resulting from spray application of finishes can cause light to be reflected off the surface in a direction slightly away from the nominal specular direction. Measurement at 25° may be chosen as the near-aspecular angle when less sensitivity to application differences is desired. However, in critical color matching applications, batches should be resampled and re-sprayed to match surface texture of the standard specimen and adjusted to an acceptable color match at the standardized 15° near-aspecular angle.

E2194 also provides a ray-tracing procedure to determine the effective aspecular angle and sets tolerances for the percentage of rays that may deviate from the expected angle. The Society of Automotive Engineers standard J1545 [11], "Instrumental Color Difference Measurement for Exterior Finishes, Textiles, and Colored Trim," also recommends the angles standardized in E2194.

Fig. 5 shows a uniplanar geometry, i.e., the illumination axis, the viewing axes, and the normal to the specimen surface are all in the same plane. Some commercial instruments provide *annular* or *circumferential* measurement or illumination. Annular geometry provides measurement (or illumination) distributed continuously and uniformly throughout the 360° of azimuth of the measurement. Circumferential measurement (or illumination) is an approximation of annular, using a discrete number of sensors (or illumination beams) distributed at uniform intervals throughout the 360° of azimuth of the measurement. These measurements minimize directional effects such as surface irregularities or preferential flake orientation. For example, when paint is sprayed on a vertical surface, the Earth's gravity may cause the flake to tilt rather than remaining parallel to the surface as the paint dries. If two halves of such a painted panel are viewed side-by-side, both in the same orientation as when sprayed, they will appear as a good color match, regardless of aspecular viewing angle. However, if one half is rotated 180° in its own plane, the flakes in the two halves are now tilted in opposite directions and the two halves will no longer match. This is referred to as the *venetian-blind effect*. Annular or circumferential instruments will average out the directional effects of tilted flake and measure the two halves as being the same. They would be the appropriate instruments if the goal is to neglect these effects. However, often in the presence of the venetian-blind effect, these instruments will provide measurements that do not agree with visual assessments. If a measurement neglecting the rotational effect is desired, it can be achieved with a uniplanar geometry by averaging several measurements taken while rotating the panel orientation with respect to the instrument after each reading. Another drawback is that annular or circumferential geometry requires symmetry. Either the illumination or the viewing axis must be on the normal or else determination of the aspecular angle is ambiguous. This limits the maximum aspecular angle to something less than 90°, short of the 110° recommendation for critical color matching.

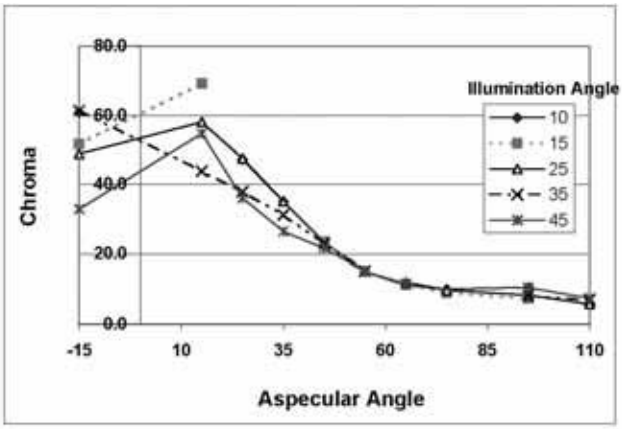
TABLE 1—ASTM E2194 angles for metallic color measurement

Aspecular Angle	Preferred angle for Critical Color Match	Acceptable Range
Near-aspecular	15°	15°–25°
Mid-aspecular angle	45°	45°
Far-aspecular angle	110°	70°–110°

MEASUREMENT OF COLORS CONTAINING INTERFERENCE FLAKES

A commercial automotive color, Mystichrome, containing Chromaflair®[2] interference flake was measured on a *goniospectrophotometer*. This measurement is shown in Fig. 7 with hue angle as a function of aspecular angle at several different illumination angles. Unlike metallics, where color

[2] Flex Products Inc., 1402 Mariner Way, Santa Rosa, CA 95407.



Note: Some data points are missing because of the physical limitation of the goniospectrophotometer to measure at angles requiring close proximity of the light source and the detector

Fig. 8—Chroma shifts observed in strong interference colors.

is a function of only aspecular angle, hue of colors containing interference flakes is also a strong function of illumination angle. Hue is also dependent on whether viewing is in a positive or negative direction away from the specular. Thus the hue at aspecular angle minus 15° is very different from that at plus 15°. It is only at aspecular angles greater than about 55° that the hue shifts are seen to be independent of illumination angle. Fig. 8 shows that chroma of this color also has a strong dependency on angle of illumination and aspecular angle, with the curves beginning to overlap at an aspecular angle of about 45°. The degree of color shift and its dependence on illumination angle is obviously a function of the particular flake used, its content in the color and the types of other pigments in that color. The interference flake by itself would exhibit a stronger color shift. Fig. 9 shows hue shifts for a Chromaflair® interference flake in a clear paint containing no other pigments. It shifts from blue-green, through purple to green-yellow when viewed 10° off specular as illumination angle is changed. Thus manufacturers of these flakes must measure them at a wide variety of illumination angles, each at multiple viewing angles. ASTM E2539 [12], "Standard Practice for Multi-angle Color Measurement of Interference Pigments" covers the instrumental requirements and parameters needed to make instrumental measurements of thin film interference

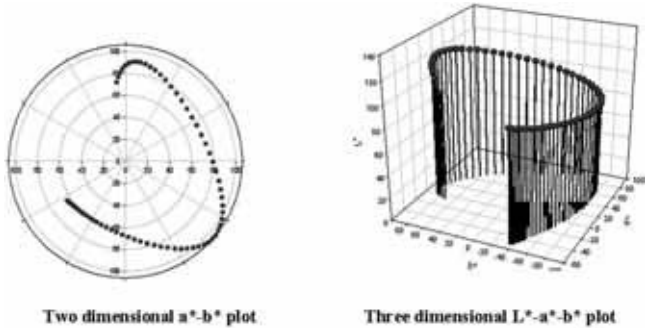


Fig. 9—A Chromaflair®, flake shifting from blue-green, through purple to green-yellow when viewed 10° off specular as illumination angle is changed. Courtesy of Michael Nofi, Flex Products Inc.

TABLE 2—ASTM E2539 Specified Geometries for Measuring the Color Range due to Interference. Note: This table gives the minimum geometries for the quality control application. For other applications, additional geometries, such as 65°:50° (as 15°), may be desirable or needed

Illumination Angle	Detection Angle	Aspecular Angle	Designation
45°	–60°	–15°	45°:–60° (as –15°)
45°	–30°	+15°	45°:–30° (as 15°)
15°	–30°	–15°	15°:–30° (as –15°)
15°	0°	+15°	15°:0° (as 15°)

pigments. The Standard states that these "pigments are typically evaluated for color and appearance in a medium such as paint or ink." The geometries specified for measuring these pigments are shown in Tables 2 and 3.

The physics of light interference shows that the hue shift in interference pigments occurs only from flake oriented so as to act as specular reflectors of the illumination source to the detector. A term to address this is *color angle,* not used in E2539 but defined in E284. The discussion of this term in E284 states "flakes in a coating have an angular distribution, and the interference effect will be exhibited in a given measurement geometry only by the flakes that are oriented so that they behave as specular reflectors." Color angle is defined as half the angle between the illumination and detection axes of the measurement geometry. Fig. 10 is an *a*-b** plot of the measurements of Mystichrome. The curves show loci of constant aspecular angles with changing illumination angle. The slightly curved "spokes" emanating from a point close to the origin are loci of constant color angle. Each spoke is at approximately the same hue angle. This suggests that measurements at color angles could be useful in characterizing the hue shift of interference colors. Another potentially useful term in E284 is *flake*

TABLE 3—ASTM E2539 Specified Geometries for Measuring the Color due to Scattering or Orientation. (Note: The three angles designated with an asterisk (*) refer to preferred angles for critical measurements as specified in E2194.) (Note: Given a geometric configuration, the reverse geometry is considered equivalent, if all other components of the instrument design are equivalent.)

Illumination Angle	Detection Angle	Aspecular Angle	Designation
45°	–30°	15°	45°:–30° (as 15°)*
45°	–20°	25°	45°:–20° (as 25°)
45°	0°	45°	45°:0°(as45°)*
45°	30°	75°	45°:30° (as 75°)*
45°	65°	110°	45°:65° (as 110°)*

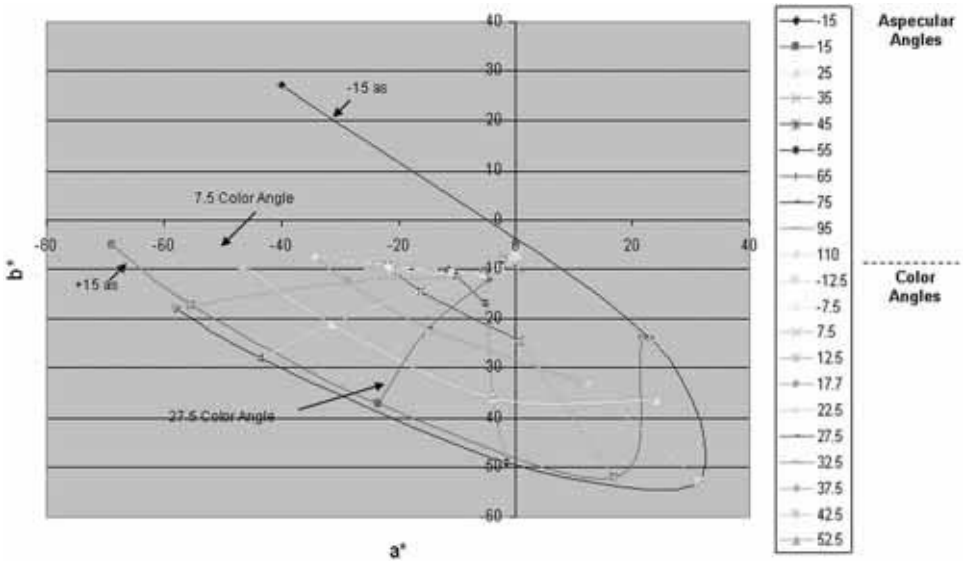


Fig. 10—Color loci for constant aspecular angles and for constant color angle in an automotive color with interference flake.

angle, defined as the angle subtended at a point on a pigment flake by the pigment flake normal and the specimen normal line through that point. Flake angle could be useful in characterizing the chroma shift of interference colors.

A task not yet addressed is to determine whether characterization of real colors containing interference flakes require the same set of angles as those in E2539. A subset may be sufficient for some products, e.g., automotive colors containing these flakes do not exhibit hue shifts as strong as the flakes themselves.

COLOR DIFFERENCE MEASUREMENT FOR QUALITY CONTROL OF COLORS CONTAINING INTERFERENCE FLAKE

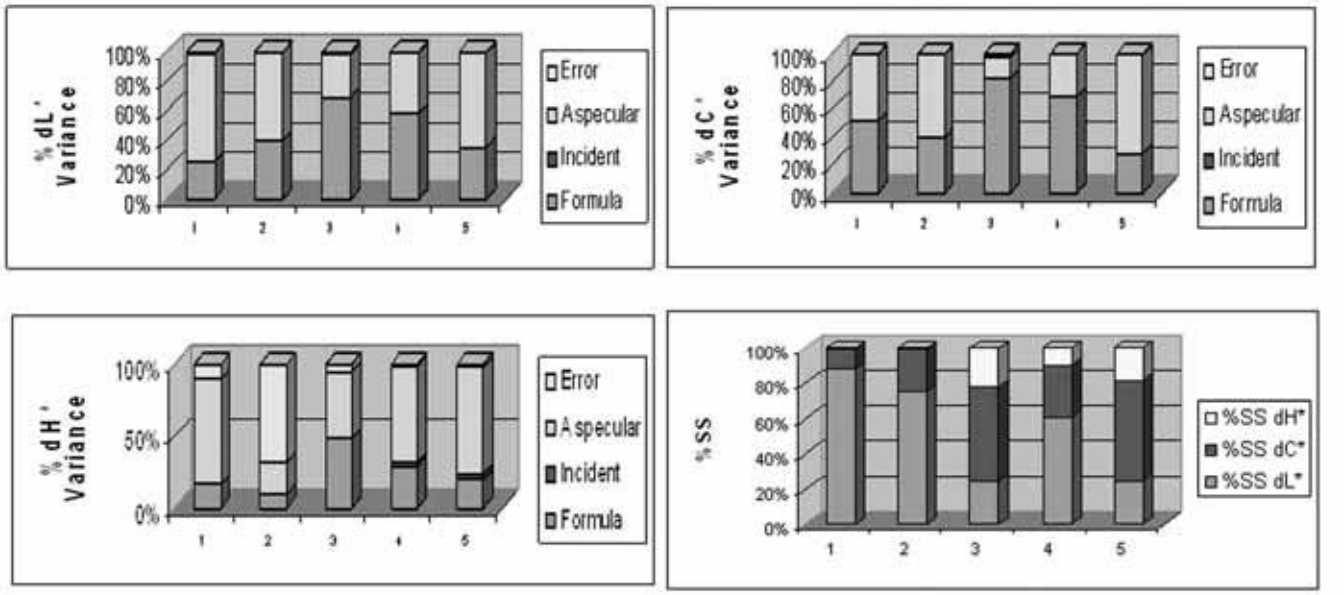
Absolute color measurement is important when a manufacturer is matching a new color standard of unknown pigmentation. Spectral measurement must be used in order to identify the correct pigmentation and avoid a metameric match. The scope of Subcommittee E12.12 encompasses the goal to "study the color measurement of metallics and *pearlescents* looking at quality control aspects." Quality control requires measurement of color difference versus a standard rather than absolute color. After establishing the correct pigmentation, measurement of color difference from the standard is sufficient to adjust colorant ratios, shading the color to a visually acceptable match. Routine, repetitive manufacture of a color uses measurement of color difference from a standard color, generally of the same pigmentation as the batch being made. Interference flake manufacture would also entail measurement of color difference from a standard. E2539 addresses measurement geometry for that process. However, it has not been established that these same measurements are necessary for paints or other products containing interference flakes.

The sub-committee conducted a preliminary experiment to determine the importance of incident angle versus aspecular angle in color difference measurement of realistic automotive colors. Bronze and violet automotive colors were chosen and the interference pearl content increased to the limit of current color styling practice for real automotive colors. In each case a standard panel was weighed and sprayed. Additional panels were made by sequentially iterating each ingredient to provide color differences of 2 to 3 CIELAB units. Duplicate panels were sprayed to determine variation due to application. Measurements were made at aspecular angles of 15°, 25°, 45°, 75°, and 110°, each at incident angles of 15°, 30°, and 45°. Goniospectrophotometer limitations did not allow 25° and 110° aspecular measurements at all three angles of illumination. So the analysis included only the 15°, 45°, and 75° aspecular angles. Color differences (ΔL*, ΔC*, ΔH*) were calculated versus the standard. Analysis of Variance (ANOVA) analysis showed that the greatest variation is from the ingredients themselves (Table 4). This of course allows for ingredient adjustments to match the color. The incident angle variation is extremely small compared to the aspecular angle. In fact even under the controlled conditions of the experiment, application variation was more significant than the incident angle.

Steenhoek [13] extended this study to five automotive colors containing interference pigments with a reflective inner layer. These pigments show very strong interference effects. Analysis of Variance (ANOVA) analysis again showed that the greatest variation is from the ingredients themselves. Fig. 11 shows the variances in ΔL*, ΔC*, ΔH* for each of the five colors. A significance test ($p < 0.05$) showed that the only significant variables were the formula itself and the product of the formula and the aspecular readings.

TABLE 4—Summary of ANOVA results

Main Effect and Interactions	Ingredient	Aspecular Angle	Application	Incident Angle
Mean Sum of Squares Variation % for ΔL*, ΔC*, ΔH*	101.1	48.0	6.1	3.3
	Note: Variation can exceed 100 % because interactions between effects are included			



	1. Silver			2. Purple-Blue			3. Appasionate Blue			4. Pappilion Silver			5. Mystichrome		
	dL*	dC*	dH*	dL*	dC*	dH*	dL*	dC*	dH*	dL*	dC*	dH*	dL*	dC*	dH*
Formula	<.0001	<.0001	<.0001	<.0001	<.0001	<.0001	<.0001	<.0001	<.0001	<.0001	<.0001	<.0001	<.0001	<.0001	<.0001
Formula * Incide	0.9992	0.8328	0.9983	0.9995	0.9856	0.3804	1.0000	0.7632	0.9957	1.0000	0.9999	0.2836	1.0000	0.9970	0.1061
Aspecular	0.8666	0.2336	0.3528	0.8889	0.2816	0.2382	1.0000	0.9999	1.0000	0.0183	1.0000	0.0580	0.1882	0.0579	0.8693
Incident	0.9666	0.4147	0.7439	0.9716	0.8431	0.3046	0.6503	0.8523	0.8866	0.9535	0.5351	0.1796	0.9771	0.9446	0.7679
Formula*Aspecula	<.0001	<.0001	<.0001	<.0001	<.0001	0.0007	<.0001	<.0001	<.0001	<.0001	<.0001	<.0001	<.0001	<.0001	<.0001

Fig. 11—Color difference for specimens containing interference pigments with reflective inner layer.

These results suggest that currently used spectrophotometers with a fixed angle of illumination may be used for quality control of real automotive colors. They are, however, based on only two colors, not necessarily representative of all interference colors in automotive or other industries. Future automotive colors may include more dramatic interference effects. Further study is required to:

- Address more automotive interference colors, including those containing higher concentrations of strong interference effect flakes.
- Consider colors containing other pigments with gonioapparency resulting from diffraction effects, liquid crystals, etc.
- Optimize the choice of incident angles.
- Verify whether optimum aspecular angles are the same as currently standardized for metallic colors.
- Address any specific needs of industries other than automotive.

COLOR METRICS

To be useful, color measurements must be reduced to metrics correlating to color as seen by human observers. Color difference equations for solid colors have evolved since 1931 when the International Commission on Illumination (CIE) adopted the "Standard Observer." The CIE recommendation in 1976 of CIELAB and CIELCH, together referred to as CIE76, was a major milestone in relating these measurements to how we see color, but not uniform enough throughout color space to allow instrumental pass/fail judgements. CMC, CIE94, and CIEDE2000 [14] have been a series of improvements based on CIE76. They all start from ΔL^*, ΔC^*, ΔH^* from CIE76 dividing each by weighting functions S_L, S_C, S_H respectively to correct for the nonuniformity of CIELAB. All these equations were possible because of a large body of experimental data of observations on a variety of color differences on solid colors made from paints, textiles, and more recently video color displays. Very few observation data on gonioapparent colors have been published. Subcommittee E12.12 has been working with the Detroit Colour Council (DCC) J1545 Committee to create such data sets. Experience with gonioapparent colors dictates that a larger ΔL^* is visually acceptable in lighter gonioapparent colors. This relationship was recognized in the S_L function used in the CMC equations. The samples in the CMC study were threads wound on cards used for color judgments in the textile industry. Textiles have a texture that apparently makes human judgments more forgiving of lightness differences in lighter colors. CIE94 was based on glossy automotive solid colors and assigned S_L the value of unity, regardless of lightness. Colors containing flakes also have a visual texture. So they would be expected to have a similar tolerance for larger lightness differences in lighter colors.

Spectrophotometers measure reflectance factor, which is "the ratio of the flux reflected from the specimen to the flux reflected from the perfect reflecting diffusor under the same geometric and spectral conditions of measurement" [1]. Very light metallics can reflect more light in the near-specular direction than the perfect diffusor and hence their reflectance factor and L* may exceed 100 %. The S_L function used in the CMC equations is non-linear and should not be used at L* greater than 100, which would be extrapolating the function beyond its experimental conditions. DCC and E12.12 did visual assessments of lightness differences on a series of silver gray metallics over a wide lightness range. This established a linear relationship

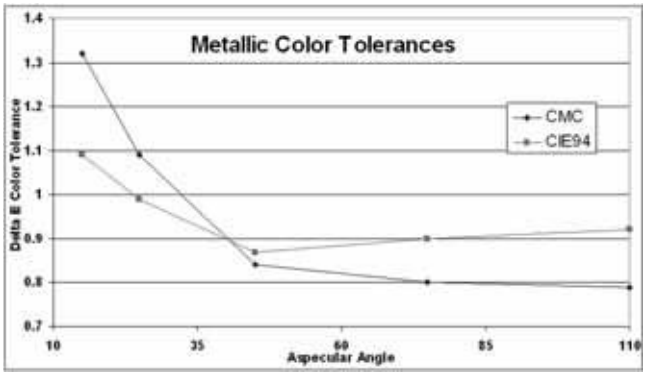


Fig. 12—Relative metallic color tolerances as a function of aspecular angle using CMC and CIE94 Equations.

between S_L and L* [15]. Modifying the CIE94 equations when used for metallic colors by dividing ΔL^* by this S_L function gave excellent agreement with the visual data. CIEDE2000 uses a V-shaped function for S_L, contrary to the findings of the DCC and E12.12 experiments. At this writing, CIEDE2000 has not been tested for gonioapparent colors.

These studies were extended to a few real automotive colors: beige, silver, gold, and teal metallics. Color difference pairs of these colors were shown to 20 observers in a Macbeth Skylight®[3] viewing booth at 15°, 25°, 45°, 75°, and 110° aspecular angles. They were asked whether they would accept the color match if seen on their own car. The frequency of acceptance as a function of color difference was analyzed to determine acceptability tolerances at each of these angles in both CMC and the modified CIE94 systems. Tolerances averaged over all colors are shown in Fig. 12. Both equations performed well. However, CIE94 gave more nearly equal tolerances at all aspecular angles. It should be noted that these are relative *color tolerances*. Actual commercial tolerances must be agreed upon between customer and supplier. However, these experiments suggest that these color difference equations could be used in setting those acceptability tolerances. Work continues to extend these studies to include larger numbers of current automotive colors including those containing interference flakes. It entails identification of a preferred experimental procedure for making simple pass/fail judgments by comparison to an anchor color difference pair. This will result in the creation of a database of observations on gonioapparent color differences allowing testing of existing color difference equations as well as development of improvements if necessary.

It should be noted that color difference is just one factor in determining acceptability of a color match. Even with solid colors, surface gloss or texture differences can cause a color difference pair measuring identically to be observed as an unacceptable match. It follows that in such cases, a pair judged as an acceptable match would very likely measure as having an appreciable color difference. Thus it is advisable to prepare color samples equal in appearance to the standard being matched before measuring or visually assessing color acceptability. Gonioapparent colors have additional appearance attributes, which must be accounted for. Both metallic and interference flakes differ in size, shape and surface texture. These can result in differences in sparkle and coarseness of visual texture. These appearance differences too can be a function of angle of illumination and view. All these factors must be considered in determining acceptability of a color match.

THE FUTURE OF STANDARDIZATION OF GONIOAPPARENT COLOR

Much progress has been made in measurement and determining color and color difference of gonioapparent colors. Standardizing organizations such as ASTM, DIN, CIE and SAE communicate with each other on this subject and membership sometimes overlaps. However, while standards have been clearly established for metallics, considerable research on interference colors is still underway. E2539 addressed measurement of interference pigments. The measurement of products containing these pigments has not been standardized. Different standardizing bodies do not always agree upon identical standards. The starting point must be agreement on terms and their definitions, followed by conventions (e.g., for designation of measurement geometry) and finally good experimental data to allow for data-based decisions in standardization. There must be openness to change. In the early days of instrumental color matching, diffuse measurements worked very well. Metallics required acceptance of the aspecular angle concept and optimized multiangle measurement. It is now accepted that absolute measurement of interference colors requires more than one illumination angle. Requirements for optimizing absolute color measurement may be more demanding than for color difference. The standardization process has to recognize and address the needs of different users of gonioapparent materials, the flake manufacturer, the coatings manufacturer, and the final user of the coating.

In addition to color measurement of gonioapparent colors, there is need for understanding and determining metrics for their special appearance characteristics such as flake sparkle and visual texture. Instruments aimed at such measurements have recently been available (BYK-mac[4] and X-Rite MA98[5]). Once these metrics are established, will color difference equations have to again be modified to account for them? For example, would the S_L factor be a function not only of L* but also sparkle and texture? Just as texture makes assessments of lightness differences more forgiving in lighter colors, would strong hue shifts in interference colors allow for larger tolerances of hue differences? There are many questions that must still be resolved. As one class of gonioapparent color is understood and its measurement standardized, a new class of gonioapparent flake is offered to the delight of color stylists and consumers. This is clearly a work in progress.

ACKNOWLEDGMENTS

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[3] Macbeth, a division of X-Rite, 4300 44th St., Grand Rapids, MI 49512.

[4] BYK-GardnerGmbH, LausitzerStrasse 8,482538 Gerestried, Germany.

[5] X-Rite, 4300 44th St., Grand Rapids, MI 49512.

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Protective Coatings and Inorganic Anti-Corrosion Pigments

Lucien Veleva[1]

INTRODUCTION

COATINGS ARE IMPORTANT WIDELY USED PRODUCTS that provide corrosion[2] protection of metals and other substrates. Paints that contain anti-corrosion pigments account for about 65 %–70 % of all areas protected by anti-corrosion coatings. Paint[3] provides a number of desirable attributes including relatively low cost, simplicity of application to simple and complex structures, aesthetic beauty, ease of repair and restoration, as well as metal corrosion protection that is markedly enhanced when anti-corrosion pigments are present.

Coatings may be classified in various ways such as by their end use, surface character, and so on. For example, an end-use classification might include coatings for transportation vehicles and associated hardware, such as boats, ships, piers, and other items subject to marine environments, such as reactors, drums, piping, buildings, etc., exposed to harsh industrial environments; pipeline coatings, architectural coatings; artists' paints that have aesthetic, aging, substrate nature needs; and many others. Each of these classes has different requirements. Marine coatings must be resistant to high humidity, chloride presence, and aqueous immersion; pipeline coatings must be resistant to crude oil, natural gas, water and aggressive aqueous solutions, and solvents; and so on [1–5]. Each end use will have its own particular requirements. Various chapters in this manual deal with coatings for a variety of end uses.

The three main components of an organic paint are pigment, binder, and volatile vehicle.[4] The pigment is an insoluble, finely ground material that provides color and opacity as well as corrosion resistance and water barrier properties when particular pigments are used. The binder is the polymeric, nonvolatile portion of a formulated coating. It is the important ingredient that forms a film[5] as paint dries, and it holds the pigment particles or other additives in a separated, suspended state within the paint film. Binders are either polymeric in nature or are capable of reacting and forming a thermoplastic or thermoset polymeric film under specified conditions. They are comprised of oils, epoxides, alkyds, polyesters, acrylics, vinyls, and the like. The volatile vehicle dissolves or disperses the binder, and it allows the coating to form in a thin, continuous film. In certain formulations, a curing agent[6] or hardener will be incorporated into the system. In the case of ultraviolet-radiation curable coatings, the curing agent will be a photoinitiator that effects rapid polymerization of combinations of monomeric and oligomeric species.

Completed coatings are comprised of one or more film layers with the number of layers and their individual thickness dependent on the particular end use involved and on specifications. For example, a three-layer coating system[7] might be composed of a primer that is directly applied to the substrate surface, a color coat or decorative layer, and a clear topcoat that protects the color coat and provides gloss. Appliances may have two coats, a primer and a colored topcoat. Automobile body coatings usually have four layers—an electrodeposited primer, a primer-surfacer, a color coat, and a topcoat. Powder coatings are often used as single-layer coatings. The most important layer in the coating system is the primer since it is primarily responsible for protection against metal corrosion. It must have excellent wetting and adhesion to the metal surface and to the next applied coating. Components of the primer, when used as an anti-corrosion paint, are various corrosion inhibitors[8] that are also known also as anti-corrosion pigments. Primer coatings are sometimes named after a pigment, for example, "zinc-rich primer (ZRP)," whose formability may be examined as described in ASTM D4146, Standard Test Method for Formability of Zinc-Rich Primer/Chromate Complex Coatings on Steel.

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[2] Corrosion: The physical-chemical interaction of metal (alloy) with its environment that results in change of metal properties (up to its final destruction) and characteristics of the environment; general characteristics of corrosion are described in "Glossary of Corrosion-Related Terms," NACE International, 1998.

[3] Paint: A pigmented liquid or paste coating material, or a coating resulting from the application of such a material.

[4] Vehicle: The liquid portion of a formulated coating material.

[5] Film: A thin, not necessary visible, layer of material.

[6] Curing agent/hardener: A chemical substance used for curing ingredients in a coating formulation.

[7] Coating system: The complete number and types of coats applied to a substrate in a predetermined order. (When used in a broader sense, surface preparation, pretreatments, dry film thickness, and manner of application are included.)

[8] Corrosion inhibitor: Chemical mixture comprised of a combination of substances that, when present in the proper concentration in the corrosion system, prevents or reduces the rate of metal corrosion.

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An organic coating system protects metal substrates against corrosion by means of one or more of several mechanisms:

- Decreasing the rates of anodic (oxidation) and/or cathodic (reduction) corrosion half-reactions that occur on the metal/paint interface.
- Introduction of high electrical resistance into the circuit of the metal/electrolyte corrosion cell[9] that is caused by the nonconductive organic film that is applied on the metal substrate.
- Acting as an effective physical barrier against the transport of aggressive species, such as water, which is the basis of the electrolyte/humidity conditions; oxygen, which is the oxidizing agent; and various corrosion ions (Cl^-, SO_4^{-2}, etc.) to the metal surface. In general, the anti-corrosion efficiency of an organic primer film is a function of four factors:
  - The nature of the metal substrate, that is, its susceptibility to oxidative corrosion.
  - The state of the metal/primer interface—for example, its electrical resistance and capacity, the nature of ions or molecules present in this region, etc.
  - The composition of the primer film and efficiency of the anti-corrosion pigments and any other inhibitors.
  - Corrosion aggressivity[10] of the environment and the characteristic nature to which the coated metal is exposed.

CERTAIN DEFECTS AND COATING APPLICATION

Although anti-corrosion pigments play an important role in protecting metals from corrosion, those applying the coating must make sure a number of considerations are met to ensure the coating properly functions. Blistering (Fig. 1) is probably the greatest cause of coating failure. It can be identified by small- to medium-sized bubbles or blisters that form under the paint film. These result in partial or complete detachment of the coating from the metal substrate. Blistering is caused by painting on a damp or wet surface, which causes trapped moisture to expand the paint film; painting in direct sunlight on a "hot" substrate, which dries the paint surface too quickly and traps solvent vapor in the film; painting during rain or in a very high humidity environment, including heavy dew; by painting over an insufficiently dried coating; or a low-quality paint that is porous.

When blistering occurs, the efficiency of anti-corrosion pigmented coatings is significantly diminished, and they cannot prevent metal corrosion; in fact, the process may well be accelerated. The corrosion products[11] formed in delaminated areas are usually voluminous in nature and exert pressure on the coating film. This pressure buildup will lead to cracking[12] or the appearance of micro-fissures and further loss of adhesion.

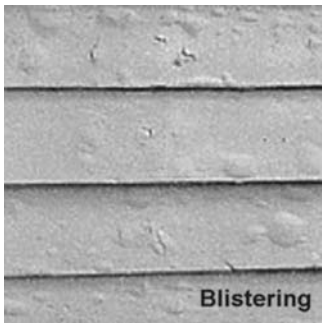

Fig. 1—Blistering of paint coating.

Blooming[13] and filiform corrosion[14] are failures that result in coating damage. These failures usually occur in coating areas that are defective or in areas that have low mechanical strength and physicochemical degradation (aging). Thus, from the corrosion protection standpoint, good substrate adhesion of the various layers is needed. Good adhesion will result in a surface with high ionic resistance that inhibits formation of local anodes and cathodes on the metal surface thus improving corrosion resistance. Since 1979, it has been suggested that the coatings having a critical resistance of less than $10^7\ \Omega\ cm^{-2}$ are not protective. Therefore, it is highly recommended that the electric resistance applied coatings, including any defective areas, be measured. This will provide important information for the analysis of degree of coating protection and failures. ASTM D5162, Standard Practice for Discontinuity Testing of Nonconductive Protective Coating on Metallic Substrates, is a practice for electrical detection of minute discontinuities. Some corrosion failures in paint coatings are shown in Fig. 2.

SURFACE PREPARATION

When the term "coating system" is used in a broad sense, surface preparation, pretreatments, dry film thickness, and manner of application are included. The protective efficiency and life of a coating system are markedly dependent on proper surface preparation, which may be costly but is a needed portion of the paint application process. It has been shown that over 80 % of all paint failures (peeling, efflorescence, etc.) can be attributed to poor or improper surface preparation (Fig. 3). Therefore, paint manufacturers often make comments such as "good paint deserves a good surface" or "the quickest way to achieve paint failure is inadequate surface pretreatment."

COATING CHARACTERIZATION METHODS

Investigation of the parameters that characterize coatings can be carried out according to specific methodologies established in international standards (ASTM, NACE, ISO,

[9] Corrosion cell/galvanic cell: The combination of different electrodes (anode and cathode), connected in series, in contact with an electrolyte (ionic conductor); see "Glossary of Corrosion-Related Terms," NACE International, 1998.

[10] Corrosion aggressivity/corrosiveness: The tendency of an environment to cause corrosion.

[11] Corrosion products: The substances formed as a result of the metal corrosion process. Usually they comprise a majority phase of various oxides and hydrated oxides (hydroxides) and sometimes a minority phase of carbonates, chlorides, sulfides, sulfates, or other.

[12] Cracking (of coating): Breaks in coatings that extend through to the substrate.

[13] Blooming/blushing: Whitening and loss of gloss of a coating, caused by moisture.

[14] Filiform corrosion: Corrosion that occurs under coating in the form of randomly distributed threadlike filaments.

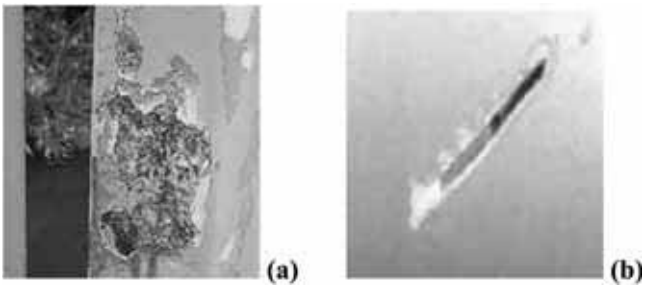

Fig. 2—Corrosion failures in protective paint coatings: (*a*) Area of corrosion of a substrate and appearance of red rust on steel. (*b*) Corrosion products ("rust") forming on steel, where the protective coating system has been damaged mechanically (scratch).

etc.). Several ASTM International documents are listed in the references section. These and other standards can be used to characterize, develop methods, and analyze coating failures. To select an appropriate anti-corrosive coating for an environment of interest, two tests are recommended—a natural weathering or field test under actual conditions and an accelerated laboratory test under selected, artificial conditions that is carried out in a test chamber. Accelerated laboratory tests provide rapid comparative results in a short time because they usually use higher values of some parameters (temperature, humidity, particular radiation, and aggressive environment) than those encountered in real or field conditions [6–8].

A new group has recently been investigating a method termed "accelerated test in natural conditions." Their efforts may result in an improved correlation between field testing and accelerated weathering. The "black box" test, in which the resistance of materials to solar radiation filtered through glass is evaluated, has been found to be a useful tool [9]. Procedures that deal with the black box test can be found in ASTM D4141, Standard Practice for Conducting Black Box and Solar Concentrating Exposures of Coatings; ASTM G24, Standard Practice for Conduction Exposures to Daylight Filtered Through Glass; and other standards.

INORGANIC ANTI-CORROSION PIGMENTS

Anti-corrosion pigments are coloring components of paint that can influence and control the corrosion of metal substrates by moderating the rate at which corrosion takes place. Because of this moderating effect, these pigments are also known as corrosion "inhibitors." These coating components are usually introduced into the primer layer.

A variety of metals such as aluminum, chromium, lead, iron, and zinc are known as effective anti-corrosive pigments, and they are introduced into the coating formulation as finely ground metal or powdered metal oxide. Oxides of lead, chromium, and iron (burnt sienna,[15] burnt umber,[16] and Tuscan red[17]) have been extensively used in the past. Currently, their usage is restricted because of toxicity considerations and their effect on the environment. However, it should be pointed out that the inhibiting protection provided by pigments such as red lead (also called *minium*, Pb_3O_4 or $2PbO \cdot PbO_2$), yellow zinc chromate ($ZnCrO_4$), and red zinc chromate ($ZnCrO_4 + Fe_2O_3$) is very satisfactory. Anti-corrosive primers based on such compounds have been used for a long time to satisfactorily protect metal structures exposed to a variety of hostile environments.

Zinc phosphate (ZP), barium metaborate, and strontium chromate pigments are also common ingredients in corrosion-inhibiting coatings. Thin wash-inhibiting primers are often formulated with chromate or phosphate pigments that are introduced in a synthetic polymeric binder such as a vinyl chloride copolymer. The variety of inorganic corrosion-inhibiting pigments includes also lead carbonate, strontium chromate, zinc oxide, and ZP.

Chromate-Based Compounds

Due to their excellent cost/efficiency ratio, chromates are one of the most used chemicals in corrosion protection systems for metallic surfaces. These anti-corrosive pigments are incorporated into paints in the form of solid, fine particulate materials that are dispersed throughout the paint film. They function as inhibitors, affording protection by an electrochemical mechanism. The chromate-containing, corrosion-inhibiting pigments include the sparingly soluble chromates of the alkaline earths, Ca, Sr, Ba, and Zn. They provide a source of active, inhibiting Cr^{6+} compounds that act as very powerful, effective corrosion inhibitors.

Chromate-based compounds are used in primers throughout industry as a component in corrosion protection systems for a range of metal substrates—even substrates exposed to aggressive environments of high chloride/chromate ratios. The oxo-anions of hexavalent chromium uniquely inhibit the corrosion of many metals and alloys, and they have been particularly useful for protecting the high-strength aluminum alloys against corrosion. Chromates are excellent inhibitors of oxygen reduction in near neutral and alkaline solutions. In these environments, they can stifle corrosion by suppressing the cathodic oxygen reduction that is the necessary partial reaction of the corrosion process.

The inhibition mechanism appears to involve reduction of Cr^{6+} to Cr^{3+} at a metal surface and formation of an irreversibly adsorbed Cr^{3+} hydroxide surface layer of near-monolayer thickness [10]. The results indicate that the adsorbed Cr^{3+} film formed by Cr^{6+} reduction is a powerful inhibitor of oxygen reduction on surfaces of aluminum and its alloys. This is due both to occupation of any active chemisorption sites and to inhibition of electron transfer. In the context of corrosion protection, Cr^{6+} acts as a "site-directed" irreversible inhibitor that migrates to active sites

[15] Sienna: Natural yellow-brown color pigment, the mineral limonite FeO (OH) · nH_2O, used in the production of oil paints. Along with ochre and umber, one of the first pigments used by humans for painting. Chemically, burnt sienna (a warm mid-brown iron oxide pigment) is formed by burning raw sienna.

[16] Umber: Natural brown clay pigment that contains iron and manganese oxides. The dark brown pigment burnt umber is made by heating umber, and it is used for oil and water color paint.

[17] Tuscan red: The mineral hematite (ferric oxide), it is the principle coloring agent in red ochres, such as Indian red, Terra Pozzuoli, Venetian red, etc. These pigments are basically hematite associated with varying proportions of mineral impurities such as clay, chalk, and silica.

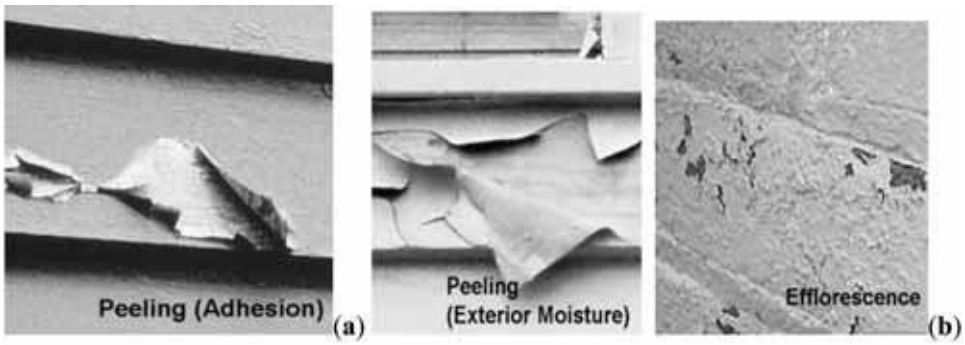

Fig. 3—Peeling (*a*) and efflorescence (*b*) failures in paint coatings.

for the oxygen reduction reaction. Here it is reduced to Cr^{3+} and forms a permanent inhibiting monolayer. The Cr^{3+} film formed is nonconductive and inhibits further Cr^{6+} reduction and outer-sphere redox processes. Evidence from older and more recent studies indicate that inhibition of aluminum corrosion is derived from both inhibition of oxygen reduction and inhibition of metal dissolution reactions mainly due to a delay in the onset of pitting. Inhibition of corrosion by chromates appears to be closely linked to their ability to irreversibly adsorb onto metal and oxide surfaces.

Chromates can also inhibit corrosion by slowly leaching from the protection system and migrating through moisture on the substrate surface where reaction with actively corroding sites takes place. This scheme results in passivation and suppression of pitting and crevice corrosion [11–13]. When present in even a very small concentration (as ~$10^{-4}M$), the dichromate ions (CrO_4^{2-}) effectively decrease the metastable pit nucleation rate and minimize pit growth rates that occur as a consequence of aggressive chloride ions attack. This has a large effect in the cathodic region and no effect in the anodic region. These observations suggest and confirm that chromate or its reduction product act as efficient cathodic inhibitors.

The distribution of $SrCrO_4$, $BaSO_4$, and TiO_2 in two chromate-inhibited primers has been characterized using electron microprobe analysis, Raman spectroscopy, x-ray diffraction, and position annihilation lifetime spectroscopy [14]. It was found that TiO_2 was evenly dispersed throughout the primer, while $BaSO_4$ and $SrCrO_4$ appeared as larger particles or platelets with sizes on the order of several microns. When immersed in solutions of *p*H 1, 3, 5, and 7, $SrCrO_4$, and possibly $SrCr_2O_7$, was observed to leach out of the primers after water uptake by the primer and dissolution of $SrCrO_4$ particles. The amount of chromate leached from the primers was greatest for *p*H 1, followed by *p*H 3, 5, and 7.

Kendig and Buchheit [15] have published a critical review that deals with the aqueous chemistry of chromium and the origins of chromium toxicity.

Zinc-Rich Paints

Anti-corrosive zinc-rich paints provide corrosion protection by two principal mechanisms:

a) Galvanic or sacrificial protection.[18] This is due to the fact that the standard electrode potential[19] of zinc (–0.76 V) is more negative than that of iron (–0.44 V), therefore in a zinc-iron (steel) coupling, zinc will take the role of sacrificial anode that corrodes (oxidizes) preferentially to iron. In this manner, zinc is protecting the steel (iron) surface from corrosion. Since this occurs, it indicates that very good electric contact between the zinc particles and metal substrate had been achieved and maintained. Due to the presence of coating defects (porosity), it is understood that the zinc-rich coating acts as a porous electrode.

b) Physical barrier protection. The physical barrier behavior of ZRPs is reinforced by the nature and quantity of zinc corrosion products. These products result in formation of a dielectric layer on the steel surface; moreover, these products are less voluminous than steel products, and, as a consequence, they do not exert a great deal of pressure on the organic coating.

Different ZRPs have been tested in industrial atmospheres. For example, when primers based on silicate and on epoxide (70 % and 79 % Zn powder, respectively) were investigated, the results indicated that the primers based on silicate provided better galvanic (sacrificial) protection than the epoxy primer. It is thought that in the coating the zinc particles are in electric contact with each other and also with the metal substrate (Fig. 4). With the zinc particles interconnected, sufficient galvanic (cathodic) protection is available to protect the metal substrate. However, while the zinc corrosion products are not as voluminous as with some primer systems, they produce a number of blisters in the paint coating [Fig. 4(*a*)]. Moreover, the migration paths for anti-corrosion agents through the organic coating could be achieved through the pore defects in the coating [Fig. 4(*b*)].

Zinc Oxide-Containing Systems

Powdered zinc oxide was introduced as an inhibitive, anti-corrosion pigment for primer formulations in the past few decades. Typically the pigment was used at 33–57 mass % of the primer composition. It contributed to successful anti-corrosion protection of metallic structures exposed to marine atmospheres, i.e., highly chloride-contaminated environments. Various organic compounds such as epoxy esters, galic acid (antioxidant) polyesters, polyurethanes, and the like are used as the binder for zinc oxide coatings. It should be noted that several physicochemical properties of zinc-rich paints (specific gravity, oil absorption, and other properties of a pigment inhibitor) may be affected due to the pigment volume concentration (PVC) considerations. More than 25 years of paint evaluation at the Kennedy

[18] Sacrificial protection: Reduction of corrosion of a metal in an electrolyte (humidity) by galvanically coupling it to a more anodic metal having more positive electrode potential.

[19] Electrode potential: The potential of an electrode in an electrolyte as measured against a reference electrode.

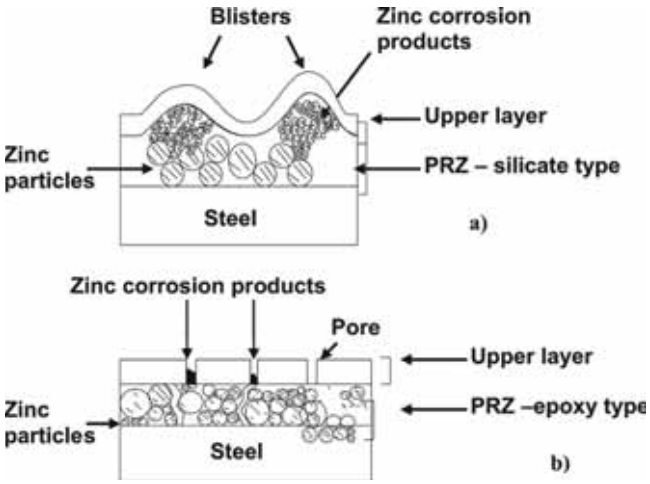

Fig. 4—Schematic representation of corrosion in steel protected by zinc-rich paint (ZRP): model of blister (*a*) and corrosive attack through the coating pore (*b*).

Space Center (marine-coastal test station) has identified the fact that zinc-rich paints are the best choice for corrosion protection of launching equipment and support equipment in service on land.

During production of zinc pigments, some zinc may get oxidized to ZnO when it comes in contact with oxygen and eventually all zinc dust will contain at least traces of ZnO as an impurity. The electrical properties of ZnO are interesting and complex. ZnO acts an inhibitor to chloride-induced corrosion, seals pores in primers, and improves the primer's barrier properties. Therefore, it has been interesting to include ZnO in a Zn-rich primer and to study its effect on corrosion-protection properties [16]. In the reported study, the effect of spherical ZnO on anti-corrosion properties was evaluated along with lamellar zinc. ZnO was added in various weight fractions to an epoxy-based primer at 60 % PVC. These coated panels were evaluated along with others for conductance, packing density, and morphology. Corrosion resistance was measured after a 3,000 h exposure in a salt spray. Open circuit potential (i.e., corrosion potential) was measured in a 3.5 wt % NaCl salt solution. When Zn and ZnO are mixed together, they quite likely formed *ap-n* junction at their interface. At a contact established between a metal and a semiconductor (known as a Schottky junction), electrons will flow from the material with the highest Fermi level to that with the lowest Fermi level, creating a positive charge in the semiconductor. This will allow electron transport in a controlled manner on the top surface of the coating, which provides better cathodic protection for the Zn-ZnO combinations rather than for Zn only. The packing density was better at 15 wt % ZnO, which implies that the compactness was enhancing junction formation. The best corrosion protection was obtained with 15 wt % of ZnO. Hence, Zn–ZnO *p-n* junction formation gives better corrosion resistance properties than either cathodic or barrier protection alone, and the combination would be the best choice for single-coat metal primer.

Electrochemical behavior of epoxy anti-corrosion paints based on zinc molybdenum phosphate and zinc oxide pigments has been studied. The main investigative tool used to describe the efficiency of epoxy-based anti-corrosion primers was electrochemical impedance spectroscopy (EIS) [17]. The film-forming material (binder) in these studies was a solvent-borne, bisphenol A epoxide polyamide, and several pigments were used with this binder. The main anti-corrosion pigment used was micronized ZnO (average particle diameter 1 mm) at loading levels of 10 % and 30 % by volume and with respect to the total pigment content. The complementary pigments used were ferric oxide (Fe_2O_3) and barium sulfate ($BaSO_4$). Twenty percent by volume of the resulting pigment mixture were replaced with zinc oxide. The ferric oxide was used because its colloidal particles are said to interact with metallic substrates and thereby increase coverage. Steel-coated samples were exposed to a 0.5*M* NaCl solution and during the test their corrosion potential was monitored every 24 h. The results indicated that addition of micronized ZnO to the base mixture had a positive reinforcement effect on the protective properties of the anti-corrosion primer. This was thought to be related to the isoelectric point of ZnO particles ($pH < 9$), which determines their positive surface charge and electrostatic attraction with the molybdate anion. In this case, the double-layer capacitor formed has a very high charge. Moreover, this strong attraction inhibits and saves ZnO particles from rapid dissolution by hydroxide. These results also indicate that there is an optimum concentration ratio of zinc molybdenum phosphate to zinc oxide that will ensure the good anti-corrosion properties.

Zinc Phosphate

ZP is the most commercially successful non-toxic inhibitive pigment used in paint formulations. Furthermore, the use of phosphates does not represent an excessive cost, and their application is even easier than other proposed alternatives for chromate pigments. This is the anti-corrosive pigment most frequently used in paints [18–21]. The massive use of nontoxic and environmentally acceptable ZPs developed an immense pressure for regulations that prohibited the use of red lead and chromated anti-corrosion pigments. Experimental results suggest that ZP and all phosphate-based pigments (zinc-aluminum polyphosphate, ZP modified with organic corrosion inhibitor, etc.) exhibit improved anti-corrosion efficiency when their concentration is increased [21].

The effect of ZP over the barrier properties of different paints has been studied using a variety of techniques. The investigations revealed that commercial ZP powder was a mixture of the dihydrate and tetrahydrate species, however, when it is blended with a polymeric binder, only the tetrahydrate form was detected. Incorporation of this pigment into a paint led to a definite improvement of the barrier properties. This was particularly apparent in the case of chlorinated rubber polymers. The finding suggests that the nature of binder-pigment interactions play an important role and should be given consideration in studies of barrier properties [22].

To improve the protective action of "environmentally acceptable" coatings, a second generation of materials aimed at combining, in a synergistic manner, the corrosion inhibition properties of phosphates and molybdates, called phosphomolybdate pigments, has been developed. Zinc molybdenum phosphate seems to be one good possibility, and it is claimed to have equal or superior anti-corrosion behavior when compared with chromate and ZP. From a corrosion point of view, when zinc molybdenum phosphate

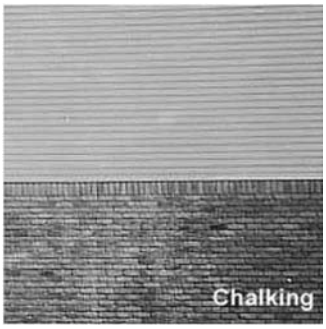

Fig. 5—Chalking of paint coating.

pigment is added to a water-borne paint and applied as a unique protective coating to a steel substrate, an interesting combination for study exists [23]. Paint with PVCs of 27 % and 10 % (v/v) of this pigment provided effective protection against weather conditions and improved properties such as chalking (Fig. 5), gloss, and yellowing. Similarly, the efficiency of zinc tripolyphosphonate (ZTPP) as an anti-corrosion pigment has been evaluated [24]. Solvent-borne paints containing $BaSO_4$, talc, and TiO_2 together with 30 % or 10 % v/v (by volume) of ZTPP, with respect to the total pigment content, have been formulated. Two polymers were chosen as film-forming materials: an alkyd and an epoxy-polyamide (1:1) mixture. The results demonstrated that ZTPP inhibited corrosion when incorporated into a paint film. It showed excellent performance when employed with the alkyl resin.

It should be pointed out that even though the literature reports indicate phosphate-based pigments to be "environmentally acceptable" and ZP is classified as "not hazardous" to human health under United States' regulations, according to other regulations of the United States and the European Union, ZP is considered "very toxic in an aquatic environment." Therefore, ZP-based pigments should not be qualified as "environmentally friendly" products. With this information in mind, the aim of a reported study [25] was to evaluate the anticorrosive performance of organic epoxy coatings pigmented with the following non-toxic pigments: ZP, zinc phosphomolybdate (ZPM), and zinc calcium phosphomolybdate (ZCPM). All of these coatings were compared with an epoxy coating pigmented with zinc chromate (ZC). The analysis was based on coated steel samples immersed in aqueous 0.01 mol/L sodium chloride solutions and in accelerated tests conducted in a salt-spray chamber. ZPM and ZCPM coatings performed best in the total immersion test, but in the salt spray test, the corrosion inhibitor performance of all three pigmented coatings was similar. This suggested that only in the less aggressive test is it possible to detect any difference between the coatings when investigating the non-toxic pigments.

Zinc Ferrites

The synthesis of zinc ferrites ($ZnFe_2O_4$) with different particle shapes for applications in anti-corrosion coatings provides a new way of protecting metals against corrosion [26]. One benefit obtained with these anti-corrosion pigments is the fact that they do not contain any environmentally harmful substances. They are synthesized through a high-temperature process that is conducted from about 600 up to 1,100°C from hematite (alfa-Fe_2O_3), goethite (alfa-FeO·OH), magnetite (Fe_3O_4), and specularite (Fe_2O_3) entering into a solid phase reaction with zinc oxide (ZnO). The formulated zinc ferrites particles have a rod-like, lamellar, and/or isometric shape. The zinc ferrites were used to prepare coatings with epoxy and with water-borne styrene-acrylate binders that were subjected to post-application tests for physical-mechanical and anti-corrosion properties. All of the synthesized pigments had good anti-corrosion efficiency in the binders studied. When compared with a commercially available anti-corrosion pigment, their protective power in coatings was demonstrably stronger.

Magnesium-Rich Primer

When two metals are exposed to a corrosive environment and placed in contact with each other, the more active metal will preferentially corrode and thereby provide sacrificial protection for the nobler or less active metal. This concept has been applied for many years by use of ZRPs for the protection of steel. Investigations using other compositions and metals, including manganese, have been made [27]. Zinc dust and magnesium-powder as pigments have been incorporated in epoxy-polyamide and butyl-titanate binders, with PVC that ranged from 20 to 74. These protective coatings were applied to mild steel substrates and immersed in an aqueous 3 wt % sodium chloride solution and the corrosion currents were measured to characterize corrosion performance. The results were found to be comparable indicating that magnesium-powder can be used an alternative to Zn-powder for metal-rich primers.

The electrochemical behavior of Mg-rich primer on aluminum alloys (specifically, AA2024 and AA7075) has been studied with EIS, open circuit potential, and potentiody-namic polarization [28,29]. Results showed that the magnesium-rich primer provides sacrificial protection for the aluminum substrate by means of a two-stage mechanism. In a first stage, corrosion of aluminum is prevented by cathodic polarization. Magnesium cathodically polarizes aluminum and shifts its potential below the pitting corrosion potential. The consequence of this polarization can be either the prevention of pit nucleation at the exposed aluminum areas or the inhibition of pit growth in the nucleated pits. During this stage, any defects on the surface will become cathodic whereas the magnesium particles are anodic. At the cathodic areas, reduction of hydrogen takes place and possibly dissolved oxygen increases the *p*H above the threshold for the precipitation of magnesium oxide. This precipitation leads to the formation of a porous layer that further inhibits corrosion by a barrier mechanism, which is considered to be the second or later stage of the protective mechanism. The typically high dissolution rate of magnesium is significantly decreased by its incorporation into the polymer matrix.

Iron Oxides

The iron oxides represent an important category of inorganic pigments in which iron is most often present in a trivalent form. Oxides, or rather hydroxide-oxides, can be used as pigments in paints [30]. Ferric oxide is usually introduced in the total pigment formula because its colloidal particles are said to interact with metallic substrates increasing its coverage. Yellow-goethite α-FeOOH with needle-shaped particles, red hematite alfa-Fe_2O_3 with granular particles, and specularite Fe_2O_3 with lamellar particles

so called iron mica, have been tested. The main features of the coatings containing these ferric pigments are the improvement of light stability and the resistance to weather conditions and ultraviolet radiation. The parallel-oriented lamellar particles of specularite moreover reinforce a paint film, improve its mechanical properties, and reduce internal tension.

Silicate-Based Pigments with Non-Isometric Particles

Talc, $Mg_3(OH)_2(Si_4O_{10})$, is a hydrated magnesium silicate that belongs to the group of silicates with a layered structure. It consists of electrically neutral layers without inserted cations, and this construction gives rise to qualities such as softness, smoothness, and lubrication. Its particles are disk-like, lamellar, or micro-fibrous. Talc is resistant to acids, has a low electric conductivity, and has high coating power. It positively influences the rheological properties of liquid paint and improves adhesion, strength, and anti-corrosion properties of the coating [29].

Wollastonite is a calcium meta-silicate, $CaSiO_3$ (structural formula: $Ca_3Si_3O_9$). It forms columnar needle-like or radial straw-like white crystals. It can be split into very fine fibers whose length to width ratio is 5:1 to 10:1 and can even exceed 20:1. Wollastonite is a chemically inert substance with low moisture content as well as suitable thermal and electrical properties. It belongs to a silicate family that has chain-like structures (SiO_4). Chain metasilicates $(SiO_3^{2-})_n$ are created by sharing of SiO_4 tetrahedron structures. The needle-shaped particles fit into each other well and reinforce the coating, improve ductility, have balancing effects, and facilitate creation of an even coating thickness.

The most effective pigment series comprises iron mica (silicate), muscovite mica [aluminum-potassium silicate, $(KF)_2(Al_2O_3)_3(SiO_2)_6(H_2O)$], and aluminum or glass flakes.

Graphite

Graphite is a key additive that provides a combination of color, conductivity, and ultraviolet radiation stability in coatings and other products. It is a high-purity, microscopic form of carbon produced by thermal cracking of a hydrocarbon raw material. The formation process consists of atomizing a heavy aromatic fraction of petroleum distillate in a preheated furnace followed by cooling and collecting the formed carbon black. The graphite lattice exists in the hexagonal structure of carbon. Graphite is found in a macrocrystalline (flaky), micro-crystalline, and even crypto-crystalline (amorphous) form. Particulate graphite (metalliferous) is rare. Unlike synthetic electrographite, natural graphite with a lamellar structure is often contaminated with various admixtures of forms.

The industrially important properties of graphite include excellent splitting capacity and plasticity, chemical and thermal resistance, and high thermal and electric conductivity. Graphite can be used in color coatings as a pigment with high chemical, ultraviolet radiation resistance and light stability. This pigment is also capable of arranging itself into barrier lamellar structures. Experimental results have shown that the best anti-corrosion efficiency is displayed by a pigment based on natural graphite due to the coating of particles with a polyaniline (PANI) layer [30]. The lamellar particles of graphite coated with the conductive form of PANI contributes to modification of conducting properties as well as to improved barrier and anti-corrosion efficiency.

Titanium Dioxide (TiO_2)

Titanium dioxide is an important white inorganic pigment that is used to provide hiding in paint. It is also called titanium white, Pigment White 6, or CI 77891. It is used as a pigment and a thickener that increases the viscosity and stability of the paint mixture and improves the suspension of added ingredients. Titanium dioxide has excellent chemical stability, heat resistance, and low electron conductivity, features that make it an excellent anti-corrosion pigment. Titanium dioxide is used in a finely suspended state and in a viscous medium to formulate paints. The medium may be a solution of a polymeric compound in an organic solvent or aqueous latex.

Titanium dioxide is a naturally formed mineral that is well known in its different structural forms as rutile (tetragonal), anatase (tetragonal), and brookite (orthorhombic). The most stable and common form is the mineral rutile. Titanium dioxide is considered as a mineral ultraviolet (UV) radiation blocker because of its high refractive index, its strong UV radiation absorbing capabilities, and its resistance to discoloration under UV radiation. In addition, it has strong photo-catalytic properties (Honda-Fujishima effect) and oxidative potential. Because of these facts, TiO_2 can directly oxidize oxygen or organic materials when, for example, it is added to anti-fouling paint. Incorporated into exterior paint for buildings, TiO_2 can substantially reduce airborne pollutants, such as volatile organic compounds (VOCs) and nitrogen oxides, because it becomes increasingly hydrophilic when exposed to UV radiation.

Titanium dioxide flocculation has a detrimental effect on opacity and other paint properties. It has been established that flocculation increases as a function of alkyd emulsion particle size. Mathematical modeling work has been used to compare theoretical light-scattering efficiency of alkyd emulsion paints with the measured scattering coefficients. An experimental proprietary flocculation-resistant grade of titanium dioxide has been incorporated into alkyd emulsion paints to demonstrate the beneficial effect on opacity that occurs when the level of flocculation in alkyd emulsion paints is reduced.

Titanates

An anti-corrosion pigment combination based on calcium titanate ($CaTiO_3$) with a perovskite[20] structure (Fig. 6) has been synthesized from titanium dioxide (TiO_2) and calcium carbonate ($CaCO_3$) in a high temperature reaction [31]. From an ecological standpoint, the application of a new anti-corrosion pigment for paints represents a highly positive trend. The synthesized pigment was used

[20] Perovskite structure: Any material with the same type of crystal structure as calcium titanium oxide ($CaTiO_3$), which is known as *the perovskite structure*. The general chemical formula for perovskite compounds is ABX_3, where A and B are two cations of very different sizes and X is an anion that bonds to both. The A atoms are larger than the B atoms. The ideal cubic-symmetry structure has the B cation in six-fold coordination, surrounded by an octahedron of anions, and the A cation in 12-fold cuboctahedral coordination (Fig. 6).

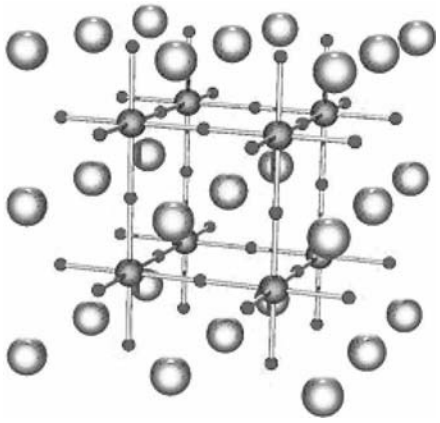

Fig. 6—Perovskite structure ABO_3. The red spheres are oxygen atoms, the deep blue are smaller (Ti^{4+}) metal cations (*B*-site) and the green/blue are the larger (Ca^{2+}) metal cations (*A*-site).

to prepare epoxy coatings with varying anti-corrosion pigment concentrations. The coatings were tested for physical-mechanical properties after exposure in corrosive atmospheres. The results were compared with the same titanium dioxide that served as a starting material for calcium titanate preparation. It was found that $CaTiO_3$ is a highly efficient anti-corrosion pigment for use in paints to protect base metals from corrosion.

Inorganic Oxoanionic Inhibitors

Inorganic oxoanionic compounds are considered as environmental safe materials. Common oxometallate anions are the molybdates (MoO_4^{2-}), phosphates (PO_4^{3-}), tungstates (WO_4^-, WO_3^{3-}), silicates (SiO_3^{2-}), vanadates (VO_3^-), and borates ($B_2O_4^{2-}$). With the exception, perhaps, of zinc, the most common inorganic cationic inhibitors are, for example, the rare earth cations, as La^{3+}, Nd^{3+}, Eu^{3+}, Y^{3+}, Ce^{3+}, Gd^{3+} [32]. However, it should be pointed out that these inhibitors have similar performance characteristics to those of chromate-based inhibitors, and they should provide corrosion inhibition over a wide *p*H range.

The use of rare earth salts of cerium and lanthanum [$Ce(NO_3)_3$ and $La(NO_3)_3$] and bis-sulphur silane (BTESPT) as chromate substitutes for galvanized steel conversion coatings has been proposed [33]. These compounds when applied by immersion and subsequent curing result in films that improve corrosion resistance and paint adherence. The two-step pretreatments result in good corrosion protection; however, the best performance was obtained with the lanthanum conversion coating. This was observed either on un-coated and coated substrates. The silane (BTESPT) by itself also shows some improved corrosion protection. The presence of the sulphur atoms on the silane molecule seems to play an important role in the deposition process. Thus, it can be suggested the presence of an internal layer rich in sulphur and zinc hydroxides/oxides together with the silane helps improve corrosion resistance.

Phospho-Molybdate Pigments

Phospho-molybdates are considered second-generation corrosion-inhibiting pigments that have been introduced in solvent- and water-based paints. Anti-corrosive pigments based on molybdate are recognized as effective corrosion inhibitors for coatings and these pigments are well established and have been commercially available for over 20 years. As environmental constraints continue to limit the use of many types of corrosion inhibitors and paints based on heavy metals, molybdate pigments are increasingly being specified for environmentally compliant paint systems.

Ongoing research has led to the development of "second generation" molybdate pigments, which are described as phospho-molybdate pigments. These compounds are believed to have exceptional corrosion-inhibiting activity. Recently completed testing, based on long-term outdoor exposure, indicates that they can provide better performance than traditional chromate-based corrosion inhibitors. In another development, phospho-molybdate pigments have been used to formulate a water-based acrylic coating system that was recently approved by the Florida Department of Transportation for bridge coatings.

Ion-Exchange Pigments

Ion-exchange pigments (IEPs) are a relatively new class of inhibitive pigments. They are one of the alternatives that could be adopted as non-toxic anti-corrosive pigments in paints. From a scientific viewpoint, they appear to be very attractive candidates. These compounds are inorganic oxides with a comparatively high surface area and that are loaded with ionic corrosion inhibitors by ion exchange with surface hydroxyl groups. As might be expected, the oxides are chosen for their acidic or basic properties to provide either cation or anion exchangers—thus, silica is used as a cation support and alumina for an anion support. The corrosion-protection behavior of these pigments is controlled by the rate of ion release by the exchanger. The ion-exchange release mechanism allows efficient use of a comparatively low loading of inhibitive pigments.

Calcium-exchanged silica, Al–Zn-decavanadate hydrotalcite (HT), and cerium (III) and calcium (II) cation exchanged bentonites have been incorporated as pigments in anti-corrosive paints. The other advantage of this approach is that it allows use of otherwise highly soluble inhibitors. With knowledge of process kinetics for ion release within the primer, it is possible to control the accessibility of inhibitors and therefore to control its diffusion onto the metal surface. The inhibition mechanism is related to the ion-exchange reaction. On exposure of paint films to an aggressive environment, water uptake occurs and exchange of calcium with hydrogen and ions and release of calcium ions takes place.

HTs, as anion exchange compounds, are layered clay materials and are used for a variety of industrial purposes. In general, they consist of a host structure with a fixed charge. Specifically, HTs are being synthesized with vanadates (HT/V), which have been shown to be excellent inhibitors of Al corrosion [34]. The ion exchange characteristic of HTs is used to release vanadates into an attacking electrolyte and stifle corrosion. In the case of HT/V, the host is a mixed Al–Zn hydroxide that is positively charged. The positive charge originates from the substitution of Al^{3+} on Zn^{2+} sites within the structure. Within the host, there are open channels or "galleries" that can accommodate anions and solvent molecules [35]. Cations may also be incorporated in the "gallery" provided that overall electro-neutrality is

maintained in the solid, but in the initial state, HT/V contains inhibiting anions in the gallery. On contact with an aggressive electrolyte containing chloride ions, an exchange reaction will occur in which the inhibitor anion is released and chloride is adsorbed into the HT gallery.

Experiments have shown that HT compounds dispersed as an additive in organic (epoxy) compounds led to potent corrosion inhibition of an underlying aluminum alloy substrate. Corrosion inhibition is derived from release of a decavanadate from crystalline Al–Zn hydroxide-based HT particles into electrolyte that has permeated the pore space of the coating. Decavanadate release is accompanied by uptake of chloride ion in an exchange reaction. The exchange of the large decavanadate anion for smaller chloride ion in the HT structure results in a predictable change in crystal structure, which can be detected by x-ray diffraction. The use of this additive also imparts the ability to detect environmental changes in the coating that are a prelude to substrate corrosion.

It was demonstrated that the anti-corrosion performance of paint pigmented with calcium-exchanged silica (Ca/Si) is at least equal to or better than that obtained with paints containing ZP [36] and closely approaching that of chromate while having better efficiency than iron oxide [37]. The results suggested a film-forming mechanism for calcium/silica coatings. Calcium, released from the silica surface, migrates to the paint-metal interface where a thin, inorganic layer is deposited. This layer is essentially impermeable to moisture/ions and hence prevents the corrosion reaction from proceeding. The anticorrosive effect of Ca/Si pigment can be described by considering two mechanisms: the exchange of calcium ions for cations (H^+, etc.) that are penetrating the coating from the environment, neutralizing the acid compounds and forming a protective layer consisting of calcium and iron silicate on the substrate [38]. Combinations with other active anticorrosive pigments (ZP/molybdate, for example) are generally possible and may be advantageous.

Novel corrosion-inhibitor pigments consisting of cerium (III) and calcium (II) cation-exchanged bentonites have been shown to provide effective cut-edge corrosion resistance in organic coated galvanized steel. The bentonite pigments were prepared from a naturally occurring bentonite with a cation-exchange capacity of 0.7 milliequivalents/g. Cation exchange was carried out by repeated washing with aqueous solutions of cerium (III) chloride and calcium (II) chloride to produce bentonites containing 31,500 ppm exchangeable cerium (III) and 13,500 ppm exchangeable calcium (II), respectively. The resulting bentonite pigments were dispersed in a polyester-based primer paint system to give a PVC of 19 %. For comparison, two similar primer systems were prepared containing a commercial calcium (II) exchanged silica pigment [Shieldex: 60,000 ppm calcium (II)] and a strontium chromate dispersion, both at a 19 % PVC. All primer systems have been applied to the zinc surface of galvanized 0.7 mm gauge sheet steel and over coated with an architectural polyester topcoat. The performance of the inhibitor pigments was compared by measuring the rate of corrosion-driven organic coating delamination from the cut edge of samples during 1,000 h of salt-spray testing. The calcium (II) bentonite pigment exhibited an anti-delamination performance similar to that of strontium chromate but superior to that of Shieldex. However, the cerium (III) bentonite pigment was superior in performance to both strontium chromate and Shieldex. Thus, the bentonite pigments represent promising, environmentally friendly, ion-exchange corrosion inhibitors that exhibit good anti-delamination performance in comparison with current commercial systems [39]. A schematic representation of the macro-structure of a bentonite clay is shown in Fig. 7.

Recent research, which focuses on the anti-corrosive protection of IEPs in alkyd coatings applied on low carbon steel specimens and formulated with anionic (vanadates-HT, HT/V 10 %) as well as cationic (calcium/silica, Ca/Si 5 %–15 %) ion-exchangeable pigments, has been reported [40]. The investigation compared the anti-corrosion efficiency of these IEPs with traditional ZC pigments. The results revealed that the anticorrosive behavior of $ZnCrO_4$ (10 %) stands out above that of the two IEPs considered in this study. The anti-corrosive performance of IEPs depends on the medium in contact with the coating. The anionic HT/V shows a tendency toward a better behavior in chloride environments (salt fog test, 0.5*M* NaCl solution) while the cat-ionic Ca/Si behaves well in non-chloride environments [humidity condensation and SO_2 (0.2 L)]. Good behavior was found for the Ca/Si pigment at the intermediate concentration of 10 %. The other two studied concentrations (5 % and 15%) afford the coatings that are highly deficient anticorrosive properties.

An electrochemical evaluation of the corrosion protection afforded by environmentally friendly coating systems that were applied on hot-dip galvanized steel samples has been reported [41]. The primers used polyphosphate (26 % P_2O_5) and anti-corrosive IEPs ($A1_2O_3$, CaO, SiO_2). Two types of coating systems were studied. The first series of metal samples was galvanized steel covered only with primer, and the second series were complete coating systems consisting of primer and topcoat. The results revealed that the pigments had a significant inhibitive effect, and they acted as cathodic inhibitors. The pigment action resulted in layer deposition on the metal surface and in reducing the corrosion rate. The barrier properties of the complete coatings (primer plus top coat) were not critical. On the contrary, the presence of low barrier properties and therefore a limited water uptake caused the pigment dissolution to induce the activation of the pigment inhibitive action.

The few studies conducted with IEPs are inconclusive about their anti-corrosive efficiency, and controversy surrounds their functioning mechanisms, interchange capacity, and anticorrosive performance.

Super Primers

The concept of a super primer is relatively new. When bis-silanes (SiH_4) are mixed with conventional primers or binders, they have been shown to impart excellent corrosion protection [42]. The concept of super primers, i.e., primers for metals with the conversion coating built in, has proven to be feasible. Such primers do not require a chromate (or other) conversion treatment of the metal and can be applied on any bare metal (Fig. 8). The VOCs content in the primer is kept low by using water-dispersed organic polymers. Because of the high concentration of organo-functional silanes contained in a super primer, its adhesion, both to the substrate and to primer overcoats,

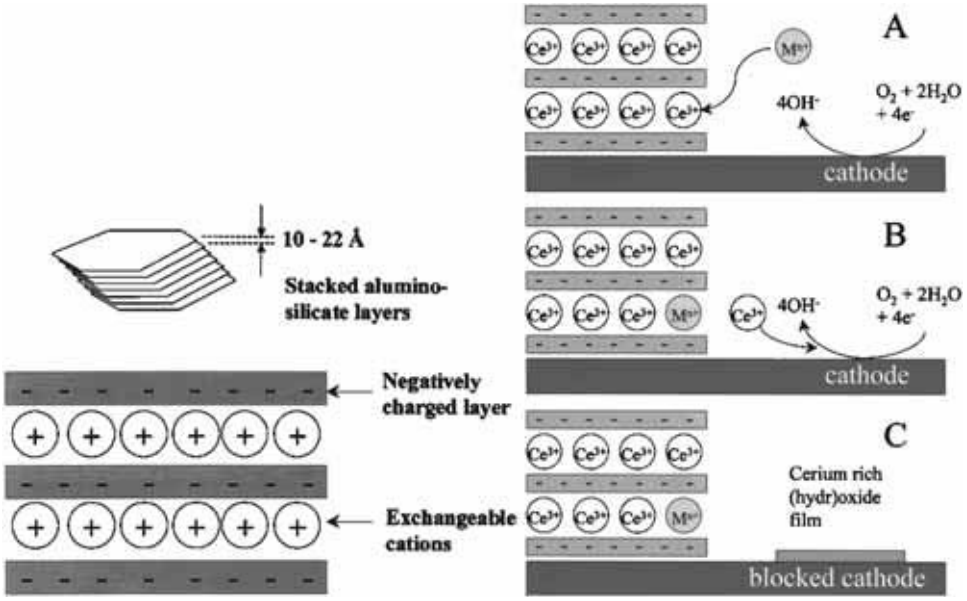

Fig. 7—(a) Schematic representation of the macro-structure of a bentonite clay. The negatively charged layers, with exchangeable compensating cations between them, are held together electrostatically. (*b*) Schematic illustration of the potential mode of operation of a cation exchanged bentonite inhibitor pigment on a corroding galvanized surface. (*c*) Schematic illustration of the negatively charged layers blocked by the numerous compensating cations between them [39].

is excellent. The corrosion resistance of the primer can be further improved by adding corrosion-inhibiting pigments such as micronized ZP into the formulation. A set of super primers has been developed, and they have been put through performance tests and characterized with a variety of methods. An attempt to explain the mechanism by which one of the coatings, the epoxy-acrylate-based primer, deposited onto aluminum, protects the metal from corrosion, is given (Fig. 9).

The corrosion-protection mechanism of the epoxy-acrylate coating, which is self-assembled into layers after it was deposited from a water-borne dispersion, is unique. The chemistry of the coating facilitates leaching of the ZP on demand when the coating is scribed and attacked by an electrolyte. The chemistry of the coating allows the ZP to act as chromate ions would act in a regular coating when the coating is exposed to salt water. The chromate ions are well known to leach out only on demand, as when a polymer coating is exposed to a corrosive environment. The extensive study of the epoxy-acrylate primer has demonstrated that ZP pigment particles can in fact function as active "on demand" corrosion inhibitors in this coating that has been formed from a water-borne polymer dispersion. In this particular coating the ZP is able to leach out only from the hydrophilic acrylate-silane-ZP layer, creating a reservoir of saturated ZP in the surrounding salt solution. At the same time, the hydrophobic epoxy layer protects the acrylate containing layer and thereby the rest of the coated metal.

Pigments for "Smart" Anti-Corrosion Coatings

Under certain conditions, the driving force of corrosion produces protective oxide films, a process typically referred to as metal passivity. In cases where passivity is difficult to achieve, for example, as with aluminum alloys in neutral sodium chloride solutions, it is conceivable that a "smart" coating can be micro- or nano-engineered to use the energy of the corrosion process to on demand generate a corrosion inhibitor for stopping or slowing corrosion at defects. Work at Rockwell Scientific Company provides evidence

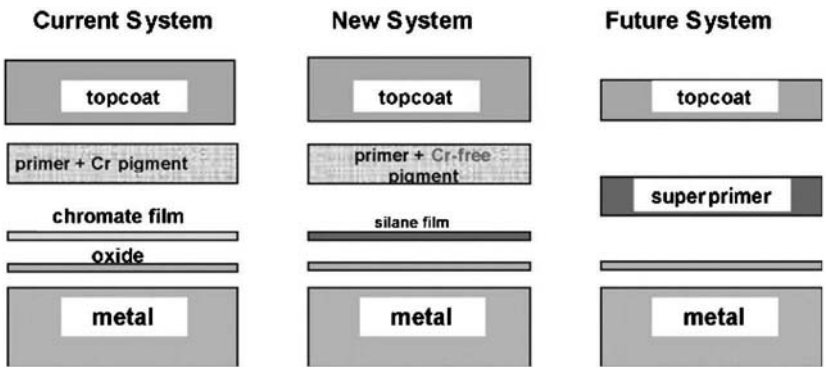

Fig. 8—Schematic of the superprimer coating system [42].

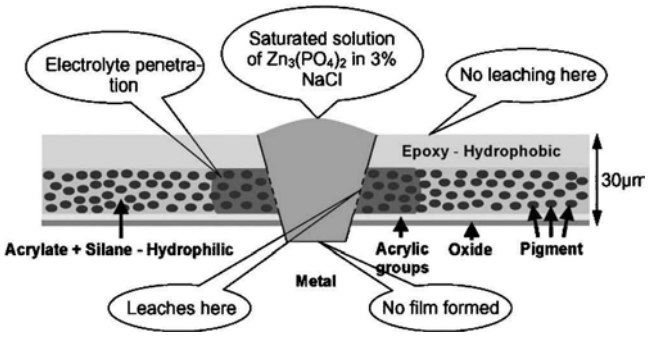

Fig. 9—Principle of the corrosion-inhibiting mechanism of the acrylate-epoxy-silane superprimer containing the ZP pigments, which protect the metal on-demand [42].

that anionic inhibitors for the oxygen reduction (cathodic) reaction, when used as dopants for conducting PANI films, inhibit corrosion of an aluminum (Al 2024-T3) substrate at a scribe [43]. In effect, the scribe polarizes the PANI, causing it to release the inhibitor.

PANI ranks high among electrically conducting polymers. Its high conductivity and chemical variability makes it suitable for a number of applications. In the course of polymerization, PANI has the ability to create thin conducting films with very good adhesion to various base materials [44]. To prove the retention of its inhibiting properties in a paint film, it was found advisable to apply this polymer in organic binders, where it would function as an organic corrosion inhibitor or an anti-corrosion pigment. Therefore, the main objective of a reported study was evaluation of the properties of organic coatings containing PANI and PANI in combination with other anti-corrosive pigments [45]. The adhesion, barrier, and anti-corrosion properties of the coatings containing PANI and selected chemically active pigments were studied as well as the combination of PANI with zinc dust. Epoxides of the bisphenol A type cured with a polyamine-based curing agent were used as a binder. To examine the synergic effect of PANI and anti-corrosion pigment in epoxy coatings, $Zn_3(PO_4)_2{\cdot}2H_2O$ with an acidic aqueous extract, $Ca_3(BO_3)_2$ with a basic aqueous extract, and $SrCrO_4$ with a neutral aqueous extract were tested. Comparison of the results of the corrosion tests revealed that the PANI plus $Zn_3(PO_4)_2{\cdot}2H_2O$ combination increased the anti-corrosion efficiency of organic coatings. Both these pigments utilize the acidic *p*H of the aqueous extract, and this may lead to very high anti-corrosion efficiency. The investigation of the total anti-corrosion efficiency of coatings with the PANI plus Zn-dust combination found that the PANI combination with a PVC of 5 % and Zn-dust [PVC/critical PVC (CPVC) = 0.65] achieves high anti-corrosion efficiency.

A new pigment for smart anticorrosive coatings, based on modified zeolite, has been proposed as a pigment for paints [46]. Alkyd paints were formulated by employing different anti-corrosion pigments: (1) 30 % by volume (v/v) of the modified zeolitic rock, (2) 10 % (v/v) of ZP, and (3) a mixture of 10 % (v/v) ZP plus 20 % (v/v) of the modified zeolitic rock. In every case, percentages were referred to the total pigment content. Titanium dioxide, zinc oxide, and barium sulfate were incorporated to complete the pigment formula. The PVC/CPVC ratio was 0.8. The performance of the resulting anticorrosive paints was assessed by accelerated tests in salt spray and humidity chambers and by electrochemical measurements of corrosion potential, ionic resistance, and polarization resistance. It was demonstrated that the modified zeolite is effective in protecting steel from corrosion when it is used in combination with ZP. There exists a synergism between the modified zeolite and ZP that allows the ZP content in anticorrosive paints to be reduced.

A group of mixed oxides with the structure of spinel and perovskite Zn–Al, Zn–Fe, and Ca–Ti inorganic pigments in combination with a conducting PANI phosphate layer were selected for the surface modification [30]. In many applications of paints, it is convenient to formulate a composite made up of inorganic particles (a pigment) with a suitable chemical composition that is coated with a functional layer of a conductive polymer. PANI has redox properties that can be used in protection against corrosion. When inorganic particles are suspended in the reaction medium used for the oxidation of aniline, they become coated with a thin (100 nm) layer of PANI. Such PANI modified particles have been tested in an attempt to find the potential synergetic effect and/or improvement of anti-corrosion properties. The study reports the anti-corrosion effects of various PANI-modified pigment particles in paints. Included in the study was another interesting group of functional pigments represented by iron oxides and silicates with various structures and diverse particle shapes. The last type of pigments included in the study was graphite of both natural and synthetic origin. Uncoated pigments and PANI powder have also been tested for comparison. Considering all the groups of pigments, the pigments coated with a PANI layer displayed the smallest corrosion loss. It is obvious that the extract of the pigments containing PANI contributes, with its optimum conductivity, to the passivation of the metal base. When testing paint films that contained mixed metal oxides, the pigments alone—that is, those without PANI coating—displayed improved corrosion resistance. The films based on iron oxides and silicate pigments exhibit similar results with regard to both PANI-coated pigments and pigments without coating. The excellent results of anti-corrosion efficiency were detected in the paint films that contained graphite-based pigments. The PANI coating of the synthetic graphite and especially of the natural form of graphite contributed to the marked enhancement of the total anti-corrosion efficiency of the paint film.

Needle-Shaped Anti-Corrosion Pigments

Use of synthesized, needle-shaped pigments in anti-corrosion paints for protecting metals is a new concept. The benefit of their use and method of synthesizing is that they do not contain heavy metals and are acceptable for the environment. The following pigments have been synthesized from oxides or carbonates at high temperatures: $ZnFe_2O_4$, $MgFe_2O_4$, $CaFe_2O_4$, $MgO{\cdot}2ZnO{\cdot}8Fe_2O_4$, and $CaO{\cdot}2ZnO{\cdot}8Fe_2O_4$ [47]. They were used to formulate epoxy coatings with a PVC of 10 % for the synthesized pigment and with the PVC/CPVC ratio of 0.3. The coatings were tested for physical-mechanical properties and in corrosion atmospheres. The test results revealed that all pigments had high anti-corrosion efficiency comparable with that of Zn–Al phospho-molybdate.

Spinel-Type[21] Pigments

Spinel pigments are oxides derived from the crystalline structure of the natural mineral "spinel," $MgAl_2O_4$. With these XY_2O_4-type oxides, the ionic charges can be balanced with three combinations of oxidation states: $X^{2+}B_2^{3+}$ (type I), $X^{4+}B_2^{2+}O_4$ (type II), and $X^{6+}B_2^{1+}O_4$ (type III). The structure of these oxides is determined by the grouping of voluminous oxygen-containing anions in a face-centered-cubic arrangement. Free cavities for the placement of cations are of two types: octahedric (coordination number 6) and tetrahedric (coordination number 4). In perovskite, the large ions, Ca^{2+} and O^{2-} and the smaller cation of Ti^{4+} located in one of the void spaces create a closely packed structure. Lamellar spinel-type pigments have been characterized as especially appropriate for high barrier efficiency coatings because they increase the diffusion path for water and oxygen. In addition, it has been shown that in addition to pigment particle shapes, their chemical compositions also plays a role.

Spinel pigments containing Zn(II), Ca(II), Mg(II), Sr(II), Fe(III), Al(III), and Ti(IV) cations have been synthesized as potential candidates for replacing toxic anti-corrosive pigments with pigments acceptable from the point of view of environmental protection [48]. Combining the cations in various oxide groups, the pigments were applied to alkyd, styrene-acrylate, epoxides, and chlorinated rubber binders. The binder containing acid groups gave aqueous extracts with better inhibitive properties than the non-reactive binders. The chemical composition of the synthesized pigments clearly shows that the compounds are ecologically harmless.

The spinel-type oxides are useful in heat-resistant organic coatings, and they are designed for applications where temperatures in a range of 200–500°C are encountered [49]. Several inorganic pigments (salts) are produced by Kremer Pigments Inc., as praseodym yellow $(Zr,Pr)SiO_4$, zirconium cerulean blue $(Zr,V)SO_4$, spinel black $(Fe,Mn)(Fe,Mn)_2O_4$, zinc-iron brown dark (metal oxide/hydroxide and 5 %–7 % of TiO_2), all of them are not classified as hazardous pigments. They are suitable for paints based on oil, acrylics, tempera, watercolor/gouache, lime/silicate binder, etc.

Metal Flake Pigments

Metal flake coating compositions are well known in the coating industry. In particular, metal flake coating compositions are widely used in automotive coatings to produce unique aesthetic effects and to provide anti-corrosion protection of metal substrates. Aluminum pigment, typically as an aluminum flake, is used in metallic decorative topcoats whereas *zinc* pigment-flake is used as anti-corrosive pigment—especially in primers. Both metal powder pigment flakes play the role of self-sacrifice anodes for rust prevention and corrosion inhibition, due to the more negative electrode potential relative to that of iron (steel). The flake-pigment is often used in the form of a pigment paste. The paste is processed and dispersed in a polymeric vehicle along with a conventional pigment to produce automotive paint coatings that have various appearance effects, such as silver metallic, gold metallic, blue metallic, and various other colored metallics.

Both aluminum and zinc pigments react in aqueous alkaline media (e.g., water-borne paints) with the evolution of hydrogen—a process known as "gassing" [50]

$$2Al + 6H_2O \Rightarrow 2Al(OH)_3 + 3H_2\uparrow$$

$$Zn + 2H_2O \Rightarrow Zn(OH)_2 + H_2\uparrow$$

The *p*H values of water-borne paints are about 8–9 and a severe problem exists with water-borne paint systems using aluminum or zinc pigments. This problem involves the hydrogen corrosion of these metals in aqueous alkaline paint media. The evolution of hydrogen during these corrosion reactions can lead to dangerous pressure buildups in containers. Therefore, inhibition against these corrosion reactions is necessary. Aluminum pigments can be stabilized with organic phosphorus compounds, but these have some disadvantages. Furthermore, aluminum and zinc pigments can be stabilized in water-borne paints by chromate (VI), which is, however, toxic. So, the investigation of alternative and especially non-toxic methods for the inhibition against these corrosion reactions has been necessary. Moreover, there is generally a great demand for environmentally friendly corrosion inhibitors (so called "green inhibitors").

It has been reported that the hydrogen corrosion of aluminum pigments can be inhibited by addition of the reducing saccharides fructose and mannose as well as with addition of the reducing ascorbic acid. Sucrose, a non-reducing sugar, did not inhibit this corrosion reaction [50]. With increasing additions of fructose or ascorbic acid, the hydrogen volumes evolved increased. This observation leads to the assumption that reaction products of aluminum and fructose or ascorbic are the actual corrosion inhibitors. The hydrogen corrosion of zinc pigment is inhibited only by ascorbic acid. So, the most efficient natural corrosion inhibitors for aluminum and zinc pigment is ascorbic acid. But corrosion inhibition of ascorbic acid on zinc pigment is much less effective when compared to aluminum.

It has also been reported that hydrogen evolution from aluminum and zinc pigments in aqueous media at a *p*H of 10 can be inhibited by several epoxy-ester polymers, which are suitable binders for anti-corrosive paints prepared with zinc pigments [51]. One particular epoxy-ester polymer was an excellent corrosion inhibitor both for aluminum and zinc pigments. These results indicate that the stabilization mechanisms of epoxy-ester polymers are similar with respect to the two different metal pigments. An increase of epoxy-ester addition results in decreasing hydrogen evolution, i.e., an increase of corrosion inhibition. Added paint binders such as saturated polyester or melamine do not significantly affect corrosion inhibition of aluminum and zinc pigments by the epoxy-ester. These results show that corrosion inhibition of aluminum and zinc pigments by epoxyesters works also in multi-component systems. The mobility of polymers dissolved in a liquid medium seems to be one general requirement for corrosion inhibition.

[21] Spinels are any of a class of minerals of general formula XY_2O_4 that crystallize in the cubic (isometric) crystal system, with the oxide anions arranged in a cubic close-packed lattice and the cations *X* and *Y* occupying some or all of the octahedral and tetrahedral sites in the lattice. *X* and *Y* can be divalent, trivalent, or quadrivalent cations, including magnesium, zinc, iron, manganese, aluminium, chromium, titanium, and silicon. Although the anion is normally oxide, structures are also known for the rest of the chalcogenides.

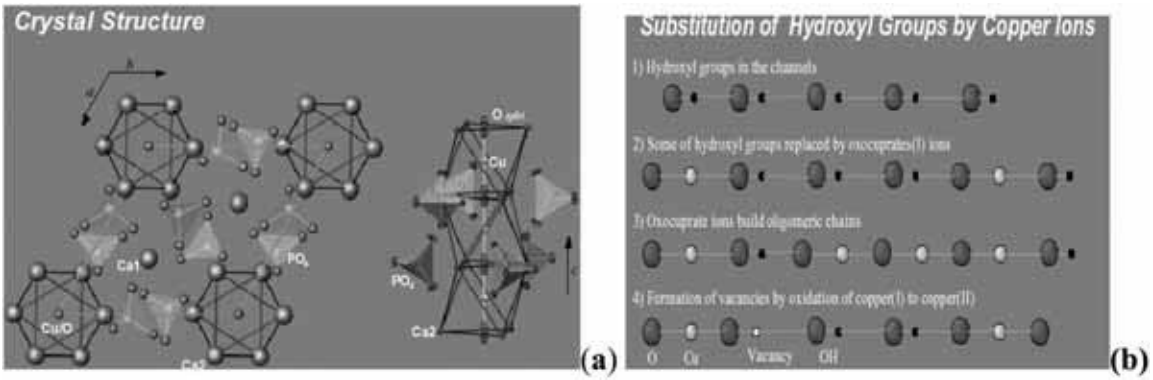

Fig. 10—Ceramic pigments: (*a*) Crystal structure; (*b*) substitution of hydroxyl groups by copper ions [54].

According to industrial company statistics, automotive color fashion dictates that in Europe 62 % and in North America 87 % of automotive paints be metallic in nature [52]. These values include metallic/pearl pigment combinations. The most important, high-demand aluminum flake products were those with a high resistance to gassing in water-based paints. As a consequence, the next step in the development of automotive paints with anti-corrosion behavior was development of encapsulated pigment technology. This technology involved production of encapsulated hydro-aluminum flakes as pigments that gave markedly improved protection properties. There were two types: chromium encapsulated with insoluble chromium III and acrylic encapsulated with a thermosetting acrylic polymer.

New, heavy metal free stabilization technology that guarantees gassing stability and optical properties comparable to chromate-passivated pigment types has been reported [53]. Silica encapsulation of aluminum flakes by means of a new sol/gel process provides aluminium pigments with long-term stability in water-based coatings. Excellent weather fastness and the best adhesion of the pigmented coating have been observed when examined after corrosion test exposure. In addition, no degradation under high shear stress could be observed.

Ceramic Pigments

Ceramic pigments are widely used and incorporated as fine particles in paints to impart color. Although many chemical compounds are effectively applied as pigments, there is still a need to find new compounds and mixtures that have bright colors and are relatively inexpensive, stable towards heat and light, non-toxic, and environmentally friendly. New types of ceramic pigments based on apatites[22] and containing linear copper (I, II) oxyanions in hexagonal channels through partial substitution of hydroxyl groups [Fig. 10(*a*) and Fig. 10(*b*)] have been reported [54]. In spite of the fact that only a small share of copper is in the divalent state, the compounds are brilliantly colored.

[22] Apatites: The most abundant and widespread of the phosphate minerals, formed in igneous/metamorphic rocks, crystallizing in hexagonal system. The apatite structure type includes no less than ten mineral species and has the general formula $X_5(YO_4)_3Z$, where X is usually Ca^{2+} or Pb^{2+}, Y is P^{5+} or As^{5+}, and Z is F–, Cl^-, or $(OH)^-$; for example, calcium phosphate $Ca_5(PO_4)_3$(F, OH, Cl).

TWO MECHANISMS FOR ANTI-CORROSION PROTECTION OF METAL

There are two mechanisms that are used to describe mechanisms for anti-corrosion behavior of different pigments/inhibitors used for metal substrate protection. These are *cathodic protection,* which involves the shifting of a metal potential to more negative values, and *metal passivation,* which involves the shifting of a metal potential to more positive values. Penetration of an aggressive electrolyte through the paint coating is accomplished through water or humidity absorption transport through the existing pores in the paint film or by the diffusion of oxygen and dissolved ions (contaminants) toward the paint/metal interface. These two processes determine the anti-corrosive paint efficiency. After the permeation of water, oxygen, and aggressive ions, a variety of corrosion reactions can occur at the metal/paint interface.

It is thought that the mechanism of coating detachment is cathodic in nature. It begins by casual formation of anodic and cathodic sites in the exposed area—a process that is necessary for initiation of the corrosion process. In an ordinary paint film, that is a film that does not have sacrificial anodes, the solid corrosion products that formed block the pores and other coating defects. In this way, the entrance of new oxygen for the iron oxidation to Fe^{2+} is limited. As a consequence, it is said that the entire coating is semi-permeable to oxygen and that the corrosion process is localized on the edges of pore defects. Because of this, the cathodic reaction that occurs on the edges of defects aids local *p*H increases from *p*H 10 to 14. The anodic reaction of metal dissolution, which occurs in the center of the coating defect, produces a local acid medium of *p*H 2 to 4. This process is depicted in Fig. 11. With these conditions existing, the high alkaline *p*H at the edges of defects diminishes the adhesion forces of the coating and causes the blister formation. Simultaneously, the lower acid *p*H in the center of the defects increases the rate of the anodic corrosion reaction.

THE CONCEPT OF PAINT MONITORING

Coatings, in a general sense, are used to increase the life or beautify of functional or decorative objects. In certain instances, both goals are important. Quite often labor costs are one of the most expensive considerations in applying and maintaining a coating. Therefore one desires and expects a long lifetime of protection and/or beauty from any applied coating. Today, prediction of the anti-corrosive

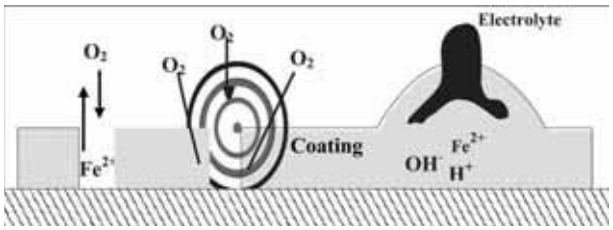

Fig. 11—Schematic representation of the three states for cathodic detachment of paint coating. The left part represents the first stage, when anodic and cathodic sites are separated in the exposed area; in the center—blocked defect, consequently transporting oxygen (O_2); and in the right—final situation.

properties of primers is one of the important lines of research in the field of organic coatings. Goals include improved protection and increased service lifetime for the coated substrates. The corrosion and degradation processes in organic/metal systems is complex. The main experimental routes used to examine different exposure processes are field testing and accelerated aging testing as in a salt fog spray cabinet. Such testing routines must be given serious planning because they are expensive to conduct. Salt spray (fog) is an accelerated test carried out with an aqueous 5 wt % sodium chloride solution, and it is one of the most widely used evaluation techniques. The practice is described in ASTM B117, Standard Practice for Operating Salt Spray (Fog) Apparatus, which provides a controlled corrosive environment for obtaining corrosion resistance of coated metals. Even though a useful tool, this practice is very subjective and does not give quantitative information about the corrosion process and its interpretation.

For this reason, various electrochemical techniques have been used to evaluate the corrosion protection performance of organic coating/metal systems: (a) anodic and cathodic polarization curves, (b) EIS, and (c) rapid testing that consists of a combination of cathodic polarization and EIS measurements (ac/dc/ac procedure). EIS has proven to be a useful technique for the study of anti-corrosive primer behavior, but to obtain good, meaningful results, long evaluation times of days, weeks, and even months are needed

The concept of inspection/monitoring is gaining importance for cost and environmental reasons. In addition to the traditional approaches of basic visual assessment and adhesion testing, new techniques for monitoring paint degradation and the resulting corrosion are emerging—these include the following:

- Thin film electrochemical sensors embedded under paint films.
- Electrochemical sensors applied to the outer surface of paint films.
- Microwave techniques.
- Thermography.
- Color and fluorescence changes (smart coatings).
- Fiber optic sensing.
- Chemical sensors for detecting surface contamination at the surface preparation stage.

SMART COATINGS

The use of "smart materials" for corrosion sensing purposes relies on a material undergoing a transformation through its interaction with a corrosive environment. It is such transformations that can potentially be used for indicating and detecting corrosion damage. Ideally the sensing function could be integrated with additional actuation and control functions designed to control corrosion damage.

Several initiatives have been launched on the front of using smart coatings as corrosion sensors, but presently the technologies reside mainly in the experimental laboratory domain. As such, they are "futuristic" in nature. Some smart coating principles including those relevant to corrosion sensing or that are potentially relevant include the following:

- Paint systems with color-changing compounds that respond to *p*H changes that result from the corrosion processes.
- Changes of coating compounds from non-fluorescent to fluorescent states when oxidation or complexation with metal cations takes place.
- Release of color dyes from incorporated dye-filled microcapsules when coating damage occurs.
- Use of pigments that absorb corrosive chemicals,
- Use of pigments that release corrosion-inhibiting chemicals on demand.
- Piezo-electric thin film applications.
- Fiber optics.

ENVIRONMENTALLY FRIENDLY PAINTS AND PIGMENTS-INHIBITORS

Due to the restriction limits on the use of toxic pigments (for example, those based on lead and heavy metals) because of health and environmental considerations, paint producers are searching for a new generation of pigments/inhibitors that are more acceptable. Numerous investigations have been performed in an attempt to evaluate promising candidate replacement inhibitors. The need for substitution of toxic pigments can be made on different levels—humanistic, economic, or ecologic. The corrosion inhibition characteristics of many inorganic compounds have been examined for more than five decades with the hope of identifying an equivalent to the excellent corrosion inhibition of chromate pigments inhibitors.

As companies search for a system with equivalent or better properties than the chromates, it is necessary to consider raw material costs. New pigments are usually more expensive than classical pigments. Although such cost difficulties may exist, the use of organic coatings remains as one of the most economical methods of obtaining corrosion protection. This is related to the relatively low application costs in comparison to protection methods such as galvanizing, enamel coating, or the use of finer materials. The true advantage of the use of paints lies in their all-purpose and easy application onto the surface of various materials.

For perhaps the past 20 years, a considerable effort has been focused on developing non-chromate corrosion-inhibiting compounds for protection of aluminum alloys. A number of chromate alternatives have been considered, including molybdates, phosphates, metaborates, zinc oxide (ZnO), vanadates, and silicates [55]. The patent literature suggests the use of sol-gel technology for generating an endless variety of non-chromate pigments. In addition to borate salts, organic acid salts of barium have been considered as corrosion inhibitors. Although barium-metaborate as it exists at *pH* 10 provides very good inhibition of Aluminum

2024, its ability to inhibit decreases with decreasing *p*H and thus decreases as corrosion takes place.

To date, no single compound has demonstrated corrosion/inhibitor potency that is comparable to chromate-based inhibitors. A promising alternative is use of a synergistic combination of two or more compounds, organic and inorganic, as a coating system. The inhibitor synergy is an additive phenomenon wherein the total inhibition provided by the combination exceeds the arithmetic sum of the individual components. However, because of the known release of inorganic pigments from organic matrices [56], and the unpredictable release kinetics of organic additives from organic matrices, the investigations have emphasized use of inorganic compounds for the replacement of chromates. Compared to chromated pigments or zinc dust, modern, environmentally friendly pigments in epoxy-ester primers have shown excellent results, especially in salt spray tests. These systems include zinc phospho-molybdate, ZP modified with organic corrosion inhibitor, calcium hydrogen phosphate, zinc-aluminum polyphosphate, etc. [21]. Reported results of the properties of a wide variety of industrially employed fillers and pigments contained in paints reveal that the formulation of steel protecting coatings can be optimized. For example, this can be accomplished by selecting the optimum filler for an epoxy coating with barrier anticorrosive properties, thickness of coatings, etc. [57].

The inorganic species considered as replacements of chromate can be divided into the following categories [10].

(a) Reducible hypervalent transition metals (compounds of Mo, V, Mn, Tc). The term "hypervalent" as used here refers to the "highest" valence state of the oxoanion, which is typically not thermodynamically stable in aqueous media. Metals, such as Mn, Tc, Mo, and V, that form oxometallates have soluble hypervalent oxoanions that reduce to form insoluble oxides in the same way as chromium. However, Mn, Cr, and Tc compounds exhibit very broad ranges in *p*H around neutral where their reduced oxides are stables, while V and Mo, exhibit relatively narrow ranges in *p*H. On the other hand, vanadium oxide is relatively more stable toward high *p*H and the Mo oxide is more stable toward lower *p*H values. However, as oxides, the elements of Mo and V will never give the same stability as seen in analogous Cr^{3+} oxide. But, they should not be completely ruled out as chromate replacements.

(b) Difficult-to-reduce transition metal oxides (Zr, Hf, Ta, Ti, Y) and covalent oxides (oxides and mixed oxides of Si, Ge, P, Te). Elements such as Nb, Hf, Ti, Zr, and Ta form very stable oxides in their highest oxidation state. Unfortunately, soluble and mobile precursors of these oxides remain difficult to stabilize in aqueous media. It is difficult to imagine how such active precursors could be retained in the resulting films in a manner analogous to the retention of Cr^{6+} in Cr conversion coatings. Both the former group (a) and this group (b) can be carried out using sol-gel methods.

(c) Precipitated coatings. These coatings include boehmite [γ-AlO(OH)] and HT [$Mg_6Al_2(CO_3)(OH)_{16}{\cdot}4(H_2O)$] coatings, and rare-earth metal coatings. The mechanism for the rare-earth inhibition seems to arise from the alkaline precipitation of protective oxide films at active cathodic sites formed on the metal surface. Cerium (Ce) species appear to offer the most effective corrosion inhibition: Ce^{3+} reversibly adsorbs on anodized aluminum, but it acts at much different sites than the Cr^{6+} oxoanions.

In a broad examination of the literature in which the substrate material is not specified, compounds identified as having promising performance include barium metaborate, vanadium-based compounds, rare-earth compounds, molybdates, zinc-based compounds, calcium silicate, thioglycolates, calcium oxide, phosphate salts, calcium silicofluoride, and benzotriazole among others. Additional studies have been made studying synergistic effects achieved by combining promising candidate inhibitors. The corrosion-inhibition efficiency of 27 candidate compounds has been studied and the inhibitors selected for continued testing were: barium metaborate, cerium chloride, cerium oxalate, lanthanum chloride, and sodium metavanadate. Sodium meta-vanadate appeared to be a possible candidate as a chromate replacement [34]. Zinc-molybdenum phosphate could also be a good possibility as a replacement of heavy metal compounds. It is thought that its anticorrosive protection efficiency is similar or superior of that of ZC or ZP.

While all coatings are important in that they protect a wide variety of objects from the harshness of various environments, they also provide us with aesthetic beauty. Studies such as many of those described in this chapter and that are ongoing in many laboratories strongly suggest that new solutions to environmentally and health-acceptable anticorrosion pigments and inhibitors will be found.

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ASTM documents related to anti-corrosion pigments and their use in coatings

D16	Standard Terminology for Paint, Related Coatings, Materials, and Applications.
D34	Standard Guide for Chemical Analysis of White Pigments.
D49	Standard Test Methods of Chemical Analysis of Red Lead.
D50	Standard Test Methods for Chemical Analysis of Yellow, Orange, Red, and Brown Pigments Containing Iron and Manganese.
D81	Standard Specification for Basic Carbonate White Lead Pigment.
D126	Standard Test Method for Analysis of Yellow, Orange and Green Pigments Containing Lead Chromate and Chromium Oxide Green.
D480	Standard Test Methods for Sampling and Testing of Flaked Aluminum Powders and Pastes.
D610	Standard Practices for Evaluating Degree of Rusting on Painted Steel Surfaces.
D660	Standard Test Method for Evaluating Degree of Checking of Exterior Paints.
D661	Standard Test Method for Evaluating Degree of Cracking of Exterior Paints.
D662	Standard Test Method for Evaluating Degree of Erosion of Exterior Paints.
D714	Standard Test Method for Evaluating Degree of Blistering of Paints.
D772	Standard Test Method for Evaluating Degree of Flaking (Scaling) of Exterior Paints.
D822	Standard Practice for Filtered Open-Flame Carbon-Arc Exposures of Paint and Related Coatings.
D870	Standard Practice for Testing Water Resistance of Coatings Using Water Immersion.
D913	Standard Test Method for Evaluating Degree of Resistance to Wear of Traffic Paint.
D964	Standard Specification for Metallic Copper Powder for Use in Antifouling Paints.
D1014	Standard Practice for Conducting Exterior Exposure Tests of Paints and Coatings on Metal Substrates.
D1301	Standard Test Methods for Chemical Analysis of White Lead Pigments.
D1641	Standard Practice for Conducting Outdoor Exposure Tests of Varnishes.
D1648	Standard Specification for Basic Lead Silicochromate Pigment.
D1654	Standard Test Method for Evaluation of Painted or Coated Specimens Subjected to Corrosive Environments.
D1735	Standard Practice for Testing Water Resistance of Coatings Using Water Fog Apparatus.
D1844	Standard Test Methods for Chemical Analysis of Basic Lead Silicochromate.
D2092	Standard Guide for Preparation of Zinc-Coated (Galvanized) Steel Surfaces for Painting, Historical Standard.
D2200	Standard Practice for Use of Pictorial Surface Preparation Standards and Guides for Painting Steel Surfaces.
D2247	Standard Practice for Testing Water Resistance of Coatings in 100 % Relative Humidity.
D2486	Standard Test Methods for Scrub Resistance of Wall Paints.
D2803	Standard Guide for Testing Filiform Corrosion Resistance of Organic Coatings on Metal.
D3003	Standard Test Method for Pressure Mottling and Blocking Resistance of Organic Coatings on Metal Substrates.
D3258	Standard Test Method for Porosity of White or Near White Paint Films by Staining.
D3260	Standard Test Method for Acid and Mortar Resistance of Factory-Applied Clear Coatings on Extruded Aluminum Products.
D3276	Standard Guide for Painting Inspectors (Metal Substrates).
D3322	Standard Practice for Testing Primers and Primer Surfaces Over Preformed Meta.
D3359	Standard Test Methods for Measuring Adhesion by Tape Test.
D3623	Standard Test Method for Testing Antifouling Panels in Shallow Submergence.
D3723	Standard Test Method for Pigment Content of Water-Emulsion Paints by Low-Temperature Ashing.
D3843	Standard Practice for Quality Assurance for Protective Coatings Applied to Nuclear Facilities.
D3891	Standard Practice for Preparation of Glass Panels for Testing Paint, Varnish, Lacquer, and Related Products.
D4141	Standard Practice for Conducting Black Box and Solar Concentrating Exposures of Coatings.
D4146	Standard Test Method for Formability of Zinc-Rich Primer/Chromate Complex Coatings on Steel.
D4213	Standard Test Method for Scrub Resistance of Paints by Abrasion Weight Loss.

D4214	Standard Test Methods for Evaluating the Degree of Chalking of Exterior Paint Films.
D4228	Standard Practice for Qualification of Coating Applicators for Application of Coatings to Steel Surfaces.
D4288	Standard Specification for Calcium Borosilicate Pigments
D4417	Standard Test Methods for Field Measurement of Surface Profile of Blast Cleaned Steel.
D4487	Standard Test Methods for Analysis of Calcium Borosilicate
D4541	Standard Test Method for Pull-Off Strength of Coatings Using Portable Adhesion Testers.
D4585	Standard Practice for Testing Water Resistance of Coatings Using Controlled Condensation.
D4587	Standard Practice for Fluorescent UV-Condensation Exposures of Paint and Related Coatings.
D4752	Standard Test Method for Measuring MEK Resistance of Ethyl Silicate (Inorganic) Zinc-Rich Primers by Solvent Rub.
D4797	Standard Test Methods for Chemical and Gravimetric Analysis of White and Yellow Thermoplastic Traffic Marking Containing Lead Chromate and Titanium Dioxide.
D4828	Standard Test Methods for Practical Washability of Organic Coatings.
D4938	Standard Test Method for Erosion Testing of Antifouling Paints Using High Velocity Water.
D4939	Standard Test Method for Subjecting Marine Antifouling Coating to Biofouling and Fluid Shear Forces in Natural Seawater.
D5043	Standard Practice for Field Identification of Coatings.
D5178	Standard Test Method for Mar Resistance of Organic Coatings.
D5894	Standard Practice for Cyclic Salt Fog/UV Exposure of Painted Metal (Alternating Exposures in a Fog/ Dry Cabinet and a UV/Condensation Cabinet).
D6280	Specification for Zinc Phosphate Pigments.
D6442	Standard Test Method for Determination of Copper Release Rate From Antifouling Coatings in Substitute Ocean Water.
D6577	Standard Guide for Testing Industrial Protective Coatings.
D6695	Standard Practice for Xenon-Arc Exposures of Paint and Related Coatings.
D7087	Standard Test Method for An Imaging Technique to Measure Rust Creepage at Scribe on Coated Test Panels Subjected to Corrosive Environments.
F1428	Standard Specification for Aluminum Particle-Filled Basecoat/Organic or Inorganic Topcoat, Corrosion Protective Coatings for Fasteners.
SSPC-PS Guide 8.00	Guide to Topcoating Zinc Rich Primers.
G85	Standard Practice for Modified Salt Spray (Fog) Testing.
G90	Standard Practice for Performing Accelerated Outdoor Weathering of Nonmetallic Materials Using Concentrated Natural Sunlight.
G113	Standard Terminology Relating to Natural and Artificial Weathering Tests of Nonmetallic Materials.
B117	Standard Practice for Operating Salt Spray (Fog) Apparatus.

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Oil Absorption of Pigments[1]

Charles W. Glancy[2]

MIXING A PIGMENT WITH LINSEED OIL AND MAK-ing a paste is a preliminary test applied to pigments that has been in use in a systematic manner for almost a century and perhaps even longer in a less defined manner. This proved to be a practical means to qualitatively characterize the approximate color and texture of pigments quickly with materials and tools readily at hand. The work of mixing and the flow properties of the resulting paste provided an estimate of the rheological impact of a new pigment under consideration or a proposed pigment composition change. Thus, valuable insight of the dispersion performance of a pigment or formulation change in a mill base could be estimated. Further extension of the test was found to be useful in predicting the consistency of finished products. Mills [3] indicated that if equal volumes of "oil absorption paste" are mixed or thinned with equal volumes of thinners, the paints prepared have equal resistance to flow, viscosity, or consistency. While the application of oil absorption values as a formulation tool originated many years ago in the age of oil- and alkyd binder-based paints, the ability to use this information to calculate the binding power index of latex binders, latex porosity index of latex paints, and free binder continues to demonstrate the value of pigment oil absorption data today to solve coatings formulation problems. This is especially true for the field of interior and exterior architectural paints.

If the oil absorption test is conducted in a quantitative manner, the result is a measure of the oil needed to wet the surface area of the pigment and to fill the voids in and among the pigment particles. If this result is achieved, profoundly important information is obtained of high value to pigmented paint and coatings development. A number of relatively simple test procedures have been developed to measure oil absorption of pigments. The difficulty generally to successfully applying these tests has been in two areas. First, great care and effort is required to reach and interpret the oil absorption end point. Secondly, one must obtain particle separation in the test to the same degree as achieved with the formulation in the pigment dispersion manufacturing process to which oil absorption value is to be related.

Two ASTM pigment oil absorption test methods are available, which cover two incorporation methods. The different methods result in different end points and therefore different oil absorption values. Stieg [4] found that if the oil absorption value is determined by the ASTM D281 (Test Method for Oil Absorption of Pigments by Spatula Rub-Out) and expressed on a volume basis, it is proportional to the critical pigment volume concentration (CPVC) of alkyd wall paints. Later he and others demonstrated the extension of oil absorption values to calculate the CPVC of pigment compositions to predict the performance of latex paints and other calculated factors useful in formulating these coatings. Gardner–Coleman oil absorption, ASTM D1483 (Test Method for Oil Absorption of Pigments by Gardner–Coleman Method), values have been related to pigment paste viscosities and found useful in estimating consistencies by comparison to a reference standard pigment behavior in the same dispersion machinery. A number of non-ASTM methods for the determination of oil absorption values have been reported in the literature and a few will be listed below.

MECHANISM

When the oil absorption test is performed, the surface of each pigment particle is wet and saturated to a certain extent with oil and thus is encased in an oil shell that has been estimated to be as thick as eight molecules [4,5]. The amount of oil needed depends on the specific pigment area, which is a function of particle size, roughness, and porosity. With temperature and humidity constant, the oil adsorption value depends on the duration and vigor of the rubbing operation and on the affinity of the oil for the pigment. As oil is added beyond the particle encasement stage, the interstices between the oil-encased particles become filled with oil. The amount of oil required for this stage of the test is a function of the type of packing taken on by the particles [6]. Packing can range from rhombehedral to cubic. In addition, the presence of aggregates, which are clusters of pigment not broken up by the rubbing process, and agglomerates, which are clusters of pigment formed after the pigment has been wet, have an effect on the amount of oil needed. Agglomeration is affected by the nature of the oil, and linseed oil with an acid number of 3 ± 1 and that meets the specifications shown in Appendix A should be used. More extended discussions of oil absorption theory and practice can be found in the literature [7–11].

METHODS FOR DETERMINING OIL ABSORPTION

There are two ASTM methods for determining oil absorption that will be described briefly as well as related methods tabulated and referenced in Table 1.

Spatula Rub-Out Method

This is the classical method and the following directions summarize those of ASTM D281 [12], first published by ASTM in 1928 and updated from time to time with the

[1] *This chapter is an abridged and modified version of the chapters with the same title found in the previous editions of this manual [1,2].*
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TABLE 1—Various non-ASTM methods for determination of oil absorption values

Method	Comment	Ref.
Azam	Method same as ASTM D281 except end point is where paste just adheres to the spatula. See text.	[15]
Bessey-Lammiman	An indirect method. Pore volume of a compressed pigment wafer is determined. From this, an oil adsorption number is calculated.	[9]
British Standards Institution BS EN ISO 787-5:1995 and German Institute for Standardization DIN ISO 787-5	Method is similar to ASTM D281. A defined weight of pigment or extender is placed on a glass plate. Linseed oil is slowly added by burette to the sample and mixed in using a palette knife. The volume of oil required to form a smooth paste-like mass is noted and the oil absorption is expressed as milliliters or grams of oil required per 100 g of sample.	. . .
Density End Point	Assumes density of pigment and oil are additive. Can have void volume errors associated with it.	[16]
National Lead Company	Method is similar to ASTM D281 and Azam methods, but an attempt is made to regulate rubbing pressure and contact area of spatula and rubbing plate	[17]
Smith-Stead	Pigment is added to oil in this method and a mechanical muller is used to better define the rubbing effort.	[18]

latest reapproval in 2007. It is approved for use by agencies of the U.S. Department of Defense. In this test, linseed oil is added in a dropwise manner to the pigment while it is being thoroughly rubbed with a spatula until a stiff putty-like paste is formed. It differs from the Gardner-Coleman Method [13], which requires only gentle folding and stirring, whereas the rub-out test requires a thorough rubbing action of the pigment and oil with a steel spatula.

Raw linseed oil that meets the specifications in Appendix A but with an acid number of 3 ± 1 is slowly added in a dropwise manner to a known amount of pigment. The amount of pigment should be sufficient to require 1 mL or more of oil. After the addition of each drop of oil, the oil is incorporated into the pigment by working or rubbing the two together with the spatula. The end point is taken to be the point where sufficient oil has been incorporated into the pigment to produce a very stiff, putty-like paste that does not break up. The weight of oil is determined by multiplying the volume of oil by its density (0.93 g/mL). The oil absorption value is reported as the grams of oil used per 100 g of pigment. Various stages in the spatula rub-out test are described in Fig. 1.

The test requires extreme care to obtain acceptable precision. The method is very tedious yet requires close attention to avoid over-shooting the end point. Test results by a single operator are often considered satisfactory if within ±5 %, but comparisons between different operators is much more problematic. As reported in ASTM 281, results by a single operator and between different operators in different laboratories that differ by more than 14.3 % and 38.0 %, respectively, are suspect at the 95 % confidence level. Stieg has reported that lack of a clear understanding of the end point accounts for the differences reported between operators [14]. He reported almost perfect correlation between CPVC calculated from oil absorption values and experimentally determined CPVC values when the end point is determined by the very least amount of oil that will cause the pigment mass to cohere while not causing it to wet either the glass plate or the spatula. Then the method is repeated with a slightly smaller amount of oil to be sure that no lower oil value can be obtained. A comprehensive study [7] of oil absorption measurement by the British Standards Institution method found individual operator capable of accuracy of about ±3 %, but results between different operators were of the same order of magnitude as reported in ASTM 281.

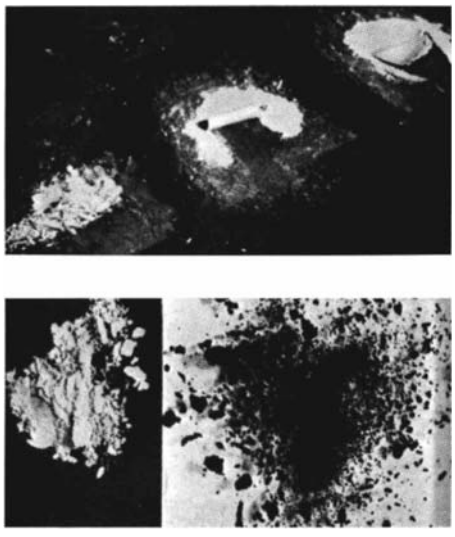

Fig. 1—[1]—A, B, and C in the top photograph represent 1 g of zinc oxide that has been mixed with increasing amounts of linseed oil. Rub-out A (top left) is crumbly and breaks up when an attempt is made to lift it with a spatula. Rub-out B (top middle) is coherent and tends to form a roll when deformed with the spatula. Rub-out C (top right) contains too much oil and does not roll. It can be lifted as a sheet and the mixture is beyond the end point. The bottom two photographs are additional examples of the mixture condition just before the end point is reached. A single drop of oil will convert the crumblings into coherent masses.

The wider range between operators was attributed to the difference in effort expended during the rubbing of the oil into the pigment rather than end point determination, and that the amount of effort that should be expended cannot be rigidly defined. Clearly, where comparisons are to be made between operators, extreme care must be exercised to ensure that the same mixing effort and end point determinations are made. Oil absorption values obtained by this test and the Gardner–Coleman test are given in Table 2.

AZAM METHOD

The Azam Method [15] is essentially the same test as ASTM D281 with the main difference being a more rigorously defined end point. The end point is defined as the point where the paste just adheres to the spatula and the paste was termed a "complete" paste. Azam found that a complete paste absorbed no more oil when immerse in oil, but an "incomplete" paste would absorb oil in an amount sufficient to make it a complete paste. The end point check was made by immersing the rub-out mass in a known amount of oil and then determining the change after two or three days.

Rowland-Stieg Simplification of ASTM D281

This modification [19] of the classical method reports oil absorption volumetrically in terms of milliliter of oil per milliliter of pigment. This simplified procedure eliminates several sources of error and is the logical procedure where the objective is to calculate the CPVC rather than to report the oil absorption value. The abbreviation OA_V was selected to identify the volumetric oil absorption determined by this procedure. The specified pigment sample size in grams equal to 1.25 mL is calculated by multiplying the pigment bulking value in pounds per gallon by the factor 0.15 (the exact value is 0.15006). This provides a sample size of about 5 g for the majority of architectural paint pigment compositions. The measured volume of oil from the titration multiplied by 0.80 (to express milliliter of oil per milliliter of pigment) is OA_V.

TABLE 2—Oil absorption values, grams of oil/100 g of pigment, of some common pigments [1]

Pigment	Gardner-Coleman Test	Spatula Rub-out Test
Barytes	13.5	. . .
Basic carbonate of white lead	18	13.0
Basic sulfate of white lead	30	12.8
Blanc fixe	30	15.0
China clay	51	30.0
Gypsum	33.5	. . .
Lithopone	33	21.5
Silica, crystalline	23	. . .
Silica, amorphous	32	29.0
Talc	60	. . .
Titanox	26	18.5
Whiting	32	17.5
Zinc oxide	52	19.5

Gardner–Coleman Method

This method or some variation of it has been in use for about three quarters of a century. The current method, ASTM D1483 by Gardner–Coleman Method [13], has been in use for over 45 years. In this test, a soft paste is formed from the pigment by drop-wise addition of raw linseed oil that meets the specification in Appendix A but with an acid number of 3 ± 1 from a burette to the gently stirred pigment. As the oil is slowly added, the mixture is continuously stirred and folded so the oil strikes dry pigment as long as any remains. The mixture is not vigorously rubbed as in the rub-out method. Eventually the mixture collects in small lumps that gradually coalesce. The rate of oil addition is reduced as the end point is reached. The amount of oil required to form a paste is used to calculate the oil absorption value. The end point for paste formation is taken to be the point when the lumps of wet pigment form a single ball or when an excess of oil smears the wall of a container (see Fig. 2). This will take place within one or two drops of oil. It is important that there is no rubbing or grinding when this test is carried out. Although the current test calls for use of a steel spatula with particular dimensions and a glass flask for the test, variations of these tools have been used [20,21].

Oil Absorption, *A,* is expressed as grams of oil per 100 g of pigment and is calculated as follows:

$$A = \left(\frac{(M \times 0.93)}{P} \right) \times 100 \quad (1)$$

where *M* is the mL of oil used, *P* is the amount of pigment used in grams, and 0.93 is a constant that represents the density of the linseed oil. Test results by a single operator and between operators in different laboratories that differ by more than 9.9 % and 15.3 %, respectively, are suspect. Oil absorption values obtained by this method and the rub-out method are given in Table 2.

Characterization of Dispersions at the Oil Absorption Point

Examination of the dispersions (pastes) formed between oil and pigment at the oil absorption point is a source of considerable information. Large differences exist in such

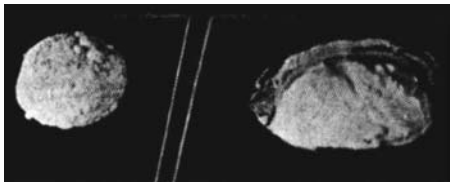

Fig. 2—[1]—Critical states in the Gardner-Coleman test. Left photograph is the oil/pigment mass just before the end point where the mass retains its rigidity. The right photograph is the mixture at the end point where the mass undergoes slight flow and smears the glass.

pastes with some being long, stringy, and soft in character. Others are tough and short, others have a high gloss, others have a dull appearance, others are soft and easy to spread, and still others are stiff and require a large pressure spread or flatten. The amount of oil needed is not closely related to these attributes, and one is led to the conclusion that pigments with essentially the same oil absorption value can yield pastes with markedly different character.

Daniel and Goldman [22] developed a scheme for evaluating dispersion character by using the paste obtained at the end of the spatula rub-out test. The amount of liquid needed to wet the pigment and produce flow is determined. From this information and the types of flow exhibited by the pastes, dispersions are classed as good, fair, or poor. From 10 to 20 g of dispersion is worked with a fairly stiff steel spatula in the test. The oil absorption value is called the *wet point*. From this point, oil addition is continued until the *flow point* is reached. In well-dispersed systems, the flow point is the stage where a substantial portion of the paste flows from a vertically held spatula without leaving jagged flow edges. In poorly dispersed or flocculated systems, the flow point is the stage where the paste drops from a vertically held spatula. Cases intermediate to these two are difficult to define. At the instant when paste drops from the spatula, it elongates at the edge. If a paste does not flow after addition of 10 %–20 % more liquid than is required for the wet point, a portion of the diluted paste is placed on the tip of a horizontally held spatula. The spatula is then tapped near the handle with a finger. The tapping is gentle at first and then more vigorous. The paste may then become glossy and flow over the edge of the spatula, in which case it is passively dilatent, or it may tend to rise or otherwise decrease the interface between it and the blade, in which case it is flocculated. Characteristics of pastes tested in this manner are given in Table 3. A test such as this can yield practical rheological results without sophisticated testing equipment.

Plasticizer Absorption By Pigments

Although linseed oil is used to obtain the oil absorption values, it is obvious that a variety of liquids can be absorbed by pigments. Typical data for selected plasticizers as well as raw linseed oil are given in Table 4.

CRITICAL PIGMENT VOLUME

For a long time, the paint industry formulated on a weight basis. In 1926 Calbeck [23] concluded from a statistical study of house-paint test results that the pigment/binder system should contain at least 28 vol % pigment. Not long after this, Wolff [24,25] related optimum performance of exterior paints to their critical oil contents, and simple graphical methods for determining this parameter were devised [26]. When Elm [27] investigated this concept, he confirmed Wolff's findings, but found it necessary to reverse the point of reference so it expressed the critical composition in terms of pigment content as in the work of Calbeck. Later Vannoy [28] studied the matter and concluded that replacement of certain pigments by others on a volume basis was the manner in which formulating should be approached. From such studies, the relationship known as the pigment volume concentration (PVC) came into use. It is a simple percentage calculated in the following manner:

$$\mathrm{PVC} = \left(\frac{\text{pigment volume}}{\text{pigment volume} + \text{vehicle solids volume}} \right) [100] \quad (2)$$

Studies such as these led to the CPVC concept, and its importance to paint formulation was established by Asbeck and Van Loo [29] in 1949. They illustrated the CPVC concept by relating marked changes in gloss, rust, blistering, and permeability over a relatively narrow (3–6) PVC range. Many other properties including dry hiding, scrub resistance, stain holdout, enamel holdout, and film tensile strength also transition over this range. The CPVC may be defined as the PVC where there is just sufficient binder present to fill the interstices between pigment particles at the densest possible packing and wet the pigment surface in the dry film. The packing characteristics of the pigments determine the void volume to be filled with binder. The surface characteristics of the pigments determine the amount of vehicle that is tightly bound to the surface. Usually the formulator's task for both economic and performance reasons is to define the highest CPVC possible for the raw materials and pigment dispersion processes available. The CPVC relationship is expressed in the following equation:

$$\mathrm{CPVC} = \frac{\text{volume of pigment}}{(\text{volume of pigment} + \text{volume of absorbed vehicle} + \text{volume of void space vehicle})} \quad (3)$$

TABLE 3—Characteristics of pastes from oil absorption studies [1]

Observation Point	Good Dispersion	Fair Dispersion	Poor Dispersion
At wet point	Shines without tapping or with light tapping; dry and difficult to knead	Shines when sharply tapped	Remains dull even when sharply tapped
At intermediate stage	. . .	Flows only on tapping; occasionally has a resistance to suddenly applied pressure	Rises on tapping; has no resistance to suddenly applied pressure; has a high yield value
At flow point	Flows without tapping; offers resistance to suddenly applied pressure	Falls with elongation at breaking line; no resistance to suddenly applied pressure; has visible thixotropy	Falls without elongation at breaking line
Gap between wet and flow points	Very small	. . .	Very large

TABLE 4—Plasticizer absorption for some typical pigments [1].

Pigment	Absorption, g Plasticizer/100 g Pigment		
	Tricresyl Phosphate	Dibutyl Phthalate	Raw Linseed Oil
Barium titanox	27.6	24.2	17.0
Carbon black, super	179.0	147.0	106.0
Calcium titanox	37.2	39.4	22.0
CP cadmium red	26.0	26.2	14.0
CP cadmium yellow	48.4	50.5	37.2
CP Chinese blue	145.0	136.5	41.1
CP chromium oxide	29.5	24.7	17.0
CP chrome orange, med.	19.5	21.0	7.5
CP glen green DD	78.0	72.5	28.9
Chromium hydroxide, green	80.0	76.6	53.0
Lampblack	118.0	126.0	145.0
Lithol toner	65.0	50.5	50.0
Lithopone, high strength	35.4	32.5	24.0
Madder Lake	106.0	81.0	51.4
Titanium dioxide	54.3	47.2	22.5
Toluidine red	31.9	20.0	35.0
Ultramarine blue	65.0	55.0	31.6
Zinc oxide	28.3	25.2	14.5
Zinc sulfide	37.2	34.1	15.7

The CPVC is also the point where the dry coating film transitions from a two-phase system of pigment and binder to a three-phase system with the introduction of air in the voids in the matrix. The discontinuity of the binder phase and presence of voids bring about air interfaces, surface pores, and changes in mechanical, barrier, and optical properties that cause the transition characteristics noted above.

The preference of the industrial coatings segments of the industry where coatings are often well below the CPVC continues to be formulation on the basis of the ratio by weight of pigment to binder (P/B). However, a better understanding of the relationship between changes in pigmentation and performance continues to be derived from formulating on a volume basis. This is especially the case in the architectural segment and other segments of the industry where products are formulated over a very wide PVC range but often above or below the CPVC. Usually this range is broadly defined as a PVC/CPVC ratio of 0.7 to 1.3. The importance of formulation by volume is largely due to the existence of the CPVC, which is largely determined by particle packing on a volume basis. Therefore, the real value of any apparent CPVC as determined by any precise method is as a guide to the relative performance of dissimilar paint systems. From this it follows the ratio of the PVC to CPVC, lambda, is also a valuable reference point in reformulation studies [30]. While the use of oil absorption measurements is very old technology, it is still used today to characterize pigments and to calculate CPVC to determine the PVC for a desired PVC/CPVC ratio in solvent and waterborne coatings [31–35].

CPVC calculated from the pigment linseed oil absorption is a good model for the case of a solution binder coating because of relatively similar viscosity and wetting characteristics. This is not the case with latex binders, which are unable to wet the pigment and flow into voids between the pigment particles to the same degree as linseed oil or solvent-borne binders. Latex paints invariably have lower experimentally observed coatings CPVC values because of physical limitations during the film drying process imposed by polymer particle size and size distribution, polymer modulus characteristics, and possibly inadequate coalescent solvent. However, as will be covered later in this chapter, linseed oil determined CPVC values are useful in formulation studies of latex coating.

Performance properties required of a coatings system determine whether the PVC is above or below the CPVC and to the degree of the difference. Rarely is a system formulated at the CPVC. For economic considerations, the pigmentation should be selected to favor efficient packing to maximize the CPVC and thereby introduce the possibility that less binder may be required above the CPVC for a desired PVC/CPVC ratio and perhaps less hiding pigment may be required in coatings below the CPVC because of superior hiding pigment spacing.

High dry-hiding power resulting from air interfaces in the voids above the CPVC typically is relied upon as a major contributor to hiding power in interior architectural paints requiring the PVC to be above the pigmentation CPVC. While dry hiding increases as the CPVC is exceeded by a greater margin, other desirable properties such as scrub resistance, stain resistance, and enamel holdout decline. For example, a ceiling paint does not need to have excellent scrub resistance, and usually this paint type requires only a very flat appearance, and high dry hiding. Therefore, paint such as this will usually be formulated with a PVC well above the CPVC. Interior flat paints require a balance of competing properties highly dependent upon the void volume ratio to the other two phases. Therefore, the CPVC of the pigment composition is a crucial consideration that the formulator must monitor as adjustments of the pigment composition and binder type and concentration decisions are made to optimize performance and cost. Commonly as the pigment composition and binder changes are made, the formulator will maintain lambda, the ratio PVC/CPVC, as a technique to maintain similar void volume while making composition changes. Exterior flat paints are formulated below the CPVC for adequate durability, but the excess binder must not be too large to avoid dirt pick-up. Therefore, the relationship of PVC to CPVC is an important consideration here as well. Semi-gloss and high-gloss enamels are formulated well below the CPVC, and it is PVC rather than CPVC that has the most significance. However, here proper hiding pigment spacing via small particle size extender often is an issue where the measurement of CPVC of the pigment blends based upon oil absorption measurements can be useful.

Identification of the optimum coatings composition providing the desired performance can be a laborious process involving PVC ladders and testing for many properties. Stieg [14] was the first to propose that pigment oil absorption values could eliminate some of the repetitious laboratory work in developing architectural paints by quickly focusing the work on the region most likely to provide the desired results. As will be detailed later, his approach was first successfully applied to solvent-borne paints and later extended to latex paints. First the oil absorption of proposed pigment blends at various ratios are determined and then the CPVC is calculated. Consequently several proposed pigment blends offering the highest possible CPVC can be identified that can be compared in paints in laboratory test at equal porosity index or free binder based upon calculating the required PVC for the various paints.

Useful Equations Based upon CPVC Calculated from Oil Absorption Data

The porosity index of solvent coatings, latex porosity index of latex coatings, and percent free binder may be calculated using oil absorption measurements of pigments or pigment blends. The recommended method for measuring oil absorption for these calculations is the spatula rub-out test ASTM D281. Stieg defined the end point for his work as the very least amount of oil that will cause the pigment mass to cohere, while not causing it to stick to glass or the spatula. Then the operator repeats the test with slightly less oil to verify that no smaller amount will satisfy this condition [14]. The careful determination of the oil absorption CPVC provides the formulator a ready means to assess the packing characteristics of pigments and pigment blends for use in these calculations or to test CPVC results provided by sophisticated computational means. Although not included below, several articles have been published on a simple computational method using individual pigment oil absorption data of extenders and hiding pigments and an experimentally determined packing correction factor applied to the small particle size fraction (hiding pigment) of the pigment composition to calculate the CPVC of a pigment composition [36,37]. Also a method to calculate CPVC based on pigment particle size distribution and oil absorption data has been proposed, but the necessary particle size data is not widely available [30].

Several assumptions or conditions are implied when Stieg's equations are applied to coatings reformulation work. First it is assumed that CPVC is independent of PVC over the range of the experiments. For practical purposes, this has proven true, probably because the PVC range usually is plus or minus 5 % or less limiting the impact of possible PVC effects. Secondly, although CPVC is a system dependent parameter, the oil absorption derived CPVC of the pigment composition is accepted as a measure of the packing characteristics and thus a pigment property useful for making these relative comparisons with both solvent and latex coatings. Also implied is that the pigment dispersion process and additives that prevent flocculation and maintain stability are equally effective in all cases. By definition the range of pigments to which these equations are useful is limited to inorganic hiding and extender pigments such as those commonly used in architectural paints. A more comprehensive review of the entire CPVC subject including the calculation of CPVC from pigment oil absorption values may be found in Ref. [38].

CALCULATION OF CPVC

Stieg found in 1954 that CPVC [39,40] of a pigment composition calculated from oil absorption values, converted to a volume basis rather than a weight basis, determined by the spatula rub-up method (ASTM 281), provided a useful working approximation of a pigment composition's CPVC. Further he demonstrated that the calculated CPVC of a solution-based paint can be related to the CPVC transition of enamel hold-out and color uniformity over sealed and unsealed surfaces. Also, Stieg showed that oil absorption based calculated CPVC of a number of common pigments is related to the bulk density of the dry pigment establishing a strong correlation between the calculated CPVC value and a basic pigment value depended on packing. The CPVC may be calculated from oil absorption measurements by the following equations:

$$\text{CPVC} = \frac{\text{test volume of pigment}}{(\text{test volume of pigment} + \text{end point test volume of oil})} \quad (4)$$

The equation for CPVC shown below is more convenient and uses the volumetric oil absorption (OA_V) method [19] described earlier. The equation is applicable to solvent systems (x = 1.0) and latex systems where the latex binding power index is known. The determination of the binding power index will be discussed in a following section.

$$\text{CPVC} = \frac{1}{1 + \text{OA}_V / x}$$

OA_V = volumetric oil absorption, mL oil/mL pigment

x = latex binding power index (1.0 for solution binder) (5)

The following CPVC equation was published by Ramig [41] and is useful to calculate the CPVC of any latex formulation from binding power index, density and oil absorption of the pigment composition.

$$\text{CPVC} = \frac{(\text{BI})(100)}{(\text{OA})\ \text{Dp} + (\text{BI})(100)}$$

OA = pigment oil absorption in grams/100 g of pigment

BI = binding power index

Dp = density of pigment (6)

CALCULATION OF FILM POROSITY INDEX

The porosity index is a numerical expression of film porosity and can be calculated from the oil absorption CPVC of a pigment composition [42]. The greatest value of the porosity index concept is as a means to guide the optimization of the dry hiding of interior flat paints, while minimizing to the extent possible the negative characteristics of porosity driven paint properties. The porosity index is the fraction of pigment air voids in a paint film *not* filled by the formulation PVC binder volume divided by the binder volume required by the pigmentation at CPVC. It is easily calculated for solution binder systems by the equation

$$\text{PI} = 1 - \frac{\text{CPVC}(1 - \text{PVC})}{\text{PVC}(1 - \text{CPVC})}$$

PI = porosity index

CPVC = pigmentation CPVC calculated from oil adsorption

PVC = formulation PVC (7)

This equation provides a way to balance or maintain constant porosity related properties such as permeability, stain or enamel hold-out, and dry hiding power when making pigment or extender changes. For example, the porosity index of an existing formulation can be calculated from the PVC and the oil absorption determined CPVC. If an extender pigment adjustment is made, the PVC change necessary to maintain equal porosity index can be readily calculated by using the oil absorption of the new pigment mix after rearranging the equation and solving for the PVC required. Frequently a new composition is tested in the laboratory at the same PVC/CPVC (lambda) ratio as the original with a 5 (or more) paint PVC ladder centered on this PVC. Evaluating performance at the lambda ratio of equal porosity index should more accurately provide a center point for further testing.

The equation for latex systems is the same as for solvent systems except that the binding power index, discussed in the next section, is included to take the film-forming capability of the latex into account. Stieg has published several articles that discuss useful graphical methodologies that may save considerable laboratory time when dealing with pigment or latex substitutions with a need to balance dry hiding and porosity-dependent performance properties [19,43]. Plotting the percent pigment, binder and air on a volume basis on triangular co-ordinate graph paper is a convenient means to obtain the porosity index and the percent air volume or porosity of the composition [44]. The porosity index is indicated at the point a line from the pigment apex strikes the pigment-air axis, that also intercepts the point that a line from the air apex to the formulation PVC on the pigment-binder axis crosses the formulation CPVC line. The CPVC line is the formulation CPVC line running from the pigment-binder axis to the pigment-air axis. With latex paints the CPVC line in this graph must be the value determined experimentally (apparent CPVC) or the PVC at zero porosity calculated from the latex porosity equation below where LP= 0. The percent air in the coating film may also be determined by reading from the intercept point on the CPVC line horizontally to the pigment-air axis.

$$\text{LP} = 1 - \frac{\text{CPVC}(1-\text{PVC})}{\text{PVC}(1-\text{CPVC})}(x)$$

LP = latex porosity index

CPVC = pigmentation CPVC calculated from oil adsorption

PVC = formulation PVC

x = vehicle volume fraction = binding power index (8)

Because the binding power index is a primary latex property that does not vary with pigmentation changes [41], the porosity-dependent properties of two different latex paints may be matched by formulating at a constant latex porosity index using the binding power index and the oil absorption CPVC of the pigment blends. The PVC change required to match the latex porosity index of the paints can be calculated by the relationship below:

$$\frac{\text{CPVC}_a(1-\text{PVC}_a)}{\text{PVC}_a(1-\text{CPVC}_a)}(x_a) = \frac{\text{CPVC}_b(1-\text{PVC}_b)}{\text{PVC}_b(1-\text{CPVC}_b)}(x_b) \quad (9)$$

In the case where the same latex is being used and the pigment composition is changed, the above equation may be used omitting the binding power index term on both sides of the equation. With the oil absorption CPVC values of both pigment compositions determined, the PVC adjustment to maintain equal latex porosity index in the new formulation can be calculated. Since the binding poor index is constant x is omitted, and the terms of the equation reverts to the solvent binder form.

CALCULATION OF LATEX BINDING POWER INDEX

Berardi [45] developed the concept that a constant ratio exists between oil absorption and latex polymer concentration required at the CPVC. This relationship can be expressed as

$$\text{BI} = \frac{V_o}{V_l} \quad (10)$$

V_o = volume of oil required to bind 100 g of pigment as determined by oil absorption; V_l = volume of latex binder required to bind 100 g of the same pigment as determined by an experimentally determined CPVC.

Stieg [46] eventually concluded the vehicle fraction factor x he had developed to adapt the porosity index (PI) equation developed for solution paints to latex paints was identical to Berardi's binding power index. The formula he developed to calculate the binding power index (x) of a latex may be derived by rearranging the latex porosity equation to solve for x when LP is zero. See Ref. [46] for a detailed discussion of this subject.

$$\text{latex porosity (LP)} = 0 = 1 - \frac{\text{CPVC}(1-\text{PVC})}{\text{PVC}(1-\text{CPVC})}(x) \quad (11)$$

$$\text{For LP} = 0 \quad x = \frac{\text{PVC}_0(1-\text{CPVC})}{(\text{CPVC}(1-\text{PVC}_0))}$$

PVC_0 = apparent CPVC, PVC of zero porosity

CPVC = CPVC calculated from oil absorption

x = vehicle fraction factor = binding power index (12)

PVC_0 may be determined by the detection of dry hiding in a formulation with no or a low concentration of opaque pigment. Schaller [47] published an excellent method for determining the PVC at zero porosity with a PVC ladder in a single extender pigment paint. He determined PVC_0 by the appearance of dry hiding by measuring the contrast ratio. The method is precise and relatively easy to perform and very suitable to determining the binding power index of a latex. Schaller demonstrated in his paper that the PVC_0, the apparent CPVC, of latex paint systems is dependent on the latex particle size and polymer modulus. It was demonstrated that increasing latex particle size and the polymer modulus detract from efficient filming and packing of the latex particles in the pigment matrix leading to latex binders exhibiting a lower apparent CPVC value compared to solution binders in the same pigment composition. Coalescent solvent effective for the latex must be included in the single pigment test to accurately access PVC_0. In systems with high white hiding power pigment, the end point must be determined by tinting a PVC ladder of the formulations with a constant amount of lampblack colorant and determining the break in apparent tintorial strength or *S*-values calculated from the Kubelka-Munk relationship assuming constant *K*-value. The Pierce-Holsworth or the

Cole methods discussed in a later section may be used for determining CPVC of a formulation with a high concentration of opaque pigment.

Ramig [41] provided a proof of the equivalency of Berardi's binding power index and Stieg's vehicle fraction factor x. In the referenced paper he demonstrated that the CPVC in latex systems is more than a basic pigment characteristic and also that the binding power index is a fundamental latex property that remains constant in any pigment composition. Ramig derived another equation to determine the binding power index in terms of oil absorption, pigment density and PVC_0.

$$BI = \frac{(OA)(PVC_0))Dp}{(1 - PVC_0)(100)}$$

PVC_0 = apparent CPVC, PVC of zero porosity determined experimentally

OA = pigment oil absorption in cc/100 g of pigment

D_p = density of pigment (13)

CALCULATION OF FREE BINDER

When making necessary formula adjustments in exterior paints, a means to adjust either the pigment or vehicle to maintain constant durability has long been desired. In the days of linseed oil paints, the concept of free binder was developed as a formulation principle [48,49] that held that if a formula's oil content was adjusted up or down with pigmentation changes to maintain equal viscosity, equal free binder was maintained. Fortunately the optimum viscosity for durability and brushing coincided for oil-based paints. This approach was, of course, not applicable to latex paints. Stieg defined an equation [50–52] below to express the free binder of a paint as the excess vehicle above the amount required for the CPVC of the formula pigmentation calculated as a percentage of the total binder volume. This equation was derived from one published by Dintenfass [53] on the theoretical relationship between the relative viscosity of a dispersion, as compared to that of its vehicle, as a function of the volume occupied by its settled pigmentation. The percent free binder present in any oil-based or soluble binder-system is calculated by the following equation:

$$\%\ \text{Free Binder} = \frac{(CPVC - PVC)}{CPVC}(100)$$

CPVC = Pigmentation CPVC calculated from oil adsorption

PVC = Formulation PVC (14)

The equation indicates that the higher the CPVC of the pigmentation is increased by pigment composition adjustments, the higher the PVC may be for a constant percentage of free binder.

For latex paint systems the binding power index will be less than 1.0 and this must be taken into account to calculate the free binder. The following equation was derived in Refs. [51,52] for latex paints:

$$\%\ \text{free binder} = (1 - PVC) - \frac{PVC(1 - CPVC)}{CPVC(x)}(100)$$

CPVC = pigmentation CPVC calculated from oil adsorption

PVC = formulation PVC

x = latex binding power index (15)

OTHER METHODS FOR DETERMINING CPVC

Asbeck–Van Loo Method of determining CPVC

The Asbeck–Van Loo [10,29] Method of directly determining the CPVC is based on the observation that the packing pattern of a pigment in a paste persists when the dispersion is diluted for sedimentation tests if nonpolar liquids are used for the dilutions. Thus, to measure the voids in a dry paint film, it is only necessary to obtain the pigment in the form of a filter cake and measure the volume of the cake. Then, the cake volume is subtracted from the actual volume of the pigment calculated from density data. The ratio of the actual volume of the pigment to the volume of the cake is the CPVC.

PIGMENT PACKING FACTOR

Asbeck and coworkers [10] proposed the term "pigment packing factor" (PPF) as a name for a pigment parameter that replaces or supplements the oil absorption value. PPF is the CPVC for a single pigment in a standard vehicle with the term CPVC being applied to a single or mixture of pigments present in a paint. The investigators suggested a blend of 4 mL of heat-bodied linseed oil and 50 mL of naphtha as the dispersing vehicle. The PPF is determined by placing 54 mL of the vehicle in a 1/4 pt can or glass jar that is half filled with steel balls. To this, 6 mL of pigment (the weight in grams of pigment equal to the specific gravity times 6) are added. The system is dispersed by machine shaking for exactly 3 min. 20 mL of the dispersion are then used to determine the PPF using the same procedure as that used for CPVC. If the PPF is to be compared with oil absorption values, it must be converted to a weight basis, PPF_{weight}, by means of the following equation:

$$PPF_{weight} = \left(\frac{(100 - PPF)(\text{specific gravity of oil})}{(PPF)(\text{specific gravity of pigment})}\right)(100) \quad (16)$$

The PPF and OA values are compared in Table 5. If values are ranked from highest to lowest, the values calculated from the PPF are highest, those from Gardner–Coleman fall next, and those from the spatula rub-out test are lowest. Explanations for the difference based on conditions existing at the endpoint are tabulated in Table 6.

Cole Method for CPVC

The CPVC depends on pigment particle packing or orientation [10,29], and Cole [54] noted that spherical particles might pack similarly in both liquid and dry films. To demonstrate this, a dry-film method was developed. The method is based on the fact that below the CPVC dry film volume, V, is a sum of the pigment volume, V_p, and binder solids volume, V_b

$$V = V_p + V_b \quad (17)$$

and that above the CPVC the volume of the voids must also be considered with

$$V = PV_p \quad (18)$$

where P is the relative pigment packing factor (the ratio of bulk volume to true volume). Two graphical and calculation methods were used to obtain CPVC.

TABLE 5—Comparison of pigment packing factors, calculated and experimentally determined oil absorption values [1]

Pigment	PPF	Oil Absorption Values		
		Calculated from PPF	Gardner–Coleman Method	Spatula Rub-out Method
Carbon black, medium	10	456	212	124
Chrome green	34	41	33	20
Chrome yellow	27	46	33	24
Iron oxide, light red	37	32	24	19
Lampblack	29	128	70	51
Magnesium silicate	39	50	27	25
Midori blue	33	104	87	51
Phthalocyanine blue	20	225	55	34
Silica, diatomaceous	24	131	105	65
Toluidine red toner B	25	199	62	48
Zinc oxide	27	45	19	12

Pierce-Holsworth Method for CPVC

This method [55] also used paint films, but it treated the data in a different manner by introducing specific volume concepts. The specific volume, v, of a dry paint film can be expressed as:

$$v = \frac{V}{W} = \frac{V}{W_p + W_b} = v_p f_p + v_b f_b \tag{19}$$

where V is the dry film volume, v, v_p, and v_b are specific volumes of the dry film, pigment, and binder, W, W_p, and W_b are weights of dry film, pigment, and binder, and f_p and f_b are weight fractions of pigment and binder, respectively. Since the sum of f_p and f_b is unity, the expression can be arranged to

$$v = (v_p - v_b) f_p + v_b \tag{20}$$

If v is plotted as a function of f_p, a straight line of slope $(v_p - v_b)$ and intercept of v_b should result.

Above the CPVC, the volume of the film is given by

$$V = P v_p W_p \tag{21}$$

where P is a packing factor. If both sides of this expression are divided by W, the expression

$$v = P v_p f_p \tag{22}$$

TABLE 6—Physical conditions that exist at the end points of pigment packing factor and oil absorption test [1,10]

Parameter	PPF	Gardner-Coleman	Spatula Rub-out
Dispersion	Aggregates are completely broken down.	Only a few of the largest aggregates are broken down and the interstices are filled with oil.	More aggregates are broken down than in the Gardner-Coleman methods and the interstices are filled with oil.
Electrokinetic equilibrium	Agglomeration is complete because of high system fluidity.	Agglomeration is incomplete because of low system fluidity.	Agglomeration is incomplete because of low system fluidity.
Pigment surface requirements	Satisfied	Not completely satisfied	Substantially satisfied
Work of dispersion	Defined and very high (approaching maximum)	Undefined but low	Undefined but relatively high
Work of packing	Defined and very low (approaching zero)	Undefined but low	Undefined but relatively high

TABLE 7—Comparison of the critical pigment volume concentration calculated by the Pierce-Holsworth method [28] and comparison with results from physical property measurements [1]

Paint system	Critical Pigment Volume Concentration			
	Pierce–Holsworth Method	Tensile Strength Method	Elongation at Break Results	Water Vapor Permeability Results
Acrylic latex exterior House Paint A	47	47	42	46
Acrylic latex exterior House Paint B	41	42	41	42
Poly (vinyl Acetate) latex masonry paint	44	44	44	45
Acrylic exterior masonry paint (from House Paint A above)	48	47	44	48

is obtained. If dry film specific volume, v, is plotted against the weight fraction of pigment, f_p, a straight line of slope Pv_p passing through the origin results. The intersection of this line with the previously described straight line should occur at a value of f_p corresponding to the CPVC. Results obtained by this method are presented in Table 7 along with the CPVCs obtained by tensile strength, elongation, and water vapor permeability. The good agreement is apparent.

APPENDIX A

Properties of raw linseed oil from Table 1 ASTM D234a

Property	Requirement	ASTM Method
Specific gravity, 25/25°C	0.926–0.931	D1963
Acid value max	4.0	D1639
Saponification value	189.0–195.0	D1962
Unsaponificable matter, max, %	1.50	D1965
Iodine value (Wijs), Min	177	D1959
Loss on heating at 150 to 110°C, max %	0.2	D1960
Clarity	Clear and Transparent At 65°C	D2090
Color (Gardner), max	13	D1544
Foots, volumetric heated oil, max, %	1.0	D1954
Foots, volumetric, chilled oil, max, %	4.0	D1954
Gravimetric foots, max, %	0.25	D1966
Flash point, min, °F	250	D93

[a]ASTM D234-82 (Re-approved 1987). Unfortunately, ASTM D234 Standard Specification for Raw Linseed Oil was discontinued in March 2007. The historical method will still be available from ASTM.org.

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Part 7: Additives

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In preparation of this chapter, the contents of the 14th edition were drawn upon. The author acknowledges the author of the 14th edition, Vanja King. The current edition will review and update the topics as addressed by the previous author, introduce new technology that has been developed, and include up to date references.

Bactericides, Fungicides, and Algicides

Janet H. Woodward[1]

PREFACE

MANY BACTERIA, FUNGI, AND ALGAE CAN CAUSE problems in the paint and coatings industry. These problems arise during manufacturing, in-can, and post application. To minimize or prevent the growth of these microorganisms, the appropriate microbicide (algicide, bactericide, and fungicide) must be effectively applied. Generally, the microbicides are divided into two general categories: Those used for in-can preservation and those used for dry-film preservation. Knowing the groups of organisms against which a microbicide will target is very important in selecting the best chemical to use. The organisms involved are discussed in more detail elsewhere in this manual.

TECHNICAL TERMS

microbicide—a substance that kills organisms; synonym for biocide; the term is further defined (bactericide, fungicide, algicide) to indicate the target organisms.

microbiostat—a substance that prevents the growth of microorganisms and their spores, but does not necessarily kill them.

aerobes—organisms that grow in the presence of oxygen, utilizing the oxygen as a terminal acceptor.

facultative anaerobes—organisms that grow in the presence or absence of oxygen.

anaerobes—organisms that grow in the absence of oxygen; oxygen can be toxic to these organisms.

efficacy—the effect of a microbicide on the target organism or group of organisms; can be measured in percent kill compared to control, but should be defined in the test method; the result is usually expressed as the minimum inhibitory concentration (MIC) against a specific organism.

spectrum—describes the efficacy of a microbicide.

broad spectrum—microbicide is effective against more than one group of organisms.

narrow spectrum—denotes activity against one group or sub-group of organisms.

DESCRIPTION OF MICROBIAL PROBLEMS

In-can Preservation

Water-based paints are prone to contamination and spoilage by bacteria and occasionally unicellular fungi (i.e., yeast) and filamentous fungi. Bacterial growth requirements include water, a carbon source, an energy source, oxygen for aerobes, and other macroelements, such as nitrogen and phosphorus. The majority of bacteria grow between 10 and 50°C and *p*H range of 3–11. Paint formulations provide an adequate supply of the minimal nutrients at the ideal pH and temperature to maintain bacterial growth.

In-can contamination may originate from a number of sources. The aqueous raw materials, such as defoamers, surfactants, wetting agents, and pigment slurries, are themselves susceptible to bacterial degradation. Powdered materials, including starches, fillers/extenders, and pigments may contain bacterial endospores and fungal spores that can germinate under appropriate conditions. The most common source of contamination is the process water. Along with good housekeeping procedures, proper microbicides must be used in the raw materials and water to minimize bacterial contamination.

The problems commonly encountered in water-based paints are shown in Table 1. These do not necessarily happen at the same time but develop as the microbial population changes due to oxygen requirements. Because of the initial oxygen-rich environment, aerobes and facultative anaerobes will often initiate the degradation. They can utilize a variety of paint components for nutrients. They can produce enzymes, including proteases and glucanases. The breakdown products resulting from numerous enzymatic activities act as nutrient sources for other bacteria. As oxygen is depleted, the facultative anaerobes and strict anaerobes will thrive. The metabolic processes produce acids that can lower the *p*H; produce gasses, such as hydrogen (H_2), carbon dioxide (CO_2), and hydrogen sulfide (H_2S), which can cause bulging cans and odors; and produce organic acids and other metabolic end products that cause odors. Acids will also react with any calcium carbonate to produce CO_2. Anaerobes also produce cellulases. The cellulases catalyze the breakdown of cellulose-based materials such as thickeners. As the thickener is degraded, viscosity is lost. More thorough discussions on these metabolic processes can be found in Refs. [1–4].

To prevent these problems from occurring, the appropriate microbicide must be incorporated into the coating formulation. In addition to being cost-effective, the microbicide should be compatible with all coating components,

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TABLE 1—Problems caused by contamination of water-based paints and coatings

Type of Problem	Common Cause
Viscosity Loss	Cellulase enzymes from bacteria or fungi catalyzing degradation of cellulose thickeners
*p*H changes	Acids produced from metabolic processes, typically from anaerobic bacteria
Odors	Organic acids and other metabolic end products, such as hydrogen sulfide from anaerobic bacteria
Gassing—bulging or exploding cans	CO_2 or H_2 production from anaerobic bacteria or yeast
Discoloration	Colored pigmentary moieties from bacterial and yeast metabolism; sulfide from sulfate-reducing bacteria
Foaming	Degradation of antifoam agents via bacteria

be stable within a range of *p*H, temperature, and time period, have no effect on rheology, impart no discoloration or odors to the coatings, be water soluble in concentrations used, and be environmentally acceptable [5–7].

Dry-Film Preservation

Microorganisms involved with dry-film problems include bacteria, algae, and fungi. Bacterial growth requirements are noted in the above paragraphs. In addition to sources of carbon, nitrogen, and hydrogen, most fungi require a relative humidity of 60 % or greater. All filamentous fungi are aerobic whereas the unicellular yeast can be aerobic or anaerobic. The ideal temperature range for fungi is 20–35°C. Although fungi can grow in alkaline conditions, the ideal *p*H range is 4.5–6.5. Algae are photosynthetic; they require light, carbon dioxide and water (i.e., moisture) to produce energy. They survive in alkaline conditions and temperatures of 15–30°C.

The most understood problem associated with dry-film preservation is the defacement and discoloration of the film itself when applied to surfaces such as interior and exterior walls of buildings, bridges, and ships [4, 8–10]. Algae are more of a serious problem in temperate and tropical regions and especially on masonry surfaces because of the alkaline conditions [11,12]. Algal growth may produce minor defacement; however, it will increase moisture retention, which can lead to other problems [10]. In hard, calcium-rich fresh water, algae can also cause the precipitation of calcium carbonate onto submerged surfaces, including antifouling paint [13]. Fungi can produce mycelia and spores that will disfigure dry-film. If the mycelia can grow through the coating, subsequent problems can include the film losing adhesion, the initiation of corrosion, and the deterioration of wooden structures. Table 2 lists problems in paint and coating film preservation.

TABLE 2—Problems in paint and coating film preservation

Type of Problem	Common Cause
Defacement/discoloration/dirt entrapment	Algae and/or fungi; some bacteria growing on film
Loss of adhesion	Fungi growing under film
Deterioration of structure (wooden)	Fungal enzymes catalyzing the breakdown of cellulose, hemicellulose, and lignocellulose
Antifouling paint failures on marine crafts, etc.	Bacteria, algae (including diatoms), fungi, barnacles
Corrosion	Bacteria, such as sulfate reducers, and moisture from fungi initiating corrosion
Destruction of cultural material	Bacteria, algae, and fungi growing on paintings, statues, and buildings

Studies [14,15] have indicated the succession of microbial populations on dry-film as well as surfaces coated with antifouling paint. Initial colonization is from bacteria that produce extracellular capsular material. The resulting conditioning of the surface allows for the subsequent growth of fungi, algae, and other organisms. These studies indicate the need for a dry-film preservative to be broad-spectrum in its activity, i.e., it must be effective against bacteria as well as fungi and/or algae. Other requirements for a dry-film preservative include stability over a wide *p*H range, temperature stability, low water solubility to prevent or retard leaching, UV stability, long-lasting efficacy, compatibility with the other materials in the formulation, no discoloration or odors imparted, and environmental acceptability [6,7].

GROUPS OF MICROORGANISMS RELATED TO BIOCIDAL EFFICACY

It is important to know the activity of a particular microbicide against the types of organisms encountered during in-can or dry-film preservation. For this purpose, the most important groups of microorganisms are:

Bacteria
Aerobic bacteria
  Gram positive bacteria
    endospore-forming bacteria
  Gram negative bacteria
Facultative anaerobic bacteria
  Gram negative bacteria
Anaerobic bacteria
  Gram positive bacteria
    endospore-forming bacteria
  Gram negative bacteria
Oxygenic, photosynthetic
bacteria (Cyanobacteria, formerly called the 'blue-green' algae)

Fungi
Multicellular (molds)
Unicellular (yeasts)

Algae
Green algae
Brown algae

MODE OF ACTION OF MICROBICIDES: SPECTRUM OF ACTIVITY

The spectrum of activity of a microbicide will describe which organisms or group of organisms will be the targeted by the biocide. Typically, microbicides are considered narrow spectrum, i.e., activity against one group or sub-group, or broad spectrum, i.e., two or more groups of organism will be affected. Thus, microbicides can be generally categorized as bactericides, fungicides, and algicides. Because algae and fungi are eukaryotes, their overall cellular structures are different and somewhat more complex than the prokaryotic bacterial cells. Thus, fungicides and algicides are generally more toxic than bactericides.

Concentration will also affect a microbicide's spectrum of activity. At higher levels, some bactericides are effective against fungi. The reverse is also true; some fungicides at lower concentrations will act as bactericides. Another aspect of concentration is the difference of a chemical being microbiocidal (or biocidal) and microbiostatic (biostatic). At low concentrations, some microbicides will be microbiostatic; instead of killing organisms, a microbiostat will react with a physiological activity of a group of organisms to prevent their growth.

Various microbicides used for in-can preservation are listed in Table 3. These agents are incorporated into a paint or coating formulation to prevent microbial contamination of the final product; they are not added at elevated concentrations to treat a contaminated component of the formulation. Therefore, for any in-can preservative to be effective, it is assumed that microbial contamination during the manufacturing process has been kept to minimal levels.

Common microbicides for dry-film preservation are listed in Table 4; most anti-fouling agents are not specifically covered in this chapter. Dry-film preservation actives differ from in-can actives because of two factors. Firstly, as described above, dry-film contamination is typically caused by fungi and algae rather than bacteria alone. Secondly, dry-film preservatives have to be effective for extended periods of time; this can be years as compared with months for in-can preservatives.

Table 5 lists some other microbicides used in paints and coatings, especially during the manufacturing process. As stated above, contamination of raw materials must be kept to a minimum. The process water must also be kept as clean as possible. Disinfection of process vessels and pipes along with general good housekeeping procedures should also help to decrease microbial contamination.

MODE OF ACTION OF SOME ANTIMICROBIAL AGENTS

The following is used to give a general overview of the more common modes of action of the microbial agents listed in Tables 3–5.

Formaldehyde-Releasing Agents

Many microbicides are classified as formaldehyde-releasing compounds. They are produced by reacting formaldehyde with amides (N-formals), with alcohols or glycols (O-formals) or with amines or aminoalcohols (N,O-formals) [7]. As implied by the category, some are biocidal due to the release of formaldehyde. However, under application conditions, certain microbicides in this category do not rely on the release of formaldehyde for their specific mode of action. The liberation of formaldehyde is also related to *p*H; at alkaline *p*H, little or no formaldehyde will be released.

Aldehydes including formaldehyde deactivate protein by interacting with amine groups on the protein. Proteins are found on the outer layers of microorganisms. Also, all enzymes, i.e. catalysts for many metabolic reactions, are protein. The deactivation of protein leads to disruption in cellular metabolism and transportation across cell walls and membranes and ultimately leads to death of the organism.

Formaldehyde can also be classified as an electrophilic agent, i.e., a compound that reacts with the nucleophilic components of a cell.

Agents that React with Nucleophilic Groups

Nucleophilic groups are described as those species that are electron rich. The nucleophilic groups that are commonly found in microorganisms are thiols ($^{-}$SH) and amines (NH_2). Both are found in various amino acids, the building blocks of protein. Proteins are distributed throughout microbial cells, especially in cell membranes and cell walls. Nucleophiles are attracted to electron-poor species, i.e., electrophiles. Thus, microbicides containing electrophilic groups react with the nucleophilic areas of the microbial cells, deactivating the organisms.

Coating components may contain nucleophilic groups and consequently an electrophilic biocide will react with these components. If the typical concentration of microbicide is used in these instances, a portion of the biocide is essentially deactivated and will not be available as a preservative. Therefore, a general knowledge of a microbicide's mode of action will prevent failures in both in-can and dry-film preservation.

Agents that Chelate Metals

Metals are trace elements needed for microbial growth and metabolism. They serve as co-factors for enzymes and are components of some vitamins. Microbicides that are chelating agents will tie up these trace metals; the consequence is disruption in some metabolic processes and eventual microbial death.

STRATEGIES FOR MINIMIZING RESISTANT STRAINS

There are several mechanisms by which microorganisms become less susceptible to microbicides. Reduced susceptibility can be due to intrinsic properties, such as cell structure (e.g., gram positive versus gram negative bacteria), efflux systems that remove various agents [16], and actual deactivation of the microbicides [17]. Organisms can also reduce susceptibility due to acquired mechanisms, including the acquisition of a plasmid or through genetic mutation.

Simple strategies can help minimize the appearance of resistant strains. The most important strategy is general good housekeeping during manufacturing. Allowing water

TABLE 3—Microbicides used for in-can preservation

Chemical Name	CAS Reg. Number	Target Organisms	Putative Mode of Action
4,4-dimethyl-oxazolidine	51200-87-4	Bacteria/fungi	Formaldehyde releaser
5-hydroxy-methyl-1-aza-3,7-dioxabicyclo (3,3,0) octane	56709-13	Bacteria—as a bacteriostat	Formaldehyde releaser
Hexyhydro-1,3,5-tris-(2-hydroxyethyl)-s-triazine	4719-04-4	Bacteria	Formaldehyde releaser
Hexyhydro-1,3,5-triethyl-s-triazine	7779-27-36	Bacteria	Formaldehyde releaser
1-(3-chloroallyl)-3,5,7-triaza-1-azonia-adamantane2[(Hydroxymethyl)amino] ethanol	44080-31-3	Bacteria/fungi	Formaldehyde releaser
	34375-28-5	Bacteria/fungi	Inhibits active transport; coagulates protein; hydrolysis results in release of formaldehyde
4,5-dichloro-2-n-octyl-4-isothiazolin-3-one	64359-81-5	Fungi/algae	Reacts with thiols and amines
([([(2-dihydro-5-methyl-3(2H)-oxazolyl)-1-methylethoxy] methoxy) methoxy] methanol	40382-75-0	Bacteria/fungi	Formaldehyde releaser
Sodium hydroxymethylglycinate 1-hydroxymethyl-3,5-dimethylpyrazole	70161-44-3	Bacteria/fungi	Formaldehyde releaser
	85264-33-1	Bacteria	Inhibits alcohol dehydrogenase and ethanol metabolism
1,2-dibromo-2,4-dicyanobutane	35691-65-7	Bacteria/fungi/algae	Has several highly electron withdrawing centers
5-chloro-2-methyl-3(H)-isothiazoline+2-methyl-3(H)-isothiazoline	26172-55-4 2682-20-4	Bacteria	Inhibits macromolecular synthesis (DNA,RNA, proteins, etc.) plus forms highly reactive radical
1,2-benzisothiazoline-3-one	2634-22-5	Bacteria	Reacts with thiol groups, especially those associated with the cytoplasmic membrane
2-bromo-2-nitropropane-1,3-diol	52-51-7	Bacteria	Reacts with thiol groups, especially those associated with enzymes
Blend of 1,2-benzisothiazoline-3-one+2-methyl-3(H)-isothiazoline	2634-22-5 2682-20-4	Bacteria	Reacts with thiol groups
Blend of 1,2-benzisothiazoline-3-one+2-bromo-2-nitropropane-1,3-diol	2634-22-5 52-51-7	Bacteria	Reacts with thiol groups
Blend of 5-chloro-2-methyl-3(H)-isothiazoline+2-methyl-3(H)-isothiazoline+ 2-bromo-2-nitropropane-1,3-diol	26172-55-4 2682-20-4 52-51-7	Bacteria	Reacts with thiol groups

to remain in pipes and vessels that previously contained treated material will provide diluted microbicide in non-lethal concentrations. This low-level exposure can lead to microorganisms becoming resistant. The same principle applies to the treatment of raw materials; low-level dosages of microbicides can also lead to reduced susceptibility in the microorganisms.

Another strategy commonly used to minimize the development of less-susceptible strains is to change to a biocide with a different mode of action. However, there is some debate as to the usefulness of this practice. Studies have shown that when an organism becomes less susceptible to one biocide, it will also become less susceptible to several chemically unrelated biocides [18].

Whenever the efficacy of a microbicide needs to be determined, organisms from the manufacturing plant or spoiled material should be used rather than stock cultures maintained on artificial media. The microorganism found in the spoiled material or in the production process will have been previously exposed to the existing biocide program and thus be more resistant than stock cultures. Knowledge of microbicides' mechanisms of action will also be useful when determining the appropriate treatment.

TABLE 4—Microbicides used for dry-film preservation

Chemical Name	CAS Reg. Number	Target Organisms	Putative Mode of Action
Diiodomethyl-p-tolyl sulphone	20018-09-1	Fungi	Reacts with nucleophilic cellular components
2-n-octyl-4-isothiazoline-3-one	26530-20-1	Fungi	Reacts with thiols and amines
3-iodo-2-propynyl butylcarbamate	55406-53-6	Fungi/algae	Chelates metals?
4,5-dichloro-2-n-octyl-4-isothiazolin-3-one	64359-81-5	Fungi/algae	Reacts with thiols and amines
1H-benzimidazole-2-ylcarbamic acid, methyl ester	10605-21-7	Fungi	Inhibits mitotic microtubule formation
N-(trichloromethylthio) phthalimide	133-07-3	Fungi	. . .
N′-(3,4-dichlorophenyl)-*N,N*-dimethyl urea	330-54-1	Algae	Inhibits photosynthesis
2-(thiocyanomethylthio)-benzothiazole	21564-17-0	Fungi/algae	Reacts with thiols; inactivates metal enzyme complexes
N-cyclopropyl-*N′*-(1,1-dimethylethyl)-6-(methylthio) -1,3,5-triazine-2,4-diamine	28519-98-0	Algae	Reacts with thiols; inhibits photosynthesis
2,4,5,6-tetrachloro isophthalonitrile	1897-45-6	Fungi/gram positive bacteria	Reacts with amines; chelates metals; interrupts electron transport
2-(thiocyanomethylthio)-benzothiazole+methylene bis(thiocyanate)	21564-17-0 6317-18-6	Bacteria/fungi/ algae/anaerobic bacteria	Uncouples oxidative phosphorylation; reacts with thiols
1-([2-(2,4-dichlorophenyl)-4-propyl-1,3-dioxolan-2-yl] methyl)-H-1,2,4-triazole	60207-90-1	Fungi	Inhibits demethylation of ergosterol in cell membranes
Zinc-2-pyridinethiol-N-oxide	13463-41-7	Fungi/algae	Chelates necessary metals
Barium metaborate	13701-59-2	Bacteria/fungi	Inhibits enzymes
Dodecylguanidine hydrochloride	13590-97-1	Bacteria/fungi/ algae	As a cationic surfactant—disrupts cell walls and cytoplasm
Blend of 3-iodo-2-propynyl butylcarbamate+ 1H-benzimidazole-2-ylcarbamic acid, methyl ester	55406-53-6 10605-21-7	Fungi/algae	Inhibits mitotic microtubule formation
Blend of 3-iodo-2-propynyl butylcarbamate+ 1H-benzimidazole-2-ylcarbamic acid, methyl ester+ *N*-cyclopropyl-*N′*-(1,1-dimethylethyl)-6-(methylthio)-1,3,5-triazine-2,4-diamine	55406-53-6 10605-21-7 28519-98-0	Fungi/algae	Inhibits mitotic microtubule formation and photosynthesis
Blend of 3-iodo-2-propynyl butylcarbamate + *N′*-(3,4-dichlorophenyl)-*N*, *N*-dimethyl urea	55406-53-6 330-54-1	Fungi/algae	Inhibits photosynthesis
Blend of 3-iodo-2-propynyl butylcarbamate+ 4,5-dichloro- 2-n-octyl-4-isothiazolin-3-one	55406-53-6 64359-81-5	Fungi/algae	Reacts with thiols and amines
Blend of 3-iodo-2-propynyl butylcarbamate+-*n*-octyl-4- isothiazoline-3-one+*N′*-(3,4-dichlorophenyl)-*N,N*-dimethyl urea	55406-53-6 26530-20-1 330-54-1	Fungi/algae	Reacts with thiols and amines and inhibits photosynthesis
Blend of 4,5-dichloro-2-n-octyl-4-isothiazolin-3-one+*N*-cyclopropyl-*N′*-(1,1-dimethylethyl)-6-(methylthio)-1,3,5-triazine-2,4-diamine	64359-81-5 28519-98-0	Fungi/algae	Reacts with thiols and amines
Blend of 4,5-dichloro-2-n-octyl-4-isothiazolin-3-one+2-n-octyl-4-isothiazoline-3-one	64359-81-5 26530-20-1	Fungi/algae	Reacts with thiols and amines
Blend of 2-n-octyl-4-isothiazoline-3-one+2,4,5,6-tetrachloro isophthalonitrile+*N′*-(3,4-dichlorophenyl)-*N,N*-dimethyl urea	26530-20-1 1897-45-6 330-54-1	Fungi/algae/gram positive bacteria	Reacts with thiols and amines; chelates metals; inhibits photosynthesis
Blend of 2,4,5,6 -tetrachloro isophthalonitrile+*N′*-(3,4-dichlorophenyl)-*N,N*-dimethyl urea	1897-45-6 330-54-1	Fungi/algae/gram positive bacteria	Reacts with amines; chelates metals; inhibits photosynthesis
Blend of *N′*-(3,4-dichlorophenyl)-*N,N*-dimethyl urea+1H-benzimidazole-2-ylcarbamic acid, methyl ester	330-54-1 10605-21-7	Fungi/algae	Inhibits mitotic microtubule formation and photosynthesis

TABLE 5—Other microbicides used in the paint and coating industry

Chemical Name	Target Organisms	Putative Mode of Action
Glutaraldehyde	Bacterial endospores/ bacteria/fungi/algae	Reacts with amines
Parabens	Fungi	Disrupts membrane activity
Quaternary ammonium compounds	Bacteria/algae	As cationic compounds—disrupt cell walls and cytoplasm
Chlorine and other oxidants	Bacteria/fungi/ algae	Deactivates protein

ANALYSIS AND NEUTRALIZATION OF MICROBICIDES

In many instances, it is important to be able to detect the presence and even the concentration of the microbicide in a raw material or final paint or coating formulation. This may be part of quality control, i.e., documenting that the microbicide was added at the appropriate dosage rate.

The appropriate analytical method will vary according to the microbicide's active ingredient(s). Ideally, the procedure should not destroy the original active molecule(s). For example, it would be preferable to detect the intact molecule of a formaldehyde releaser rather than the formaldehyde that may have already been released prior to analysis or released due to the analytical procedure. Nondestructive methods include nuclear magnetic resonance.

TABLE 6—Factors that positively influence microbicide efficacy

Inclusion of pigments that have antimicrobial activity	Such components could possibly reduce the amount of preservative needed
Inclusion of other materials in the formulation that have antimicrobial activity (e.g., propylene glycol) or resist degradation	Some compounds are not readily used as a food source
Choosing a suitable *p*H range for the microbicide	Because some microbicides are more effective at acid *p*H and others at alkaline *p*H, the *p*H of the formulation could be adjusted to suit the microbicide
Differences in solubility of different microbicides	Combinations of microbicides with different solubilities could increase overall efficacy
Synergism resulting from the combination of microbicides with different modes of action	Antimicrobial agents are frequently complemented in combination, e.g., methylene bis(thiocyanate)/ 2-(thiocyanomethylthio) benzothiazole

Literature from the microbicide supplier, such as the material safety data sheet, will contain information regarding the proper procedure for deactivating a microbicide. If a spill occurs, the chemical will need to be neutralized and cleaned without danger to personnel or the environment.

FACTORS IMPACTING THE EFFICACY OF SOME COMMON MICROBICIDES

Physical and chemical factors not only affect the growth of microorganisms but also impact the efficacy of any microbicide. Some factors are listed in Tables 6 and 7.

METHODS FOR THE DETERMINATION OF MICROBICIDE EFFICACY

There are many standard methods described in the literature for the determination of a microbicide's efficacy for either in-can or dry-film preservation. The ASTM methods include D2574-06, Standard Test Method for Resistance of Emulsion Paints in the Container to Attack by Microorganisms; D3273-00(2005), Standard Test Method for Resistance to Growth of Mold on the Surface of Interior Coating in an Environmental Chamber; and D3456-86(2002), Standard Practice for Determining by Exterior Exposure Tests

TABLE 7—Factors that decrease microbicide efficacy

*p*H	Knowledge of the chemistry of a microbicide should include its activity at various *p*H. Many are less effective at alkaline *p*H. Stability should not be equated with efficacy; a microbicide may be stable at alkaline *p*H but with little efficacy.
Addition temperature	Any biocide will be deactivated to some degree by elevated temperature; MSDS and other literature can provide needed information
Nonionic surfactants	Some biocides are deactivated by these, including the parabens, organic acids, and aromatic alcohols
Low solubility	Preservatives need to be water-soluble to the concentration required for efficacy.
Leachability	A dry-film preservative must maintain an effective concentration throughout the film; leaching of water-soluble actives would lead to reduction in efficacy.
Formulation components	Some biocides are deactivated by these, i.e. protein can deactivate formaldehyde releasers
UV light frequency	UV light frequency decomposes dry-film fungicides and algicides and efficacy is lost

the Susceptibility of Paint Films to Microbiological Attack. A review of industry- and government-mandated methods to demonstrate fungicide efficacy is described in Ref. [19] with testing of algicides for tropical locations described in Ref. [20].

REGULATORY ISSUES

Because of environmental concerns, many heavy metal microbicides are no longer used. In the United States, organo-mercurials were banned from interior paints in 1990 and exterior paints in 1991. The use of various tributyltins was being restricted by several countries, including France [21], Japan, the United States, the United Kingdom, and Germany [22]. In 2001, the International Maritime Organization adopted the International Convention on the Control of Harmful Anti-fouling Systems on Ships (AFS Convention). Effective January 1, 2003, ships would not apply or re-apply organotin compounds. After January 1, 2008, ships would either not have organotin compounds on the hulls, surfaces, or external parts or the ships would have a barrier coating that would prevent the leaching of the organotin compound. The AFS convention entered into force on September 17, 2008. Replacement options include copper-based coatings. However, Canada, the United States, and the Netherlands have regulated copper emissions and/or discharge into their waters [23].

The greatest challenge for microbicide manufacturers worldwide is the Biocidal Products Directive 98/8/EC of the European Union. One aim of this directive is to increase the level of protection to humans, animals, and the environment by establishing a list of permitted active ingredients. The directive was enforced beginning in May 2000 with a ten-year period for the review of all existing actives. Any new active will go through a similar assessment. Because of the anticipated costs associated with this process, it has been speculated that manufacturers may not pursue the assessment of some existing actives. This may have an impact on the actives traditionally used for in-can and dry-film preservation. Instead of introducing new actives, many microbicide manufacturers are registering formulations of blends of approved actives (see Tables 3 and 4).

The current trend in paints and also in microbicides is to produce low-to-no-volatile organic compound (VOC) products. This is being driven by stricter environmental regulations in Europe and North America and by consumers' demand for more environmentally friendly products. Most microbicide manufacturers have low- and no-VOC versions of their actives.

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Surfactants

Elvira Stesikova[1] and Heinz Plaumann[1]

INTRODUCTION

SURFACE ACTIVE AGENTS OR "SURFACTANTS" represent a diverse spectrum of chemical compounds capable of modifying interfacial interactions by means of adsorption at interfaces. Since an interface is created when any two phases of immiscible components are present, it is virtually impossible to exclude or ignore interfacial aspects from any practical application. Coatings are no exception, but rather a unique expression of various surface phenomena governing the entire application.

The advent of waterborne and water-based technologies produced more environmentally benign paint formulations, but brought along new technological challenges that did not exist in solvent-based paints. Considering that typical water-based paint consists of an emulsified binder and dispersed pigments, the complexity of paint formulations is caused not only by their multi-component composition but also their multiphase nature and inherent thermodynamic instability. In such complex systems, surfactants play an extremely important role, since they represent additives that facilitate dispersion, provide much desired shelf stability, and destabilize foam. Moreover, surfactants are used in coatings as wetting, coalescent and pigment dispersant agents to aid coating application, film formation and color development.

In addition to the challenges provided by thermodynamic instability of paint systems and kinetics of their phase separation, environmental laws and regulations introduced new standards and additional requirements that will continue to have significant impact on the coating industry. Among many actions taken by state and federal legislative parties, the Clean Air Act of 1970 defines volatile organic contents (VOCs) and stipulates its permissible limits. In addition to the body of federal regulations, an increased consumers' awareness instigated new market initiatives that drive towards alkyl phenol ethoxylate (APEO), free consumer products. All these provide rather stringent guidelines to paint formulators with regard to the selection of dispersing media and functional additives, including surfactants.

Compliance with regulations is compounded with another requirement—ever-growing performance standards. Consumers demand convenience of application, durability, efficiency, and low price. A new trend, contemporary color designs in the architectural coatings, involves deep tones and various textures. This presents new challenges to the chemical community of paint developers that have to deal with more complex issues of pigment stabilization, uniform color development, environmental stability, and potential touch-up applications. Fast-growing and highly demanded do-it-yourself application materials present their own set of challenges with regard to stability and consistency of the paints.

Undeniably, the fundamental technological challenges, legislative regulations, and market trends are the main driving forces behind the developments leading to the introduction of nonvolatile APEO-free surface-active additives on the market. However, the objective of this review is to describe some of the basic properties of various types of surfactants and to develop a rational approach for their use in various coating applications. As elaborated later in this chapter, surfactants in coatings have multiple roles and functions. Initially, surfactants are used as a dispersing aid during the pigment-grinding stage, where they provide better wetting of the pigment particles. Moreover, surfactants are required as primary and/or secondary emulsifiers to produce stable interfaces. Finally, surfactants impart certain physical properties to the water-based coatings, such as better wetting of the substrate, improved stability and film integrity, optimized color acceptance, and minimized film defects.

DEFINITION AND CHEMICAL STRUCTURE

A surfactant is a chemical compound consisting of two well-defined and sufficiently separated moieties of opposite polarity or solubility: oil soluble (lipophilic or hydrophilic) and water soluble (hydrophobic). Fig. 1 shows a general structure of a surfactant molecule possessing those two components of opposite polarity. The hydrophilic "head" group of the surfactant molecule consists of polar ionic or nonionic groups, which interact strongly with water. The hydrophobic "tail" group is non-polar, usually consists of aliphatic or aromatic hydrocarbon residue, and has little or no affinity to the aqueous phase.

This dual nature of surfactants is responsible for their so-called amphiphilic properties, the most significant of which is their tendency to adsorb at an interface and modify interfacial interactions [1,2]. At the interface, amphiphiles are allowed to orient themselves so that the hydrophobic part of the molecule can escape from the aqueous environment, whereas the hydrophilic head group remains immersed in the water phase. This peculiar interfacial orientation of surfactant molecules is responsible for lowering interfacial surface energy. The latter is one of the fundamental properties of the surfactants, which eases the formation of new surface and stabilizes the existing one.

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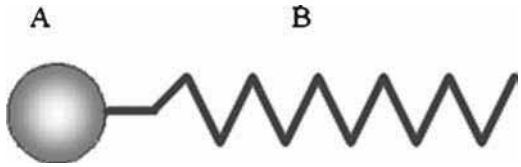

Fig. 1—Basic chemical structure of surface-active molecules with hydrophilic (a) and hydrophobic (b) components.

Owning to their ability to modify interfacial interactions, surfactants are widely used in coatings formulations. In recent times, the term "surfactant" is used as a general term for surface-active agents, which include emulsifiers, wetting and dispersing agents, and foaming and coalescent agents [3,4].

Coating surfactants differ in molecular chemistry, structure, and molecular weight. An assortment of widely used surfactant classifications exists today. This fact could be rationalized based on the diversity of molecular chemistries and the needs of the application community. One classification approach is based simply on the intended use, where surfactants may be classified as emulsifiers and wetting, dispersant, or foaming agents. Another approach is based on physical properties such as water or oil solubility, hydrophilic-lipophilic balance (HLB), cloud point, or viscosity characteristics. Alternatively, classification may be primarily based on the overall chemical structure of the materials. This latter approach provides general guidance for structure-property relationship and develops some rules for the correlation of chemical structure and interfacial activity. Therefore, the following discussion will be focused on the molecular architecture and surface activity of surfactants, whereas subsequent chapters will address physical characteristics and application aspects of surfactants in relation to coatings.

In addition to the above mentioned classifications, it is also important to distinguish between low molecular weight and high molecular weight surfactants. The former exhibit high molecular mobility [1], whereas the latter adsorb forming a thick protective layer that provides steric stabilization [5]. Overall, the molecular weight of the surfactants is relatively high and ranges between 300 and 2,000, which is essential to providing sufficient separation of the structural units and allowing them to reveal their properties.

Surfactant classification, depicted in Fig. 2 and discussed below, is based on the chemical nature of both hydrophilic and hydrophobic groups. Most hydrophilic groups of the surfactants fall into two major categories, ionic and non-ionic. The former, depending on the charge, could be further divided into anionic, cationic or Zwitterionic surfactants.

Anionic

Anionic surfactants are materials of significant practical and economical interest. They contain a negatively charged polar head group, such as sulfonate, sulfate, carboxylate, or phosphate, attached to a hydrophobic moiety, such as alkyl, alkyl phenol, alkyl ether, or alkyl phenol ether chain. The right balance of surface activity is achieved when an anionic group is linked to a hydrocarbon chain containing 10–20 carbon atoms [6]. Shorter hydrocarbon chains render the molecule too water soluble. Longer hydrocarbon chains contribute to insolubility and limited water-based applications.

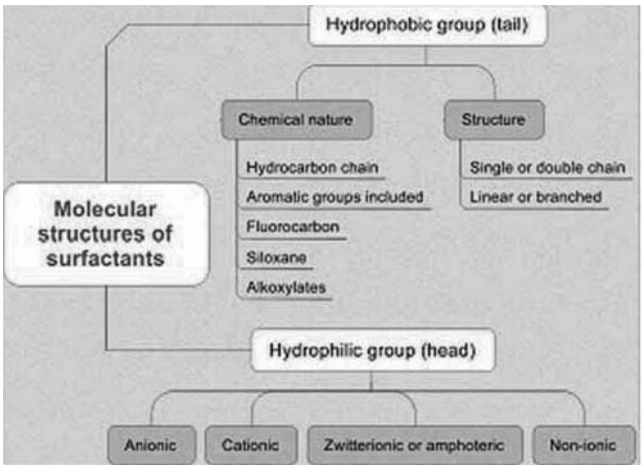

Fig. 2—Surfactant classification based on chemical nature of hydrophilic and hydrophobic groups.

These charged molecules adsorb on the surface of a particle, impart a charge, forming the so-called Helmholtz electric layer [1]. The charged layer around the particle creates electrostatic repulsive forces to guard against coagulation. The main disadvantages of anionic surfactants include the fact that they form water-insoluble salts with divalent and trivalent cations (Mg^{2+},Ca^{2+},Fe^{3+}), precipitate from brine solutions, and increase water sensitivity of the coatings.

Cationic

Quaternary ammonium compounds are the most commonly used cationic surfactants that bear a positive charge on the polar moiety of the molecules. The composition of the hydrophobic tail is similar to that of anionic surfactants and includes aliphatic, aromatic, ether chemistries, and combinations thereof. Because of their wider bactericidal activity, the major use of cationic surfactants is found in germicides and fungicides. Despite their high cost, they are also used for pigment dispersion.

Amphoteric and Zwitterionic

The term "amphoteric surfactant" is referred to amphiphilic compound that, depending on the *p*H of the media, is capable of carrying both anionic and cationic charges. *N*-alkyl amino acid is a typical example of *p*H-dependent amphoterics. However, there are amphiphiles that contain both strongly acidic and strongly basic groups and show both anionic and cationic properties independent of the *p*H. Such molecules are specified as Zwitterionic surfactants. Lecitin is an example of a Zwitterionic surfactant that has been traditionally used as a dispersant agent of organic pigments. In general, however, these surfactants are rarely used in the coatings industry since they are unable to provide electrostatic stabilization, and present only 2 % of the world surfactant market [1].

Nonionic

Despite wide utilization of anionic surfactants, chemical coagulation may be avoided by using nonionic surfactants. These molecules have no charge, but incorporate

well-defined hydrophilic and hydrophobic parts. Typically, the hydrophile is composed of ethylene oxide units and can be attached to fatty acid esters of glycerol, sorbitol, or propylene glycol. Widely used and commercially available nonionic surfactants include alkylphenol polyethoxy alcohol, having a series of various degree of ethoxylation and length of alkyl chains. For example, Emulan® (BASF), Triton® (Union Carbide), and Igepal® (Rhone-Poulenc) surfactants are very effective additives having excellent interfacial properties and are used as emulsifiers, dispersants, and wetting agents.

Due to increased environmental considerations, alkyl phenol-free surfactants are getting more attention in the industry and, in some applications, gain enough grounds to replace alkyl phenol-containing additives. Alkyl phenol-free surfactants are rather diverse and are based on EO-PO block copolymers (Pluronic® surfactant series) and alkyl alkoxylates (Lutensol® XP and XL surfactant series). Acetylenic glycols, containing a polar group surrounded by two bulky hydrophobic tails (Air product's Surfynol® surfactant series), is another example of a unique surfactant chemistry that found its applications as an effective wetting agent, defoamer, and surface tension reducer [7].

The main distinction between ionic and nonionic surfactants is the charge and the molecular weight of their molecules. The lack of ionic groups is primarily responsible for lower water sensitivity of nonionic surfactants. Because of their higher molecular weight, the water-soluble segments of nonionic surfactants extend into the water phase, forming a viscous barrier layer. This imparts steric stabilization by inhibiting the approach of another particle and preventing coagulation. Despite their unique advantages, most of the time, nonionic surfactants are used in combination with ionic amphiphiles. Such blends enhance sheer, mechanical and electrolyte stability of the paint in a wider *p*H range, electrolyte concentrations, and temperature conditions. Thus, the presence of anionic surfactant allows compensation for limited solubility of nonionic surfactants at temperatures above their cloud point. Nonionic surfactants, on the other hand, provide additional stabilization to a dispersion when anionic surfactants experience electrolyte "shock" due to shrinking double electric layer at elevated electrolyte concentrations [8].

Hydrophobic Groups

Alkyl benzene and alkylated aromatics, paraffins, and olefins (branched and linear), long-chain alcohols, alkylphenol alkoxylates, fatty acids, and their derivatives are among typical and most commonly occurring hydrophobic groups of various amphiphilic molecules [1,6].

Fluorocarbon surfactants have similar molecular structures to the hydrocarbon molecules except all the carbon-hydrogen bonds are replaced by carbon-fluoride bonds. These surfactants exhibit extremely low surface tension, an average 10–20 mN/m lower than equivalent hydrocarbon [1]. Because of the extremely hydrophobic nature of these molecules, fluorocarbons have a very strong tendency to preferentially adsorb on the interface, reducing the surface tension down to 15–22 mN/m, and provide spontaneous spreading on low surface energy substrates. Despite their unique surface activity and chemical stability, the wide use of these surfactants is limited by their high cost and poor compatibility. The latter could precipitate adhesion problems in the coatings.

Silicone-containing surfactants are another type of nonhydrocarbon-based surfactant molecules. When functionalized to produce water-soluble molecules, their surface activity falls below hydrocarbons and above fluorocarbon-based surfactants. Silicone surfactants effectively adsorb on the interface, act as effective defoamers but do not exhibit aggregation behavior such as micelle formation and solubilization [5].

Polymerizable Surfactants

In recent years, with heightened demands for reduced VOC and improved performance, polymerizable surfactants have received much attention in both academic and industrial circles [9–12]. The attraction of using polymerizable surfactants for lattices is rationalized by the fact that surfactant concentration in the aqueous media and on the surface of a latex particle depends on many factors. These include particle concentration, temperature, ionic strength, *p*H, any of which could be changed during the storage and application affecting the stability of the latex. During the film formation and particle coalescence, the surface area of the particles is significantly reduced, freeing a substantial amount of surfactant to migrate toward remaining coating/substrate and air/coating interfaces. This behavior affects paint adhesion to the substrate and re-coating ability. This could also adversely affect water resistance of the film and its gloss.

It has been shown [9–12] that many surfactant-related problems could be avoided or minimized by using polymerizable surfactants that become covalently bonded to the latex particles during the emulsion polymerization. Several types of ionic and nonionic reactive surfactants have been introduced to the market. Most of them have ethylene and propylene oxide blocks combined with a polymerizable group like allyl (Reasoap™ surfactants, Clariant's Emulsogen® surfactant), vinyl (Emulsogen®) surfactant, diallyl (Plurocoat™ RS surfactants), acrylic (Unichema's Maxemul® surfactants, Eleminol™ surfactants), and styrene (Noigen™ and Hitenol™ surfactants).

THE PROPERTIES OF THE SURFACTANTS

Hydrophile-Lipophile Balance

Solubility, and many other surfactant properties, depends on the specific chemical structure of the amphiphile and the relative contributions of its hydrophilic and hydrophobic (i.e., lipophilic) components. An increase in the length of the hydrophobic portion of the surfactant molecule increases its oil solubility and reduces affinity to water. The reverse is true when the hydrophilic portion of the molecule is increased in proportion to the hydrophobe. The balance of hydrophilic and lipophilic groups in a molecule is known as HLB.

Introduced by Griffin [13,14] and further developed by Davies [15,16], HLB is an attempt to quantify surfactants' properties to determine their affinity to hydrophilic or lipophilic solvents. Griffin [13,14] proposed a scale ranging from 1 to 20. The extremes represent predominantly lipophilic oleic acid and predominantly hydrophilic sodium oleate, respectively, while their mixtures of different compositions represent continuum between these two extremes. The balance of hydrophilic and lipophilic properties (HLB)

TABLE 1—List of hydrophilic and lipophilic moieties of surfactant molecules

	Hydrophilic		Lipophilic	
Ionic	Sulfate	$-OSO_3^-$	Linear or branched	C_6–C_{20}
	Sulfonate	$-SO_3^-$	alkyl	C_6–C_{20}
	Carboxylate	$-CO_2^-$	Alkynebenzene	
	Quaternary ammonium	R_4N^+	Fluoroalkyl	–
Nonionic	Alcohol	$-CR_2OH$	Poly(ethylene oxide)	$(OCH(CH_3)CH_2)_n-$
	Ether	–COC–		$-(OSi(CH_3)_2)_n-$
	Poly(propylene oxide)	$-(OCH_2CH_2)_n-$	Polysiloxane	

is, therefore, expressed in terms of relative amounts of each ingredient in the composition

$$\mathrm{HLB} = 1W_1 + 20W_2 \quad (1)$$

where W_1 and W_2 are the weight fractions of oleic acid and sodium oleate, respectively. Their blends of various compositions dissolved in 50/50 mixture of water/oil serve as reference standards. The state of emulsification of any commercial emulsifier could then be observed and matched to that of a corresponding standard of known HLB that exhibits similar behavior.

Another empirical relation, obtained by Davies [15,16], uses the group contributions:

$$\mathrm{HLB} = 7 + \sum H\ (\text{hydrophilic group numbers}) - \sum L\ (\text{lipophilic group numbers}) \quad (2)$$

where ΣH is the sum of contributions of hydrophilic groups, and ΣL is the sum of contributions of hydrophobic groups. This equation agrees that the higher the HLB value, the more polar and hydrophilic the surfactant, and stronger its affinity to water. The HLB group numbers are listed in Table 2. Both approaches to HLB calculation [Eqs (1) and (2)] provide satisfactory agreement, especially considering that HLB is only one factor determining interfacial activity of the surfactant.

As a general guideline, HLB > 11 corresponds to a water-soluble surfactant, and HLB > 9 represents an oil-soluble surfactant. In practice, the solubility in water itself may be used to estimate HLB value of surfactants (Table 3).

HLB is an important characteristic for selecting the right surfactant for the application. According to the HLB value, surfactants can be conventionally divided into several groups according to their application potential, as shown in Table 4.

TABLE 2—Davies' HLB Group Numbers (data from Ref. [16])

Group Type		Group Number
Hydrophilic	$-OSO_2^-Na^+$	38.7
	$-CO_2^-K^+$	21.1
	$-CO_2^-Na^+$	19.1
	R_4N^+	9.4
	–COO–	2.4
	–COOH	2.1
	–OH	1.9
	–O–	1.3
Lipophilic	–CH–	0.475
	$-CH_2-$	
	CH_3-	
	=CH–	
	$-(OCH_2CH_2)_n-$	0.33
	$-(OCH(CH_3)CH_2)_n-$	–0.15

Surface Adsorption

Surface free energy is usually associated with disruption of immediate molecular environments of the bulk phases and formation of an interface. The surface free energy per unit area, defined as surface tension σ, is the minimum amount of work required to create new unit area of that interface (ΔA):

$$W_{\min} = \sigma_o \times \Delta A \quad (3)$$

Therefore, a surface active agent is a substance that, at low solution concentrations, adsorbs on the interface and, thereby, changes the amount of work required to expand that interface, i.e., reducing surface tension. Specifically, at the air/water interface, adsorption of the surfactant is driven by unfavorable hydrophobic interactions. The

TABLE 3—Correlation between solubility of a surfactant in water and its HLB value

	HLB
No dispersability in water	1–4
Poor dispersion	4–6
Non-stable milky dispersion	5–7
Stable milky dispersion	7–10
Translucent emulsion	10–12
Clear (micellar) solution	>12

TABLE 4—HLB ranges and surfactant applications

HLB Range	Application
4–6	Water-in-oil emulsion
7–9	Wetting agents
8–18	Oil-in-water emulsion
13–15	Detergents
10–18	Solubilizers

presence of hydrocarbon groups of the dissolved amphiphilic molecule causes distortion of hydrogen bonding network of water molecules and increase of the free energy of the system. This is known as a hydrophobic effect [17]. Once the surfactant is present in the solution, substantially less work is required to bring a surfactant molecule, rather than a water molecule, to the surface. Hence, migration and preferential adsorption of a surfactant on the interface is a spontaneous process. As concentration of the surfactant in the solution increases, the formation of an oriented and densely packed surfactant monolayer with the hydrophobic tails extends away from the water and the hydrophilic head groups submerge into the water phase [Fig. 3(*a*)].

The surfactant's adsorption at an interface is a dynamic process that quickly establishes its equilibrium between two phases: surfactant dissolved in the media and molecules adsorbed at an interface. Classical equations by Gibbs and Langmuir describe quantitative relationships between the equilibrium adsorption and major affecting factors, such as interfacial surface tension and surfactant concentration Thermodynamics of surfactant adsorption from solution are reviewed in detail elsewhere [1,2,6,8,18].

The key property defining surfactant molecules is their ability to adsorb on an interface and reduce interfacial surface tension. The surfactant's ability to reduce surface tension of a solution depends on both its efficiency and effectiveness [2]. Efficiency is related to the minimum concentration of the surfactant required to produce a given surface tension reduction. Effectiveness of the surfactant is the maximum reduction in surface tension that can be obtained regardless the concentration. Efficient surface active agents have relatively low molecular weight and, therefore, high molecular mobility. Surfactants, which diffuse or migrate rapidly, impart to the paint, by definition, low dynamic surface tension and, therefore, reach equilibrium much faster than higher molecular weight surfactants.

Micellization

Adsorption of a surfactant at the interface occurs over a wide range of surfactant concentrations and is typically complete above a well-defined concentration, called critical micelle concentration (CMC). At the CMC, the interface is near its maximum coverage and, to further minimize the free energy of the system, the surfactant is forced to form aggregates in the bulk. Thus, above the CMC, the system consists of adsorbed surfactant monolayer at the air/water interface [Fig. 3 (*a*)], free monomeric surfactant dissolved in the bulk phase [Fig. 3(*b*)] and micelle aggregates in the bulk phase [Fig. 3 (*c*)]. Dynamic equilibrium is quickly

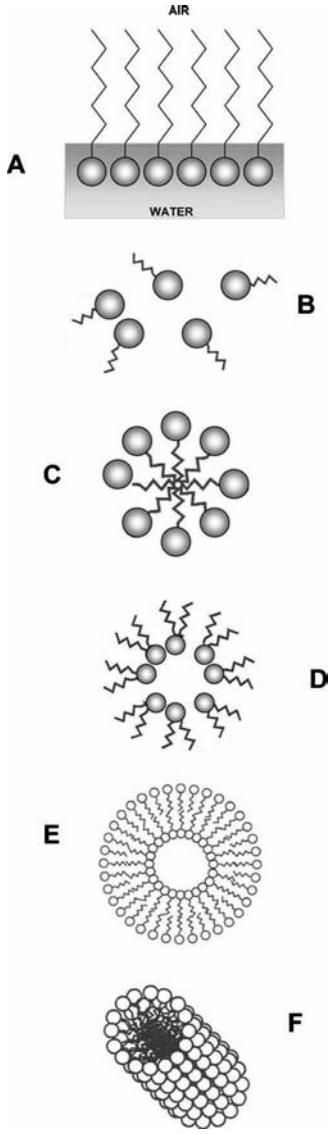

Fig. 3—Schematic illustration of surfactant aggregates: Monolayer (a), monomeric state (b), micelle (c), inverted micelle (d), liposome (e), and rod-like micelle (f).

established between all three states of surfactant existence in the system.

The same mechanism, i.e., "hydrophobic interaction," that causes adsorption of amphiphilic molecules on an interface, also leads to spontaneous association of such molecules to form aggregates or micelles, when their concentration is sufficiently high [1,2,6,8]. Micelle formation occurs over a fairly sharp, well-defined region called CMC. Above the CMC, additional surfactant molecules form the aggregates, whereas the concentration of unassociated surfactant remains fairly constant and equal to the CMC. Most importantly, at much the same concentration, a rather dramatic change in concentration dependence can be observed in common surfactant solution properties (Fig. 4). The sudden change in solution properties is attributed to a significant change in the nature of the solution and formation of aggregates or micelles in solution.

According to Hartley [19], micelles are essentially spherical aggregates with a diameter equal to approximately twice the length of the hydrocarbon chain. The

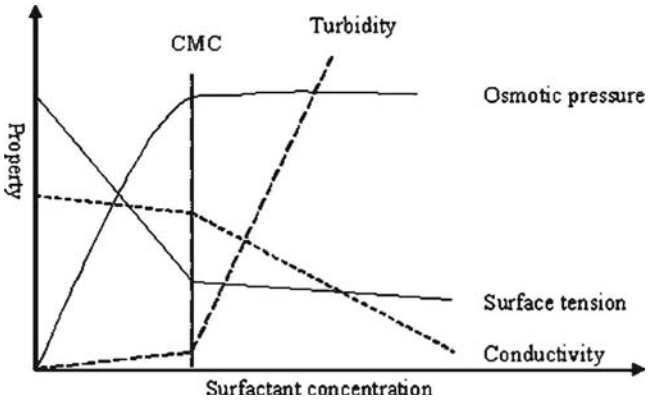

Fig. 4—Schematic representation of the concentration dependence of physical properties of micelle-forming surfactant solutions.

cluster of 50100 surfactant molecules, the core of the micelle, is essentially hydrocarbon free of water or any other polar solvent. The hydrophilic groups remain on the surface of the micelle to allow for maximum interaction with aqueous media. Counter ions are strongly or partially bound to the polar head-groups, thereby reducing lateral repulsive forces between those groups on the surface of the micelle and stabilizing the entire aggregate.

The CMC value of a surfactant depends on many factors, including the experimental method of determining this characteristic [18]. Thus, light scattering techniques are sensitive to the weight average molecular weight and particles size of the micelles. Surface tension and conductivity methods, on the other hand, depend on the number of particles in the solution. Other major factors determining CMC are the nature and structure of the hydrophobic and hydrophilic groups, the nature of counter ion, temperature, and the presence of electrolytes and additives [1,2].

The length of the hydrophobic group is one of the major factors determining CMC. For the homologous series of liner alkyl chains, the CMC decreases logarithmically with increase of carbon number, according to the Klevens equation [20]:

$$\log_{\min}(\mathrm{CMC}) = A - Bn_c \qquad (4)$$

where A and B are constants for a particular homologous series and temperature, and n_c is the number of carbons in the hydrophobic alkyl chain. This equation predicts, rather well, the behavior of linear single-chain surfactants. However, CMC values deviate significantly when alkyl chain branching, double bonds, or aromatic groups are introduced into the hydrophobe moiety. In hydrocarbon surfactants, chain branching increases the CMC value compared to the straight chain surfactant [21]. Presence of a benzene ring in the chain is equivalent to approximately 3.5 carbon atoms [Eq(4)].

Varying the nature of the hydrophilic group from ionic to nonionic has more impact on the CMC of the surfactant than the exact nature of ionic group itself since a major driving force for micelle formation is the entropy factor [1,2]. For a C_{12} hydrocarbon surfactant molecule, the CMC of ionic surfactant occurs in the range of 1×10^{-3} mole/L, while equivalent nonionic surfactant exhibits a CMC in the range of 10^{-4} mole/L.

Since ionic surfactant micelles are formed and stabilized by the interactions of water with the charged head groups, an increase in degree of ion binding (or decrease in electrostatic repulsion between ionic head groups) decreases the CMC. For a given hydrophobic tail and anionic head group, the CMC decreases in the order of $Li^+ > Na^+ > K^+ > Cs^+ > N(CH_3)_4^+ > Ca^{2+} = Mg^{2+}$. For the halide series of cationic surfactants, the CMC decreases in the order of $F^- > Cl^- > Br^- > I^-$.

Presence of electrolytes effectively shields the electrostatic repulsions between ionic head groups, thereby lowering the CMC and increasing aggregation number. Temperature effect on the CMC of ionic surfactants is relatively subtle, owing to the fact that its impact on bonding, heat capacity, and volume is very weak. Nonionic surfactants have more dramatic response to the temperature changes, as elaborated in the discussion of the Krafft and cloud points.

Other aggregates existing in surfactant solutions and described in the literature include rod-like micelles [22] [Fig. 3(*f*)], lamellar [23][Fig. 3(*e*)], and disk or cylindrical aggregates [24]. As the surfactant concentration is increased above CMC, the initially spherical micelles become more distorted in shape and form cylindrical rods and liquid crystals at much higher concentrations.

Solubilization

Solubilization is characterized by the dramatic increase in the solubility of a lipophilic material in the presence of a surfactant at the concentrations above the CMC. This characteristic is frequently used to detect the onset of micellization, even though the lipophilic material itself may affect the value of the CMC [25]. The location of the solubilized species in a micelle is determined primarily by the chemical structure of the additive. In aqueous media, polar molecules are solubilized in the polar surface of the micelle, whereas non-polar additives are strongly associated with the hydrophobic interior of the micelles. More complex molecules containing both polar and non-polar regions may partition between the polar and non-polar regions of the micelles, producing more complex structures. Such complex systems are believed to be stabilized via hydrogen bonding or dipole-dipole interaction between the solute matter and the surfactant [26,27].

Solubilization, similar to the adsorption micellization, is a dynamic process. The average residence time of solubilized molecules have been determined and depend on many factors including temperature, the nature of the solute and its concentration, type of surfactant, concentration, and CMC value [6]. Thus, solubilization increases with increasing surfactant concentration in the region above CMC level. Micelle solubilization capacity is proportional to the length of hydrocarbon chain of the surfactant, which controls CMC and micelle aggregation number. On the other side, the solubilization is expected to decrease with introduction of unsaturation, aromatic groups and hydrocarbon chain branching in the surfactant molecules due to weakened hydrogen bonding, and geometric and packing constraints. Moreover, solubilization depends on the nature of the additive that control its interactions with the surfactant molecules and its molecular size, which determine packing requirements. However, the relationship between the chemical structure of the additive and its ability to be

solubilized by a surfactant solution is rather complex and has not been quantified yet. Temperature has a combined effect on the solubilization process. First, it affects the "parent" process of micellization and may have impact on both CMC value and aggregation number. Second, temperature undoubtedly affects intermolecular interactions, such as hydrogen bonding and hydrophobic interaction, between solvent and solutes.

Cloud Point

Most nonionic surfactant solutions become visibly turbid and cloudy upon heating. Cloud point is defined as a temperature above which the phase separation of surfactant solution occurs. Observed increase in turbidity is the result of increase in aggregation number, augmentation of micelle size, and their more efficient scattering of the light. On the molecular level, more energetic thermal motions available at elevated temperatures weaken specific interactions between surfactant and the media and cause dehydration of the surfactant polar groups. Reduction or complete elimination of hydration shells around surfactant aggregates diminishes or totally eliminates protection against intermolecular interactions. As the result, the micelle-micelle interaction and their subsequent aggregation significantly increase with temperature augmentation. This process occurs in a narrow temperature range and is totally reversible upon cooling.

Cloud point characteristics depend on the chemical structure of the surfactant molecule. For poly(ethylene oxide)(PEO) nonionic surfactants, the cloud point increases with increasing EO content. For a given length of EO block copolymer, the cloud point value decreases by increasing the length of the hydrophobe, broadening the PEO chain length distribution, and introducing branching in the hydrophobe portion of the molecule. However, note that the cloud point could also be affected by the presence of electrolytes [28] and other polar and non-polar additives [29,30] present in the formulation.

The cloud point phenomenon affects many processes including solubilization, foaming, and dispersion. If application temperature is above the cloud point of the surfactant solution, destabilization of dispersion, pigment flocculation, phase separation, and defoaming may occur. The latter could be a very desirable effect since surfactants with cloud points near or below the application temperature are the most effective defoamers.

Krafft Temperature

Solubility of most solutes in water typically increases with increases in temperature. However, for ionic surfactants with low solubility, there is often a temperature at which the solubility suddenly increases very dramatically. This is known as Krafft point or Krafft temperature, T_k, and is defined as an intersection of the solubility and the CMC curves (Fig. 5). Hence, the Krafft temperature is the point at which surfactant solubility equals CMC. Below T_k, surfactant is dissolved only in a single dispersed state and the minimum achievable surface tension will correspond to the concentration of maximum solubility and not the CMC. Above T_k, additional surfactant forms micelles and the solubility rises sharply.

An abrupt increase of surfactant solubility in water with temperature was first noted by Krafft and Wiglow and had since been called "Krafft point" [31]. Originally, due to coincidence of Krafft points and melting points of the hydrocarbon chains, this phenomenon was interpreted as the melting of the hydrocarbon chains of the surfactants. However, current interpretation evolves around the transition between the dissolution of the surfactant to form ions and dissolution to form micelles [2].

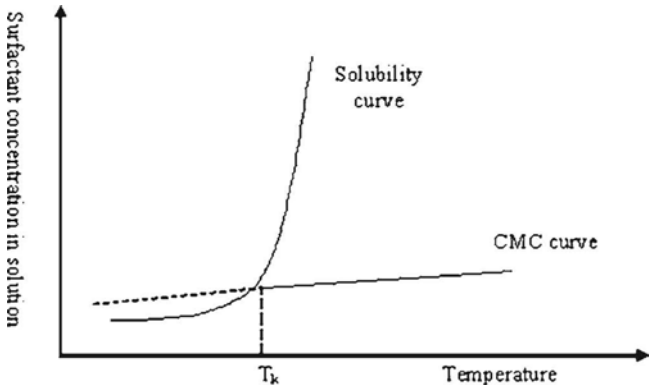

Fig. 5—The Krafft temperature T_k is the point at which surfactant solubility equals the CMC.

T_k varies as a function of both the nature of the hydrophobic group and the character of the ionic interactions between the surfactant and its counter ion. Krafft point is critical for many applications since typical surfactant characteristics such as surface tension reduction and micelle formation cannot be achieved below T_k. Because of their different mechanism of solubilization, nonionic surfactants do not exhibit a Krafft temperature. Characteristic temperature/solubility relationship of nonionic surfactants relies on the delicate balance of specific interactions promoting solubility and thermal motions that destabilize the system. As temperature increases, nonionic surfactants become less soluble and form cloudy suspension (cloud point).

APPLICATIONS

Emulsifiers

The majority of water-based paints consist of aqueous dispersions of water-insoluble polymers made by emulsion polymerization, i.e., lattices. Emulsifiers used for latex preparation are often a combination of both ionic and nonionic surfactants [3,12]. Despite numerous advantages of non-ionic surfactants, they do not completely replace anionic emulsifiers, but rather used in combination for several reasons. First, the presence of anionic surfactants during the synthesis offsets the negative temperature dependence of ethoxylated nonionic surfactants. As elaborated in the discussion of the cloud point phenomenon, temperature increase during the radical polymerization may lead to a decrease in water solubility of the surfactants and a possible phase inversion (from oil-in-water to water-in-oil emulsion). In practice, emulsion polymerizations are often carried out in semi-continuous processes, where the presence of ionic surfactants and adequate reaction cooling circumvent this problem, providing better control over the kinetics and particle size of the resultant latex.

Another reason for using a combination of ionic and nonionic emulsifiers is their enhanced electrolyte stability. Anionic surfactants provide electrostatic stabilization to the latex particles at low and moderate salt concentration.

However, evaporation of water during the storage leads to higher electrolyte concentration and subsequent particle coagulation due to higher ionic strength. Presence of nonionic surfactant provides additional steric stabilization to the latex, preventing it from immediate coagulation upon subtle change in the ionic strength.

Another advantage of using blends of both ionic and nonionic surfactants for emulsification is the fact that adsorption-desorption mechanism is dynamic and driven by many factors including molecular weight of the surfactants, affinity to the surface and media properties. Noteworthy is the fact that nonionic surfactants have a stronger driving force toward the adsorption, which is augmented by the entropy factor. As the result, the ratio of nonionic/ionic surfactants in the adsorbed layer is significantly higher than their ratio in the bulk solution. It is the nonionic surfactant that is responsible for improved sheer and electrolyte stability of the resultant lattices.

Some common ionic surfactants used for emulsification [32] are the sodium and potassium salts of naturally occurring fatty acids, salts of sulfated linear alcohols, salts of alkylbenzene sulfonates and alkylnaphthalene sulfonates, and salts of alkylphosphates. Typical nonionic surfactants may include polyethoxylated alkylphenols and straight-chain alcohols or polyethoxylated polypropylene glycol block co-polymers. Note that the length of the hydrophobic part of the molecule (propylene oxide block, alcohol, or alkylphenol) could be adjusted relative to the hydrophilic part (ethoxylated block) for targeted HLB. While this list is not exhaustive, the combinations of ionic and nonionic surfactants are truly infinite. The primary guideline for selecting the best combination of surfactants is not only the stability of the latex particles, but mainly the application performance of the final product. Since the presence of surfactant in the final dry coating increases its water sensitivity and inadvertently results in surfactant migration to the coating/air and coating/substrate interfaces, the compromise often is necessary in emulsion polymer synthesis.

Wetting Agents

Wetting agents are, by definition, used to improve the wetting of pigment particles and substrate surfaces. Wetting phenomenon involves the displacement of air from a solid surface by a liquid. It also leads to the reduction of the inter-facial surface tension between solid and liquid interfaces.

For a spontaneous wetting to occur, the spreading coefficient of water at a solid surface, $S_{w/}s$, must be positive [1,8],

$$S_{w/s} = \gamma_{s/a} - (\gamma_{s/w} + \gamma_{w/a}) \tag{5}$$

where $\gamma_{s/a}$, $\gamma_{s/w}$ and $\gamma_{w/a}$ are the interfacial surface tensions for the solid/air, solid/water and water/air interfaces, respectively. The presence of surfactant molecules in the system reduces both $\gamma_{s/w}$ and $\gamma_{w/a}$ surface tensions, providing a positive value for the spreading coefficient and prompting spontaneous wetting. Low surface tension of the surfactant solution in the media ($\gamma_{w/a}$) are usually an indication of wetting effectiveness of the surfactant in a given paint formulation.

Wetting is not an issue in the solvent-based paints since their surface tension is usually low enough to spread on any surface. Good wetting agent for a waterborne paint formulation should be a surfactant with a strong ability to adsorb on the interface and ability to reduce surface tension to that of conventional solvent-based coatings, i.e., 25–32 mN/m [3]. These requirements also imply that wetting agents should be hydrophobic surfactants with limited water solubility (HLB 7-9, Table 4). Upon paint application and formation of two new interfaces (coating/air and coating/substrate), the migration of surfactant molecules to these new interfaces is a diffusion-controlled process depending on surfactant availability in the bulk phase. This latter condition is satisfied for surfactants with high CMC, e.g., surfactants containing bulky or branched hydrophobic groups such as Pluronic® WA and Surfynol® products.

Fast surfactant migration is possible for surfactants exhibiting high diffusion coefficient [3]. Since the rate of diffusion decreases with the size of the molecule according to the Stokes–Einstein equation:

$$D = k_B T / 6\pi\eta R_h \tag{6}$$

where k_B is the Boltzmann constant, T is the absolute temperature, η is the viscosity of the solvent, and R_h is the hydro-dynamic radius of the molecule. Large size of the surfactant molecule and corresponding large hydrodynamic radius will prevent it from fast diffusion rendering it a poor wetting agent. Therefore, lower molecular weight surfactants are preferred to achieve more efficient wetting.

Dispersing Agents

Pigments provide various optical properties and special effects, influencing corrosion resistance and mechanical characteristics, adhesion and rheology, and imparting mechanical strength and protective properties. The performance of pigments, however, depends on many factors, including their chemical structure, particle size, and degree of dispersion. The latter is a function of pigment wetting and stabilization and could be largely influenced by the presence of dispersant agents or lack thereof.

Dispersing additives improve the incorporation of pigments and fillers in a coating and ensure their stability during manufacturing, storage, and application processes. Dispersant agents coat suspended pigment particle to form a barrier that, either by ionic repulsion or steric hindrance or both, prevents particle-particle contacts and aggregation [33].

A surfactant's unique ability to adsorb preferentially at the interface is the essence of their application as pigment-dispersant agents. In aqueous systems, the hydrophobic groups of nonionic surfactants are adsorbed on the particle surface, with the hydrophilic groups extending into the bulk of the aqueous media. This partitioning provides not only the reduction of interfacial tension but also steric stabilization around the particles. Such stabilization is the result of steric hindrance created by the chains of the surfactants solvated in the liquid phase. Additional charge stabilization could be provided by ionic surfactants, which adsorb to generate surface charge and repulsive forces, preventing agglomeration of two or more particles with the same charge. Better understanding of the stability characteristics of the colloidal system is provided by the well-known DLVO theory [34] that accounts for attractive van der Waals and repulsive electrostatic forces in suspensions. Both electrostatic and steric (entropic) stabilization may be

combined to achieve maximum stabilization effect in the system. Such electrosteric stabilization is very common for paint formulations.

Pigment dispersion process involves initial particle wetting, particles separation, dispersion in the media, and stabilization against flocculation. Improved pigment dispersion is realized initially by modifying the surface of the pigment. This is typically achieved by adsorbing a surfactant during pigment manufacturing without disclosing particular details of surface treatment. Dispersant agents in the paint formulation adsorb on the particle's interface to form loose assemblies and further prevent agglomeration. Block or graft copolymers are proven to be very effective dispersant agents that adsorb and anchor to the pigment particle and further lower the interfacial surface tension.

The main distinction between dispersing and wetting agents is that a dispersing agent must wet, anchor to the surface of the pigment particle, and provide a connecting link between the particle and the dispersion media. In order to be an effective dispersing agent, a surfactant molecule should meet a number of structural requirements that are somewhat different from those of wetting agents. Thus, a dispersing agent molecule must be long enough to provide adequate wetting by adsorbing on the surface and provide steric stabilization by protruding to the media. Effective anchor groups should have high affinity to the pigment and have little or no solubility in the media. Wetting agents typically have much shorter chain length and are not effective dispersants.

Organic polyelectrolyte dispersants are the most common type of dispersants of inorganic pigments used in waterborne paints [3]. Polymeric phosphates, polyacrylates, polyamines, and other polymers of relatively low molecular weight have the advantage of providing sufficient anchoring at the particle surface. This is favored by polymeric structure of the molecules and quick adsorption rate, which is controlled by keeping the molecular weight of the molecules relatively low.

Organic pigments are generally more hydrophobic than inorganic pigments and require the use of various types of ionic and nonionic surfactants for their dispersion. Alkylbenzene sulfonates and alkylphenol ethoxylates with relatively long poly(ethylene oxide) chains of 20–30 ethylene oxide units are the most commonly used dispersant agents. However, with the increased attention to the perceived environmental effect of alkylphenol ethoxylate surfactants and their slow biodegradation, they are gradually being replaced by linear and branched alkyl alcohol ethoxylates. Unfortunately, even after matching the HLB values of alkylphenol ethoxylate, fatty alcohol ethoxylate are still lacking the benzene moiety that provides additional electron donor-acceptor mechanism of interaction with pigment surfaces.

Due to vast diversity of pigment structures, particle size, and paint formulations designed for different applications, there is no universal wetting or pigment dispersant agent that would work in every formulation. Preference is given to a particular surfactant based on performance and environmental considerations, cost, and availability.

Foaming and Antifoaming Agents

Foam is created when air is introduced into paint during manufacturing or application. Complex paint formulations include several vehicles that promote foam stabilization, i.e., wetting agents, dispersants, and emulsifiers. These surfactants stabilize the foam due to one or several mechanism available to them including hydrogen bonding, ionic, and van der Waals forces. Foaming is highly undesirable and almost unavoidable. It reduces manufacturing efficiency and causes film defects. This necessitates the use of foam control agents—surface-active additives that prevent, reduce, or eliminate foaming during manufacturing and application.

Physically unstable foam composed of thin lamellae-structured film of surfactant with water molecules trapped inside. Foam stabilization mechanism is associated with well-known Marangoni–Gibbs effect [3,18]. The thinning of the foam lamellae leads to a surfactant's concentration gradient, which, in turn, establishes a surface tension gradient. The surface transport of the surfactant molecules from low to high surface tension region (Marangoni flow) will eliminate the gradients, but will also pull water molecules in the process, thus restoring the width of the lamella and preventing it from complete drainage. Ionic surfactants assist in foam stabilization by creating electrostatic repulsion between the two sides of the film. Additionally, they provide high osmotic pressure due to the presence of high concentration of counter ions. Since none of these mechanisms are available in the absence of ions, nonionic surfactants produce less foam and less stable foam, thus offering a substantial benefit of utilizing nonionic surfactants in coatings.

Foaming is resolved by creating inhomogeneities in the surface tension of the foam lamellae to cause instability and ruptures. Such effects can only be achieved if defoaming additives have a very limited compatibility with the aqueous media. These molecules also must have a positive entering (E) and spreading coefficients (S) to enter the foam lamellae and spread at the interface, and be able to adsorb the surfactant and drastically reduce lamellae stability [18],

$$S = \sigma_f - \sigma_{a/f} - \sigma_a \tag{7}$$

$$E = \sigma_f + \sigma_{a/f} - \sigma_a \tag{8}$$

where σ_f is a surface tension of the foaming medium (such as aqueous), $\sigma_{a/f}$ is an interfacial tension between media and antifoam, and σ_a is the surface tension of the antifoam. Typically, foam control agents are hydrophobic molecules with low surface tension in the range of 20–25 mN/m [3], present in the small amounts, less than 5%.

In addition to quantitative calculations, the simple and most straightforward method for defoamers' evaluation is simply to shake a measured amount of surfactant solution in a graduated cylinder or other suitable container, under controlled conditions (rpm, temperature, time, and concentration), and note the amount of the foam generated and the rate of its disappearance. Defoaming effectiveness is rated in comparison to the control solution with no defoamer present [35].

There are two types of foams—macrofoams and microfoams [36]. The former consists of polyhedral foam bubbles that, once they rupture and dry, produce craters in the coating films. The latter is revealed by the existence of small spherical air bubbles dispersed throughout the paint that produce pinholes. Foam control agents are called antifoams

if they prevent or retard foam formation, or defoamers if they destroy already existing foam. All antifoams are defoamers but not all defoamers are antifoam agents.

Defoamers generally fall into two main categories: silicon-based and silicon-free organic defoamers. Silicon defoamers are based on polydimethylsiloxane chemistries and combine non-volatility with low surface tensions. They proved to be outstanding "universal" defoamers, but find limited application due to high cost and substantial contribution to coating defects, such as fish eyes, poor recoatability or loss of adhesion. Moreover, with the increased general pollution of siloxanes in Nordic countries, less toxic non-silicon defoamers are promoted by the manufacturers. For example, surfactants based on propylene oxide (Pluronic® L101 and 25R1 surfactants), silicone backbone (Gold-schmidt's Tegopren® surfactants), and fluorochemical backbones [37] are very effective "foam killers."

Unfortunately, there is no single universal defoaming agent that would prevent foam formation in all systems. Paints are very complex formulations and potentially any constituent could affect either foam behavior or the effectiveness of the defoamer [38].

Coalescent Agents

Coalescing agents aid film formation, improve leveling, gloss, adhesion, and scrub resistance. Prior to the VOC regulations, high-boiling solvents were used as coalescing agents to provide better coalescence or fusion of polymer particles by reducing the T_g in polymer particles below minimal film formation temperature (MFFT). Examples of these additives include Union Carbide's Carbitol®, carbitol acetate, Butyl Cellosolve® acetate, butyl carbitol acetate, and hexylene glycol products.

In contrast to coating resins dissolved in a solvent, latex paint undergoes several steps during the film-forming process [39,40]. Initial stages of this process involve water evaporation accompanied by significant reduction of inter-particle distances. In order to achieve direct contact, the electrostatic repulsion forces between the spheres, which originally provided for the stability of the dispersion, must be overcome. Upon further reduction of the total volume beyond the point of inter-particle contact, sufficient deformation and interdiffusion of the particles is required for true film formation. This is possible when the capillary forces and the surface tension forces are larger than the deformation resistance,

$$pressure\ of\ deformation = C\gamma_{PA}R \tag{9}$$

where γ_{PA} is the polymer/air interfacial tension, R is the particle radius, and C is a constant. Capillary forces are equally important for particle deformation. Thus, Eckersley and Rudin [41,42] illustrated that even though the capillary forces cannot cause coalescence, the combination of capillary and interfacial forces gives enough coalescing force. Later, this theory has been challenged by Dobler [43], who studied core shell latexes. The theory, describing the interdiffusion of particle surfaces, was further developed by Winnik et al. [44], who proved that PEO stabilization also promotes interdiffusion and possibly plasticization.

Deformation pressure is related to physical properties and glass transition temperature of the resin and frequently assessed in terms of MFFT. In practice, film formation process can only occur at a temperature above glass transition (T_g) of the polymer, or, more precisely, above the MFFT. As the result, the processing temperature (T_p) could be controlled either by a corresponding selection of monomers or by the addition of external plasticizers to meet the following condition:

$$T_p \geq \text{MFFT} \tag{10}$$

This theoretical and practical limitation is circumvented by the addition of film-forming or coalescing agents. Their behavior could be explained by the so-called three-phase model [45]. This model takes into consideration the fact that a coalescent agent is distributed among three phases: Water, particle nucleus, and particle shell. Only its presence in the shell of the particle is essential for the film formation. The plasticizer effect and impact on the film formation is marginal, if the coalescent agent is too hydrophobic, and predominantly located in the nucleus of the particles, or too water soluble and, thus, primarily located in the water phase.

Organic solvents, in general, are very effective coalescing aids due to their small molecular size, high diffusion coefficient, and closely matched interaction parameter. They successfully and temporarily lower the T_g of the polymer and affect polymer diffusion rate in the film prior to their complete evaporation. Alternatively, nonvolatile coalescing aids remain in the film and impart more permanent change to the polymer physical properties. Examples of nonvolatile coalescing aids used in coatings include alkylphenol ethoxylates ($C_nPhO–EO_x$), particularly NP20 ($n = 9$, $x = 20$), which was shown to increase the rate of PBMA polymer diffusion [46]. Pluronic® surfactants EO-PO-EO or PO-EO-PO of approximately 2,000 molecular weight and 50 % copolymer compositions also reduce T_g of the PBMA polymer by 3 and 8°C, respectively [47].

Coating Defects

Most common coating problems could be attributed to one of the two main causes: defects driven by surface tension and pigment dispersion problems. The former includes cratering, telegraphing, sinks and bumps, crawling, and beading. The latter manifests itself in flooding, floating, poor color development, and insufficient gloss, which could be solved, at least partially, by carefully selecting a dispersant agent better suited for a particular application.

Surface-tension-driven defects are formed in the presence of and in the vicinity of surface tension gradients caused by contaminants, such as oil, or by temperature and surfactant concentration gradients across the surface of the coating. An established surface tension gradient will cause the material to flow from low to high surface tension area until the driving force is diminished or the materials cure and resist the flow.

Poor initial wetting of the substrate and subsequent dewetting could yield crawling defects. Solution to this problem involves a better cleaning of the substrate surface or addition of wetting agents to the paint. Surfactants, however, do not differentiate and could migrate to both substrate/coating and coating/air interfaces. When used in excess, surfactants could improve wettability of the

substrate but also weaken the adhesion and cause difficulties during touch-up and re-coating applications.

CONCLUSIONS

In summary, it is important to emphasize that surfactants remain to be the key paint additives. They enable water-based paint technology to reduce paint surface tension, wet the substrates, aid in film formation, disperse pigments, and emulsify polymers. The term surfactant is used as a general term for surface active agents. In paint applications, these include wetting agents, dispersants, emulsifiers, coalescent agents, and defoamers. In addition to numerous and frequently conflicting functions of surfactant additives in paints and coatings, high paint performance standards and growing environmental concerns are important practical considerations for paint formulators. Volumes of publications and decades of experience do not change the fact that surfactants applications in coatings, although based on strong scientific foundation, mainly rely on empirical guidelines and remain to be an art. Where wetting agents are used to improve surface wetting and assist pigment dispersion, foam issues may arise and contribute to coating defects. Likewise, anionic surfactants, useful for electrostatic stability of dispersions and freeze/thaw stability of the lattices, yield excessive water sensitivity that shortens the longevity of the coatings.

Because of the complex interactions of surfactant molecules with multi-component paint systems, it is practically impossible to design universal additives, or accurately predict their impact on a particular formulation. As a result, a particular choice of surfactant additives depends on many factors including the nature of the coating formulation and its intended use. However, it also represents a delicate balance of desirable and undesirable properties for the final coating.

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Coalescing Aids

Kevin W. McCreight[1]

LATEX PAINTS CONTAIN FINE DISPERSIONS OF high molecular weight film-forming resins in water. Common film-forming resins include vinyl acetate-acrylic co-polymers, vinyl acetate-ethylene copolymers, acrylic copolymers, or styrene-acrylic copolymers although many other types of systems are also commercially available. Formulations of latex paints are complicated by the presence of pigments, surfactants, dispersants, biocides, defoamers, thickeners, freeze-thaw stabilizers, and coalescing aids. Paints must be formulated such that good stability and excellent coating properties can be achieved over a wide range of application conditions. Many important paint properties, including scrub resistance, porosity, and gloss, are linked to the quality of film formation that is achieved. Film formation in latex paints is promoted by the addition of coalescing aids, which enable the latex particles to consolidate and yield a continuous film.

HISTORY

Latex paints based on styrene and butadiene copolymer were first commercialized in about 1946 and rapidly developed wide acceptance in the marketplace [1]. Other film-formers of this period included vinyl acetate, acrylates, styrene, and vinyl chloride copolymers [2]. Since many of these latexes had relatively high glass transition temperatures, it was understood early on that plasticizers, such as phthalates or phosphates, were required in order to achieve good film formation. In a paper written by Green in 1953, it was noted that plasticizers should be liquids that are solvents for the film-forming resin and exhibit low color, mild odor, non-flammability, and minimal toxicity [3]. These comments were echoed in a paper written by Sullivan in 1954, which also stated that the primary function of the plasticizer is facilitation of film formation through solvation of the resin in the paint [4]. Subsequent work illustrated that overuse of plasticizers could lead to paint films with poor scrub resistance and increased dirt pickup [5]. These issues arose from the extremely low volatility of the plasticizers, which caused them to persist to a significant degree after film formation had occurred. In order to overcome the problems that had been encountered with plasticizers, the concept of coalescing aids was introduced. Coalescing aids have higher volatility than plasticizers, which enables them to facilitate film formation and then evaporate such that scrub resistance and dirt pickup are not negatively impacted. Early coalescing aids included hexylene glycol, ethylene glycol monoethyl ether, diethylene glycol monoethyl ether acetate, ethyleneglycol monobutyl ether acetate, and diethylene glycol monobutyl ether acetate [5]. In 1963, a patent was issued for 2,2,4-trimethyl-1,3-pentanediol monoisobutyrate (Tex-anol® Ester-Alcohol) [6], which became the most widely used coalescing aid for latex paints [7]. Coalescing aids that are currently used include glycol ethers, ester-alcohols, glycol ether-esters, esters, and glycols. These materials vary widely in evaporation rate and hydrophobicity.

INTRODUCTION TO COALESCING AIDS

In relation to latex paints, coalescence may be defined as the process by which latex particles come into contact with one another and unite to form a continuous homogeneous film. The process of coalescence is governed by the glass transition temperature (T_g) of the paint system (including coalescing aids and other additives). T_g may be defined as the temperature at which the onset of cooperative segmental backbone motion occurs in a polymer chain. In other words, a polymer below its T_g acts "glassy" since the molecules have no short-range mobility, while a polymer above its T_g is "rubbery" and the molecules are free to move. In order for film formation to occur, the polymer molecules in the latex must have sufficient mobility to interdiffuse across the boundaries between latex particles under a range of application conditions (temperature and humidity). A coalescing aid acts as a temporary plasticizer to reduce the T_g of the latex below that of the application or drying temperature to enable good film formation. Fig. 1 provides a simplified illustration of the impact of a coalescing aid on the T_g of a paint. In section A, it is seen that T_g of the paint is significantly higher than the desired minimum application temperature. Under these conditions, the latex particles cannot coalesce since the polymer molecules that compose the latex are in the glassy state and do not have sufficient mobility to enable film formation. Section B illustrates the same paint after the addition of an appropriate amount of a coalescing aid. The coalescing aid reduces the T_g of the paint below that of the minimum application temperature and enables mobility of the polymer molecules in the latex such that particle coalescence can occur. After application of the paint, the water and the coalescing aid begin to evaporate from the coating (section C). Although Fig. 1 illustrates the evaporation of the water and coalescing aid as discrete events, they actually evaporate simultaneously (although the rate of evaporation of the coalescing aid is generally much slower than that of the water, as indicated). While the coalescing aid evaporates,

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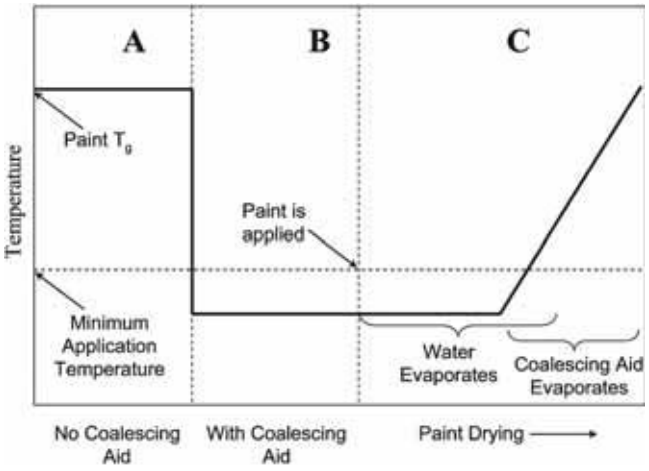

Fig. 1—Impact of coalescing aid on T_g of a paint applied at the minimum application temperature.

the T_g of the paint film increases and returns to approximately its uncoalesced value. As T_g increases, the polymer molecules become much less mobile and a well-coalesced block resistant film is formed. Plasticizers may be added to a paint formulation to enable film formation, but since they tend to evaporate extremely slowly, they must be used judiciously in order to prevent the coating from remaining tacky, which may manifest itself as problems with block resistance and dirt pickup.

AN OVERVIEW OF FILM FORMATION

There have been numerous studies on the mechanism of film formation [8–19] and while there is some disagreement as to the detailed driving forces for coalescence, there is general agreement in a three-step depiction of the process. Fig. 2 provides a general model of the stages that proceed as a latex paint dries. Initially, water evaporates from the system and the latex particles become more closely packed—also known as consolidation. As the coating continues to dry, the particles begin to contact one another, deform, and compact. This process is believed to be driven by capillary pressures or van der Waals forces that occur in the interstices between adjacent latex particles as drying proceeds. [8,9] Coalescing aids facilitate compaction by reducing the elastic modulus and yield strength of the particles. [10] Finally, coalescence occurs by the diffusion of polymer molecules across the latex particle boundaries and a strong, continuous film is formed.

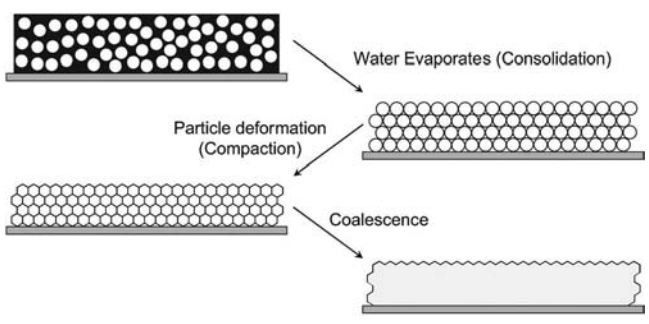

Fig. 2—A simplified view of the film formation process.

REQUIREMENTS FOR EFFECTIVE COALESCING AIDS

Coalescing aids must meet several important criteria in order to be considered for use in latex paints. The issue of primary importance involves the compatibility of the coalescent with not only the common film-forming resins, but also all of the other paint components including pigments, thickeners, surfactants, and freeze-thaw stabilizers. The coalescing aid must also efficiently reduce the T_g of the system. Many coalescing aids are considered to be volatile organic compounds (VOCs), and therefore selection of an efficient coalescent minimizes the amount of VOC that must be added to a formulation in order to meet minimum application temperature requirements. Evaporation rate of coalescing aids is important since the majority of the water needs to leave the paint system prior to the coalescent, regardless of the conditions of temperature and humidity. As a result, most coalescing aids tend to have relatively low evaporation rates in order to ensure that film formation can be achieved. Coalescing aids must also exhibit reasonable hydrolytic stability under the relatively high *p*H conditions that are common in latex paints. Hydrolysis of a coalescing aid can lead to reductions in coalescing efficiency and shelf stability. The water solubility (or insolubility) of a coalescing aid impacts the extent to which it partitions between the latex and the water. It has been found that relatively water insoluble coalescing aids function very effectively since they partition largely to the latex, which enhances their efficiency [20] Other important properties for coalescing aids include a low freezing point (so that the coalescent does not solidify at low application temperatures), low odor, low color, reasonable cost, and acceptable properties from a health, safety and environmental (HSE) perspective.

PERFORMANCE EVALUATION OF COALESCING AIDS

Coalescing Efficiency

One of the most important properties of a coalescing aid is how efficiently the material can reduce the T_g of a latex. Since measurement of the impact of a coalescing aid on the T_g of a latex is not straightforward by use of differential scanning calorimetry, a minimum film-forming temperature (MFFT) instrument is used in accordance with the ASTM Test Method for Minimum Film Formation Temperature of Emulsion Vehicles (D2354, withdrawn in 2007 but still available). MFFT may be defined as the lowest temperature at which a system can form a coherent film, and generally has a value relatively close to T_g. A MFFT instrument consists of a stainless steel plate with a specified temperature gradient along its length. By preparing mixtures of a latex and coalescing aid at various coalescent concentrations, a determination may be made as to the MFFT of a system as a function of coalescent level. Fig. 3 provides an illustration of a typical MFFT bar set with a temperature gradient of 0–18°C. Five coalescing aid/latex mixtures have been drawn down on the bar under controlled conditions of temperature and humidity, with coalescent concentration increasing from the front (near side) of the bar to the back. The part of the film that appears to be white is not coalesced since in that temperature range, the polymer molecules have insufficient mobility to interdiffuse. The

Fig. 3—Minimum film-forming temperature apparatus (temperature range of 0–18°C).

point at which the film changes from white to clear is designated as the MFFT for that particular blend. As more coalescing aid is added to the latex, the MFFT of the system decreases since the additional solvent allows sufficient molecular mobility for lower temperature film formation. From this type of test, a plot can be made of MFFT as a function of coalescent concentration for a given latex and coalescing aid combination. Fig. 4 demonstrates the impact of three different coalescing aids in a typical latex with a MFFT of about 15°C. Coalescent **A** is more efficient than coalescent **B** since at a given MFFT, a given quantity of **A** yields a lower MFFT than an equivalent amount of **B**. If a manufacturer specifies a minimum application temperature of 10°C, in order to have a reasonable margin of safety, a MFFT of 5°C might be selected. From Fig. 4, it can be seen that 3.2 parts per hundred parts of resin (phr) of **A** is necessary while 4.7 phr of **B** is required. Coalescent **C** is ineffective in conjunction with this latex since it provides no reduction in MFFT regardless of the level of incorporation. An estimate of the overall efficiency of a coalescing aid may be obtained by preparing blends of a given material with a wide range of latex types and determining the total amount of coalescent necessary to achieve a target MFFT. Paints that contain high T_g industrial maintenance type latexes require a significantly higher quantity of coalescing aid compared to the low T_g latexes that are used for interior flat paints. In addition to MFFT measurements, atomic force microscopy (AFM) proves to be a useful technique for observation and quantification of the extent of coalescence. Fig. 5 demonstrates the appearance of a high T_g (~40°C) acrylic latex with two different amounts of a typical coalescing aid—5 phr for **A** and 10 phr for **B**. The left side of each image represents the height in the vertical direction and gives a feel for surface roughness, while the right side of the image provides phase contrast between the hard and soft sections of the latex particles. Note that in **A**, there is insufficient coalescing aid to form a homogeneous film, while in **B** there is a marked decrease in surface roughness, and the particle boundaries are less well-defined.

When considering coalescing efficiency, it is important to consider the impact of substrate and substrate porosity on paint performance. Since water soluble coalescents partition predominantly to the water phase, it has been suggested that porous substrates could absorb both the water as well as some of the solubilized coalescent [21]. In this case, the residual coalescing aid in the paint may be insufficient to provide for adequate film formation, especially under adverse conditions (see illustration in Fig. 6). Perera has examined the potential for selective penetration

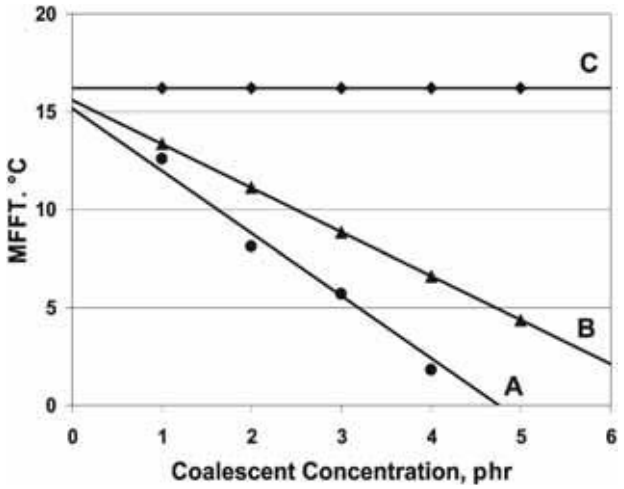

Fig. 4—Impact of coalescing aid concentration on MFFT of a typical latex.

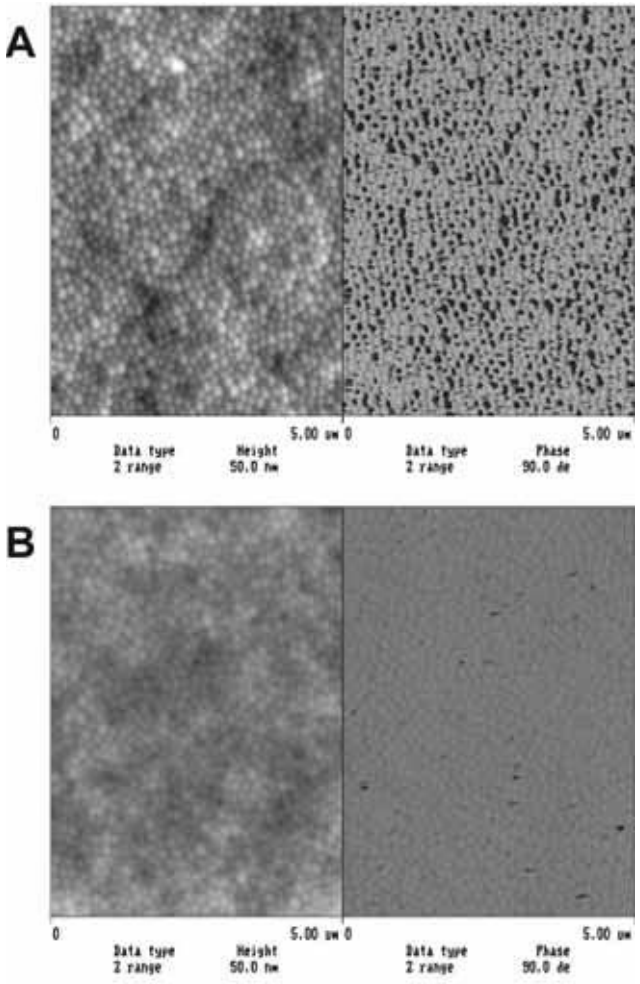

Fig. 5—AFM images of a high Tg acrylic latex with coalescent levels of (A) 5 phr and (B) 10 phr—the height image is on the left, and the phase image is on the right.

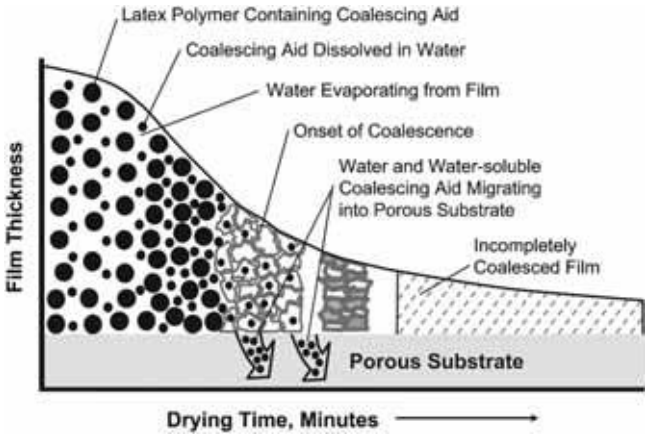

Fig. 6—Impact of using a water soluble coalescing aid in paint applied over a porous substrate [21].

of paint components into common substrates by evaluating paint T_g and the concentration of coalescent and binder in the substrate for several types of paint [22]. His work suggested that penetration of the binder and coalescing aid into porous substrates leads to increases in both the T_g and pigment volume concentration.

Evaporation Rate

The evaporation rate of a coalescing aid is measured relative to a standard such as *n*-butyl acetate in accordance with the ASTM Test Method for Evaporation Rates of Volatile Liquids by Shell Thin-Film Evaporometer (D3539). As stated previously, the evaporation rate of the coalescing aid needs to be significantly slower than that of water regardless of temperature and humidity conditions. Fig. 7 provides an illustration of the variation in the evaporation rate of water as a function of relative humidity at 25°C. A coalescent with a fast evaporation rate may not adequately coalesce a paint under high humidity conditions, while a very slow evaporating coalescent has the potential to remain in the coating too long, which may result in poor hardness development, blocking problems, and dirt pickup.

Hydrolytic Stability

Hydrolytic stability of a coalescing aid may be evaluated by combining the material with a high *p*H latex (generally above 9.0) and holding the system at elevated temperature (usually 50°C). The *p*H of the system is then monitored over a period of four weeks. Dramatic reductions in *p*H are often associated with hydrolysis of a coalescing aid, which can negatively impact paint performance.

Water Solubility

Water solubility of a coalescing aid may be determined by preparing a 50/50 v/v mixture of coalescent and distilled water which is agitated. If separation occurs, samples can be taken from each of the layers to be quantified using a technique such as gas chromatography (GC). Alternative measures of water solubility are the ASTM Test Method for Partition Coefficient (N-Octanol/Water) Estimation by Liquid Chromatography (E1147) and the ASTM Test Method for Measurements of Aqueous Solubility (E1148). In general, water insoluble coalescents function with maximum efficiency since the majority of the solvent partitions to the latex particles where it can effectively act to reduce the T_g of the film former. The extent of partitioning may be expressed by means of the distribution coefficient, which is the ratio of the concentration of coalescent in the water to its concentration in the latex. Distribution coefficients may be determined experimentally by a centrifugation/GC technique [20]. In addition, models have been developed to predict partitioning behavior of coalescents [23]. There is some data to suggest that hydrophobic coalescing aids (which partition more extensively to the polymer) lead to an increase in latex particle size while hydrophilic coalescents can actually lead to slight reductions in particle size [24]. A simple model for the location of a coalescing aid in a latex paint has been developed by Mercurio [25]. As shown in Fig. 8, the location of a coalescent in a paint system can be characterized by location **A** (the interior of the latex particle), **B** (the surface of the latex particle), **C** (the aqueous phase), or a combination. The most efficient coalescing aids tend to reside in the **AB** region, which encompasses the most critical region for film formation.

Odor

Although odor is becoming an increasingly important property in paints, particularly for institutional use, it also tends to be very subjective. Coalescing aids can contribute to odor in latex paints, but the impact a single raw material on the odor of a paint formulation is not easily quantified. A paper has recently been published by researchers at the

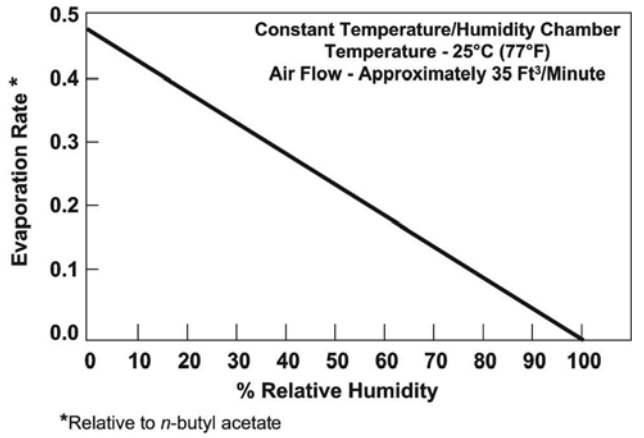

Fig. 7—Effect of relative humidity on the evaporation rate of water at 25°C.

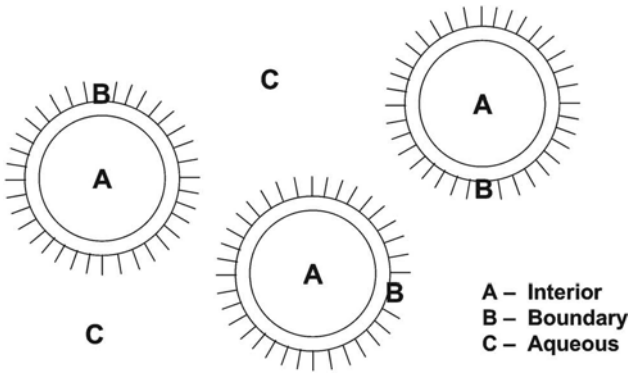

Fig. 8—General schematic for coalescing aid distribution in a latex paint (after Mercurio [25]).

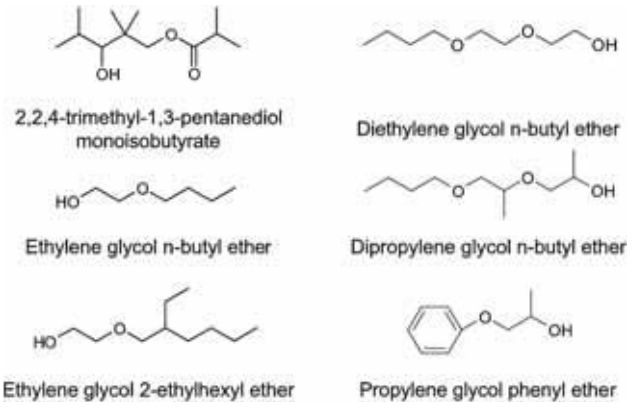

Fig. 9—Chemical names and structures of common coalescing aids.

Monell Chemical Senses Center that addresses the impact of a common coalescing aid on odor perceptions in formulated paints [26].

STRUCTURES AND PROPERTIES OF COMMON COALESCING AIDS

Fig. 9 illustrates the names and structures of some of the more widely used coalescing aids. The most common coalescents are ester-alcohols and glycol ethers. Table 1 provides a summary of the evaporation rate, water solubility, and partitioning behavior of these same coalescing aids. The majority of these materials have slow evaporation rates relative to n-butyl acetate (0.002–0.006). In the case of ethylene glycol monobutyl ether, the evaporation rate is 0.06, which is close to the evaporation rate of water at about 85 % relative humidity and 25°C. Under hot, humid conditions, a fast evaporating coalescing aid, such as ethylene glycol monobutyl ether, may evaporate at a comparable rate to the water, which may leave insufficient coalescent for complete film formation. An appropriate coalescing aid should be selected so that (1) coalescence can be achieved under the most adverse conditions of temperature, humidity, and substrate and (2) the coalescing aid will evaporate from the film at a rate that will allow adequate property development. Coalescing aids are commonly blended to provide an optimized evaporation rate for a given paint and the associated application conditions. Table 1 demonstrates that the majority of common coalescing aids have relatively minimal water solubility and partition predominantly to the latex particle and its surface (the AB region). More hydrophilic glycol ethers, such as ethylene glycol monobutyl ether and diethylene glycol monobutyl ether, are completely water soluble and partition in the **BC** region. Although these water soluble coalescing aids may not provide optimum efficiency in systems applied to porous substrates, they may improve freeze-thaw stability and open time since they have a significant presence in the aqueous phase of the paint [25].

GUIDELINES FOR INCORPORATING COALESCING AIDS

Although a properly selected coalescing aid should be compatible with the remainder of the paint components, some care must be exercised during formulation to prepare a paint with the expected performance properties. Most hydrophobic coalescing aids can be successfully added directly to the letdown, assuming the latex is relatively stable. In contrast, certain highly hydrophilic coalescents, such as ethylene glycol monobutyl ether, can "shock" or destabilize the latex if added directly to the letdown. These coalescents can be successfully incorporated by premixing with some water prior to being added to the paint. In some cases, a portion of the coalescent may be added to the grind, where it may reduce surface tension and may function as a pigment dispersant.

INFLUENCE OF COALESCING AIDS ON PAINT PROPERTIES

Coalescing aids have significant impact on the properties of paints due to their function in film formation as well as their interaction with other additives in the formulation. Not surprisingly, coalescing aids have major effects on properties that relate to the quality of film formation, such as scrub resistance, gloss, color development, and weathering.

Scrub Resistance

Scrub resistance of a coating may be evaluated according to the ASTM Test Method for Scrub Resistance of Wall Paints (D2486). This method simulates the resistance of a paint to cleaning with an abrasive cleaner and a nylon bristle brush. Scrub resistance is generally measured after the paint is allowed to dry for at least a week, during which time the majority of the coalescing aid evaporates from the coating. In common architectural coating for-

TABLE 1—Physical properties and partitioning characteristics of common coalescing aids

	Evaporation Rate (*n*-BuOAc=1)	% Solubility in Water	Partitioning Properties[a]
2,2,4-trimethyl-1,3-pentanediol monoisobutyrate	0.002	Insoluble	AB
Ethylene glycol monobutyl ether	0.060	100 %	BC
Ethylene glycol mono 2-ethylhexyl ether	0.003	0.2 %	AB
Diethylene glycol monobutyl ether	0.003	100 %	BC
Dipropylene glycol monobutyl ether	0.006	5 %	ABC
Propylene glycol monophenyl ether	0.002	2 %	AB

[a]See Fig. 8 for description of partitioning designations.

mulations, paints with no coalescing aid have minimal scrub resistance while the addition of increasing amounts of coalescent increases scrub resistance up to a point. If an excessive amount of coalescing aid is used, the latex can be softened to the point that the scrub resistance of the paint is reduced. Although plasticizers can aid in film formation, their use in paints has the potential to reduce scrub resistance since they evaporate extremely slowly, which may cause the paint film to remain soft. Early block resistance (hardness development) of a latex paint can also be reduced by overuse of plasticizer or slow evaporating coalescing aids.

Gloss

Gloss of a paint film is also related to the quality of film formation. In general, smoother coating surfaces yield higher gloss. Specular gloss is most commonly measured using a glossmeter in accordance with the ASTM Test Method for Specular Gloss (D523). A poorly coalesced film will have lower gloss than a well-formed film. Proper choice of coalescent is critical to the development of acceptable gloss under harsh conditions (for example, low temperature and high humidity). Under adverse conditions, a very volatile coalescing aid may not allow development of good gloss since the coalescent may evaporate before it can function to enable film formation.

Color Development (Low Temperature Coalescence)

Film formation may also be analyzed by comparing the color obtained from a slightly tinted paint at two temperatures (room temperature and 4.5°C) by the ASTM Test Method for Low Temperature Coalescence of Latex Paint Films by Porosity Measurement (D3793). To achieve similar color development under two temperature conditions, a coalescing aid must provide equivalent film formations in both cases. If an insufficient amount of coalescent or a coalescent that does not provide adequate film formation under adverse temperature conditions is used, the color may not match. This could be an issue if part of a room is painted under a given set of environmental conditions, and the rest of the room is painted at a later time and the temperature and/or humidity have changed drastically.

Block Resistance

Block resistance testing provides insight as to the tendency of two painted surfaces to stick together when they come into contact with one another, such as in the case of doors and windows. Testing is carried out in accordance with the ASTM Test Method for Blocking Resistance of Architectural Paints (D4946), which specifies that the painted surfaces be placed face to face at 50°C for a set period of time and applied weight. The degree to which the painted surfaces can be separated from one another to one another after testing is referred to as the block resistance. The ASTM method is sometimes referred to as a "heated block" test, and in some cases variants such as the "room temperature block" or "wet block" may also be reported, although under different conditions of sample preparation, applied weight, paint cure time, and temperature of the testing. If a paint film is too soft or poorly coalesced when tested, block resistance will be poor. Appropriate selection of coalescing aids is critical when working with high T_g latexes, which may require significant amounts of coalescent and can lead to a balancing act between achieving low temperature coalescence and maintaining block resistance. Overuse of slow-evaporating coalescents or plasticizer can lead to poor block resistance, but appropriate choice of coalescent type and level will yield complete film formation and excellent block resistance.

Exterior Durability

Exterior durability of paints is impacted by the quality of film formation as well as the composition of the latex. A well-chosen coalescing aid will reduce the porosity of a latex paint while increasing the film strength. Both of these effects can increase the potential for a paint film to withstand the forces of wood expansion or contraction without cracking and to minimize the water vapor transmission that can lead to delamination of paint from a substrate. Solvents or additives that remain in the paint film have the potential to bloom to the surface and lead to dirt pickup. As a result, it is important to select a coalescing aid with an appropriate evaporation rate at a use level that will ensure timely hardness development. Dirt collection on coated exterior panels may be evaluated by the ASTM Test Method for Quantifying Dirt Collection on Coated Exterior Panels (D3719).

Rheology

Coalescing aids interact with associative thickeners and different types of coalescent can significantly modify the viscosity of a latex paint formulation. Relatively hydrophobic coalescing aids can interact with the hydrophobic modifications present in associative thickeners, which increases viscosity and effectively increases thickener efficiency [27]. In contrast, more water soluble coalescing aids can actually interfere with the function of associative thickeners and may lead to a reduction in the viscosity of a formulation. If alternate coalescing aids are "dropped into" a formulation as a direct substitute, there is a potential for the paint rheology to be altered such that the application characteristics of the paint change.

Freeze-thaw Stability

Architectural coatings are evaluated for freeze-thaw stability by cycling paint samples between room temperature and 0°C as outlined in the ASTM Test Method for Freeze-Thaw Resistance of Waterborne Coatings (D2243). Freeze-thaw stability is often achieved through use of completely water soluble diols, such as ethylene glycol or propylene glycol, which serve as freezing point depressants. Since the most efficient coalescing aids tend to be relatively hydrophobic, these materials do not improve and may actually reduce freeze-thaw stability. Wegmann suggested that the mechanism for this reduction in freeze-thaw stability stems from the coalescing aid increasing the solubility of the surfactant in the water, which destabilizes the latex [28].

Wetting and Defoaming

Many coalescing aids effectively reduce the surface tension of water. In latex paints, this property serves to aid in the process of both pigment and substrate wetting [29]. It has been reported that hydrophobic coalescing aids can be used to activate silicone defoamers in aqueous systems [29].

TABLE 2—Summary of the progression of U.S. AIM VOC regulations (in grams per liter)

	EPA		CARB			SCAQMD			OTC	
Product Type	*2002*	*2009*	*2000*	*2003*	*2010*	*2000*	*2002*	*2006*	*2002*	*2005*
Flat	250	100	250	100	50	250	100	50[a]	250	100
Non-flat	380	150	250	150	100	250	150	50	380	150
Non-flat high gloss	380	250	250	250	150	250	150	50[b]	380	250
Primer, Sealer, Undercoater	350	200	350	200	100	350	200	100	350	200
Industrial Maintenance	450	340	340	340	250	420	250	100	450	340

[a] Postponed until 2008.
[b] Postponed until 2007.

IMPACT OF VOC REGULATIONS ON COALESCING AIDS

VOC Regulations and Test Methods

Over the past 10 years, there have been significant changes in the regulations governing the use of VOCs in architectural and industrial maintenance (AIM) coating applications. In the United States, several regulatory bodies have restrictions in place, including SCAQMD (South Coast Air Quality Management District), OTC (Ozone Transport Commission), CARB (California Air Resources Board), and the U.S. EPA. Table 2 provides a summary of the historical, current, and proposed regulations for these four organizations. From this table, it is evident that the usage of VOCs has been and will continue to be curtailed by these new regulations. The European Union (EU) is covered by the Decopaint Directive 2004/42/CE of the European Parliament, which was issued on April 24, 2004. Annex II of this directive outlines two sets of VOC limits for paints and varnishes, one that was implemented on 1/1/2007, and a more stringent standard that will come into force as of 1/1/2010. The reader is cautioned that U.S. and EU limits are not directly comparable, as both VOC definitions and test methods are different. In the United States, VOC is evaluated according to ASTM Standard Practice for Determining Volatile Organic Compound Content of Paints and Related Coatings (D3960), which is analogous to EPA Federal Reference Method 24. At low VOC, EPA Method 24 has significant error [30], and a newer method is described in the ASTM Test Method for Speciation of the Volatile Organic Compounds in Low VOC Content Waterborne Air-Dry Coatings by Gas Chromatography (D6886), although this method has not yet been adopted for regulatory purposes by the EPA. The European Union uses test methods from the International Standards Organization (ISO) titled Paints and Varnishes—Determination of Volatile Organic Compound Content Part 1: Difference Method (ISO 11890-1, for use with VOC contents above 15 % by weight) and Part 2: Gas-Chromatographic Method (ISO 11890-2, for use with VOC contents less than 15 % by weight). As more restrictive rules are implemented, significant research has been carried out in order to determine the most effective approaches to maintain paint properties within the guidelines of these regulations.

In addition to the changes observed with respect to VOC limits in paints and coatings, there has begun to be more interest in long-term emissions from painted substrates, both from the regulatory and research perspectives. Some recently published work focused on obtaining a better understanding of the fate and availability of coalescing aids in latex paints. Corsi studied the partitioning of 2,2,4-trimethyl-1,3-pentanediol monoisobutyrate in flat and semi-gloss paints over aluminum, gypsum board, and concrete substrates [31]. His work led to mass balances of coalescing aid in the substrate, paint film, and air over the period of about 1 year, which revealed that airborne recovery of 2,2,4-trimethyl-1,3-pentanediol monoisobutyrate ranged from <25 % to 90 % and was dependent on both paint type and substrate type.

Reformulating to Reduce VOC

Regulations have led to the need for extensive reformulation in the coatings industry, which has in turn spawned a desire for new lower-VOC components for latex paints. The main VOCs in latex paints are the freeze-thaw stabilizer/open time additive and the coalescing aid. Several approaches to meet lower-VOC limits have been espoused, generally including a resin modification, a coalescing aid modification, or both.

Low-VOC Coalescing Aids

From the perspective of VOC reduction through use of alternative solvents, possible solutions involve more efficient coalescents, low-VOC coalescing aids or plasticizers, reactive coalescing aids, or elimination of the freeze-thaw stabilizers. The premise for VOC reduction based on efficiency stems from the fact that if less coalescent is required to meet a target MFFT, VOC will be reduced accordingly. Lower-volatility coalescents have been considered for use in formulations based on the fact that the VOC contributions of very nonvolatile materials may be much less than 100 % according to EPA Federal Reference Method 24 (Determination of Volatile Matter Content, Water Content,

Density, Volume Solids, and Weight Solids of Surface Coatings). Some of these materials may be classified as having nearly zero VOC contribution based on the U.S. definition. Low-VOC coalescents often share similar chemistry with conventional coalescing aids, but are less volatile since they are higher molecular weight esters, glycol ethers, or ester-alcohols. As described previously for plasticizers, careful formulation is required when using low-volatility coalescents in order to avoid issues with block resistance, scrub resistance, and dirt pickup. The concept of a reactive coalescing aids involves a coalescing aid acting to promote film formation in the traditional manner and then crosslinking to become a permanent part of the coating. One approach to reactive coalescents involves esterification of relatively nonvolatile unsaturated materials that can crosslink through an oxidative cure mechanism [32]. The benefits for this technology are twofold: VOC is reduced and these products may be viewed as renewable, since many of the unsaturated materials are of natural origin. Potential shortcomings for this approach include slow hardness development due to the minimal crosslinking from the low level of coalescent incorporation, the potential for color development, and the fact that driers may be required to promote cross-linking.

Reducing VOC through Resin Modification

Alternative technology based on resin modifications includes reduction of latex T_g to limit the coalescent requirements, manipulation of latex composition or morphology (core-shell or power feed processes) to reduce coalescent requirements, or copolymerization of reactive monomers that allow cross-linking subsequent to film formation. By reducing T_g of the base latex, the paint film can form a film without using as much (or any) coalescent. While this reduces VOC, it can also lead to a softer film that is less durable and more prone to dirt pickup and blocking problems, as demonstrated by Testa in a study comparing the performance of coalesced versus coalescent-free paints [33]. There has been extensive work on cross-linking latex systems in which a functional monomer is polymerized into the latex and which may or may not require use of an additional crosslinker. These systems were initially directed more extensively toward the industrial maintenance market, but are beginning to gain some traction in the architectural area, although cost considerations are more significant in this market. Taylor and Winnick have written a comprehensive review of the technologies in the functional and thermoset latex field [1].

Currently, although there are many technologies under examination from both the additive and resin standpoints, it is clear that maintaining excellent paint properties while meeting future VOC regulations will continue to be a significant challenge.

ACKNOWLEDGMENTS

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Thickeners and Rheology Modifiers

Gregory D. Shay[1]

LIST OF ABBREVIATIONS

ASE = Alkali-swellable and/or soluble emulsion
ATRM = Associative thickener and/or rheology modifier
BP = Biopolymer
CMC = Carboxymethyl cellulose
CTRM = Conventional thickener and/or rheology modifier
DS = Degree of substitution
DUEV = Dynamic uniaxial extensional viscosity
EHEC = Ethylhydroxyethyl cellulose
EMHEC = Ethylmethylhydroxyethyl cellulose
GG = Guar gum
HASE = Hydrophobe modified alkali-swellable/soluble emulsion
HEC = Hydroxyethyl cellulose
HEEASE = Hydrophobe modified ethoxylate ester alkali-swellable/soluble emulsion
HEG = Hydroxyethyl guar gum
HEMC = Hydroxyethylmethyl cellulose
HENN = Hydrophobe modified ethoxylate nonionic non-urethane
HEUR = Hydrophobe modified ethoxylate urethane
HEUUR = Hydrophobe modified ethoxylate urea urethane
HEURASE = Hydrophobe modified ethoxylate urethane alkali-swellable/soluble emulsion
HMC = Hydrophobe modified cellulosic
HMNS = Hydrophobe modified nonionic synthetic
HMEHEC = Hydrophobe modified ethyl hydroxyethyl cellulose
HMHEC = Hydrophobe modified hydroxyethyl cellulose
HPG = Hydroxypropyl guar
HPAPE = Hydrophobe modified polyacetal polyether
HPMC = Hydroxypropylmethyl cellulose
HSV = High-shear viscosity
ITRM = Inorganic thickener and/or rheology modifier
LIQ = Liquid
LSV = Low-shear viscosity
MC = Methyl cellulose
MCC = Microcrystalline cellulose
MS = Molar substitution
MSV = Medium-shear viscosity
NA = Data not available
ORG = Organo or organic
PAA = Polyacrylic acid
pEO = Polyethylene oxide
PG = Propylene glycol
PN = Pre-neutralized
PVC = Pigment volume concentration
RM = Rheology modifier
SOLV = Solvent
T = Thickener
TRM = Thickener and/or rheology modifier
VOC = Volatile organic components
XCPS = Xanthamonas campestris polysaccharide (Xanthan gum)

INTRODUCTION

THE PERFORMANCE EXPECTATIONS OF COATINGS have grown substantially over the past few decades, and the rheological requirements for storage, handling, application, and post-application flow properties have become more demanding. Thickeners and rheology modifiers (TRMs) play a key role in many coating performance properties, and consequently, they are among the most important components in coatings systems. Although TRMs are used in minor amounts in most formulations and are generally considered additives, aqueous coatings usually contain at least one and sometimes two or more TRMs to obtain the desired balance of performance properties. Due to present-day environmental concerns and the use of TRMs predominantly in aqueous coatings, the focus of this chapter is on water-borne coatings where TRMs are used extensively in architectural, construction, elastomeric, and industrial applications. TRMs also find utility in some solvent-borne coatings—discussed later in this chapter, where they function primarily as flow modifiers and thixotropes. A list of some coating properties controlled or influenced by thickeners are found in Table 1. A recommended overview of coatings rheology and rheological test methods is found in Chapter 36 on "Rheology and Viscometry."

Thickeners

Thickeners, as traditionally defined, are chemical components that substantially increase the viscosity (resistance to flow) of fluids at relatively low concentration. The viscosity of a fluid, as discussed later in more detail, is a function of shear rate (the rate of fluid deformation), and most coatings formulations are shear thinning. That is, they decrease in viscosity as increasing rates of shear are applied. Thickeners tend to increase viscosity at all shear rates when incorporated, but for coatings, thickeners are most often incorporated to increase viscosity at moderate shear rates approximating those encountered during pouring, pumping, stirring, or mixing. The applicable shear rate (in reciprocal seconds) during these medium shear processes is in the range of about 10–1000 s^{-1} and more typically about 100 s^{-1}. The coating viscosity in this shear rate range is often referred to as the coating "consistency" or medium-shear viscosity (MSV). To be effective, a thickener should produce the desired coating consistency at a low-use level. The amount of thickener required to obtain a desired coating consistency is the "thickener efficiency," which is often expressed in units of lb thickener solids per 100 gal of liquid coating (or g/L where metric units are used). By example, for architectural coatings the total amount of thickener

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TABLE 1—Coating properties that are significantly controlled, affected, or influenced by thickeners and rheology modifiers

- Flow and leveling
- Pigment suspension
- Sag resistance
- Brushability and brush drag
- Film build and spread rate
- Roller spatter and misting
- Atomization and sprayability
- Syneresis and color float
- Pigment dispersion and hiding power
- Gloss development
- Color compatibility
- Open time
- Scrub resistance
- Wet and dry adhesion

required (thickener efficiency) is typically less than about 15 lb/100 gal (~ 18 g/L), more typically less than 10 lb/100 gal (~ 12 g/L) and can be as low as 3 lb/100 gal (~ 4 g/L) or even less depending on several factors. Among those factors are the inherent thickening ability of the thickener, coating formula solids, pigment volume concentration (PVC), vehicle type, and other components present in the formulation. As discussed later, the selection and interaction of other coating components is of particular importance when associative thickeners are used.

A coating's consistency can sometimes be sensed subjectively. For example, the depth of fluid vortex in a container at a given mixing speed provides an indication of the consistency by visual observation, or the resistance to flow can be felt during hand stirring of the coating fluid. The consistency of the coating can also be measured using an appropriate viscometer or rheometer that operates in the medium shear rate range. The high end of this range (near 1000 s^{-1}) also correlates with "pumpability," which is critical in some automated manufacturing operations. Several popular instruments for measuring consistency are described later in this chapter.

Rheology Modifiers

Rheology is the study of the flow and deformation of matter, and various rheological measurements are used to define the flow characteristics of a fluid. Many fluids including most coatings cannot be described rheologically by a single viscosity measurement. Rheology modifiers are often used in coatings to alter viscosity at low and/or high shear rates. However, there is no universally accepted definition of the term "rheology modifier" as it relates to coatings. In fact, the terms "thickener" and "rheology modifier" are often used interchangeably in commerce. The rheology modifier term is frequently used to refer to associative thickeners or to low molecular weight conventional thickeners, which are effective for modifying low or high shear viscosity. The thickener term is more often used to refer to relatively efficient conventional (non-associative) thickeners. The distinction between associative and conventional thickeners is discussed in more detail later in this chapter.

Upon close examination, all thickeners modify rheology in some way or to some degree when incorporated into a coating. Consequently, all thickeners are technically also rheology modifiers whether that is their intent or not. The converse is also generally true—most materials described as rheology modifiers are also thickeners since they increase the consistency of a coating to some degree though they may be relatively inefficient in doing so. Consequently, a true rheology modifier will usually require a higher concentration to significantly affect coating consistency. However, that same rheology modifier can be an inefficient thickener in one formulation but an efficient thickener in another depending on formulation parameters and other coating components present in the formulation. This is especially true for associative rheology modifiers. For instance, a rheology modifier that is efficient for consistency in one formulation may require only 5 lb/100 gal, but in another formulation it could be very poor for consistency requiring as much as 60 lb/100 gal (~ 35–75 g/L). Rheology modifiers are often used as secondary thickeners in a coating formulation to influence viscosity at high and/or low shear rates (generally above 1000 s^{-1} or below 10 s^{-1}). They may be very efficient for controlling rheology at the shear-rate extremes while contributing little to coating consistency. Rheology modifiers may also influence the elastic or elongational (extensional) properties of coatings, which are properties that can be measured on some high-performance rheometers. Sometimes, a single thickener or combination of thickeners is effective in meeting all of the low-, medium-, and high-shear rheological requirements of a coating formulation. If the rheological requirements cannot be met with thickeners alone, a rheology modifier is often included to augment flow properties especially at low and/or high shear rates. A common example of this is the incorporation of a rheology modifier to raise the high-shear viscosity (HSV) of a coating to increase film build (film thickness) for improved substrate protection or one-coat hiding. Another common example is the incorporation of a rheology modifier to reduce the low-shear viscosity of the coating for improved leveling of brush marks and roller pattern. In some situations, a rheology modifier is efficient enough to function as an effective thickener such as in the presence of a small-particle-size latex, water-insoluble coalescing aids, at high binder concentrations, or at high-volume solids. This effect, which will be discussed in more detail later, especially applies to associative rheology modifiers where strong interactions occur between the TRM and other coating components.

Terminology Convention

The definitions for thickeners and rheology modifiers as they apply to coatings in this chapter are shown in Table 2. Because most thickeners modify rheology and most rheology modifiers thicken coatings to some degree, these terms will be used interchangeably in this chapter with little distinction and are collectively referred to as TRMs. The term thickener is used extensively hereafter and is meant to mean either a thickener or rheology modifier.

INCORPORATION OF TRMs

Coating manufacturing operations generally consist of several stages of processing, and TRMs are often important in each. Some common stages of coating production are the "premix" (where ingredients are added prior to pigments), "grind" (where pigment is added and reduced in

TABLE 2—TRMs defined in this chapter
Thickener—any material added to a coating formulation to increase coating consistency (mid shear viscosity). Note: Most thickeners also modify coating rheology to some degree when incorporated into a coating formulation.
Rheology Modifier—any material added to a coating formulation to alter one or more rheological characteristics (e.g., low-shear viscosity, high-shear viscosity, extensional viscosity, visco-elasticity, thixotropy, yield point, or relaxation time etc.). Note: Most rheology modifiers also increase coating consistency to some degree when incorporated into a coating formulation.

size for optimum dispersion), and "letdown" (where the polymer or latex binder is normally added). Some, but usually not all, of the thickener is often added to the premix to increase viscosity in the grind for improved pigment dispersion (deagglomeration). Under laminar flow conditions, the rate of shear during grinding is set by the tip speed of the impeller and the depth of the shear gradient. One theory suggests that increased viscosity (such as from thickener addition in the grind) allows better energy transfer by decreasing turbulence at the impeller. This, in turn, increases the shearing collisions that attrite the pigment agglomerates. However, too much thickener at this stage impedes mixing and actually slows down the grinding process. The remaining thickener in a coating formulation is usually added to the letdown to provide proper suspension and product consistency. Finally, post-adjustments with additional thickener or rheology modifier may be required to bring the product "into specification" for consistency and application properties.

RHEOLOGY AND VISCOSITY

Because viscosity and rheology modification are the very essence of primary TRM function, a basic understanding of rheological concepts is helpful to fully appreciate differentiation in product performance. The rheological characterization of paints and coatings has been extensively investigated [1–14], and thorough treatment of this subject is found in Chap. 36. The following subsections provide a general overview of the two primary types of flow encountered during the preparation, storage, and application of coatings that are affected by the choice and amount of TRM present.

Viscosity is defined as "resistance to flow" and is mathematically equal to the ratio of two rheological parameters (shear stress τ/shear rate γ), where shear stress is the force exerted per unit area in the fluid shearing plane and shear rate (rate of fluid deformation) is the fluid velocity divided by the gap between shearing planes. For the case of simple shear, shear rate is just the gradient of velocity in a flowing fluid. At constant shear rate, viscosity increases with increasing shear stress. Shear rate increases with increasing fluid velocity or with a decrease in the gap between shearing surfaces. If either the shear rate or shear stress is known, the other parameter can be measured to obtain viscosity. Often, the geometry of the viscosity measurement system allows the shear rate to be known or approximated, and by plotting the measured viscosity of a fluid at several shear rates, a viscosity flow curve (i.e., rheology profile or rheogram) is obtained. Nearly all waterborne architectural coatings are shear-thinning fluids. That is, the viscosity of the coating decreases with increasing shear rate. Some coating processes operate at lower rates of shear, while others operate at moderate or higher rates of shear. Consequently, the rheology profile of the coating fluid defines the relative performance of several coating processes.

Shear Flow

Most low, medium, and high shear rate coating phenomena involve shear flow that is characterized in the laminar regime (where the shear field produces Reynold's numbers below the critical characteristic for the fluid). Shear flow in the turbulent regime (high Reynold's numbers) is not normally characterized, since most parameterizing equations fail in this regime. The vast majority of viscometers and rheometers produce laminar shear flow and measure the ratio of shear stress to shear rate (viscosity). With coatings, it is useful to determine viscosity at several shear rates to obtain a complete rheology profile (rheogram), which is normally represented in log-log form. These profiles are also conveniently divided into three shear rate regions—"fluid at rest," "fluid during processing," and "fluid during application," which correspond to the low-shear, medium-shear, and high-shear regions, respectively, as depicted in Fig. 1. A coating fluid at rest could be either a stationary fluid in a container or a liquid film after application before it dries. A rheometer is a convenient instrument for obtaining a coating fluid rheogram. The viscosity profile for a coating can also be approximated by single-point viscometer measurements of low-shear viscosity (LSV), MSV, and HSV. Some of the coating processes and properties affected in each region are shown in Fig. 1 and are further discussed later in this chapter in "TRM Functions."

Time-dependent shear thinning (thixotropy) and zero-shear yield value are two other rheological coating properties that may be very important in the rheological characterization of coatings. For example, a thixotropic fluid with high yield value may exhibit good leveling if the time required to rebuild viscosity is long compared to the time needed for flow out of brush marks or roller pattern. The viscoelastic properties of a coating may also be important, particularly in spray and roll applications. The elastic component of shear can be determined on some advanced cone-plate or parallel plate rheometers either by measuring the shear storage modulus (G') in oscillatory simple shear mode or by measuring normal forces (e.g., first normal stress difference, N_1), which is a force produced perpendicular to the plane of shear.

Elongational Flow

In addition to the simple shear flow fields generated during the mixing and application of coatings, elongational (extensional) flows may also be induced during the coating application processes of spray, roll, or blade. The study of extensional flows and their importance in coatings has been widely examined [15–17] and especially as it applies to roll coatings [18–20] and spray applications [21,22]. During these application processes, the fluid is accelerated as it approaches the applicator orifice or nip, and the polymer molecules of the thickener become stretched and aligned. The viscosity related to the induced elongational flow is termed by Glass [15] as the "dynamic uniaxial extensional

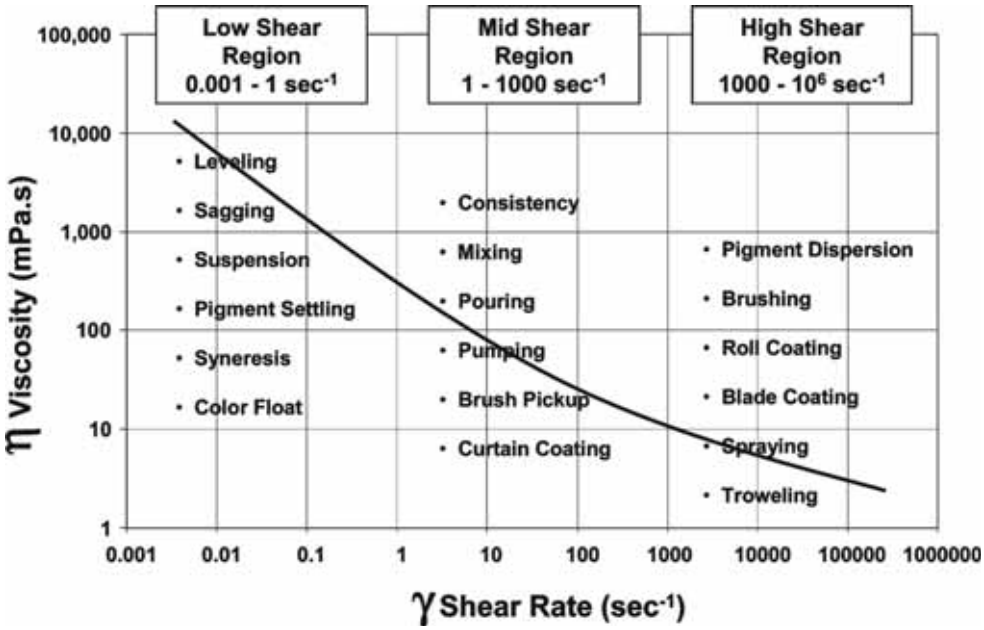

Fig. 1—Three shear-rate regions and related performance properties for architectural coatings.

viscosity" (DUEV). One coating property that has shown some correlation with DUEV is roller spatter in architectural coatings [23–25], and this undesirable phenomenon may actually be due to a complex combination of DUEV and viscoelasticity [25]. The degree of spatter can be rated using ASTM Test Method for Measurement of Paint Spatter Resistance to Roller Application (D4707-87). Other properties that have shown some correlation with DUEV are ribbing, web formation, misting in roll coatings, and atomization in spray coatings. Many viscometers and rheometers are available for the characterization of shear flow, but there are only a few instruments for the measurement of DUEV on disperse phase coating systems. Two such instruments are the Rheometrics RFX (no longer in production) and the Haake Caber 1 Extensional Rheometer. As a class, associative thickeners tend to impart lower DUEV than conventional (non-associative) thickeners, which improves some of the application properties described. Comparative representations of shear and elongational (extensional) flow are depicted in Fig. 2.

TRM CLASSIFICATION

Polymeric organic thickeners for aqueous media are often classified into two basic types: "conventional," which thicken predominately by hydrodynamic and flocculative mechanisms, and "associative," which thicken substantially by hydrophobe associative mechanism. Associative thickeners may also have some hydrodynamic thickening contribution depending on their molecular size. These mechanistic definitions are subject to some variability and ambiguity; however, a more clear distinction can be made for purposes of classification based on chemical architecture.

Conventional thickeners are defined in this chapter as viscosifying water-soluble polymers lacking hydrophobic groups capable of association. They are non-associative thickeners. Higher molecular weight conventional polymers are more efficient as thickeners, while lower molecular weight polymers of similar or different composition may function more as rheology modifiers. Associative thickeners are defined here as viscosifying water-soluble polymers that contain hydrophobic groups capable of association. The hydrophobes may be located at the ends of the polymer chains, within the polymer chains, or pendent to the hydrophilic polymer backbone The hydrophobes in these polymers are capable of nonspecific hydrophobic associations similar to those of conventional surfactants, and these associations are primarily responsible for generation of viscosity with these thickeners. Because they provide much of their thickening ability by hydrophobe association, these polymers can be much lower in molecular weight than conventional thickeners but they may also have some thickening contribution due to their molecular size. Regardless of their size, most associative thickeners are effective rheology modifiers at low and/or high shear rates and also due to their ability to modify elastic and elongational flows. Variation in chemical architecture, the number of hydrophobes present, and a further reduction in molecular weight can produce associative polymers that function primarily as rheology modifiers. It becomes readily apparent that, with proper hydrophobe modification, virtually any conventional polymer can be converted to an associative polymer, and this is what has been done in the design of several commercial associative thickener products.

The acronyms used hereafter for conventional thickeners and rheology modifiers and for associative thickeners and rheology modifiers are CTRMs and ATRMs, respectively. The various advantages and disadvantages of CTRMs and ATRMs have been extensively investigated and reviewed in the literature [26–32] and will become more apparent in

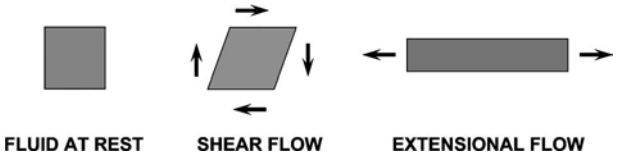

Fig. 2—Types of flow in coatings rheology (shear flow and extensional flow).

the following sections. A clearer distinction between these two major classes of thickeners will be apparent on examination of the thickening mechanisms involved. Although nearly all inorganic thickeners are conventional thickeners with respect to their thickening mechanisms, these TRMs will be treated separately later in this chapter.

THICKENING MECHANISMS

Three primary thickening mechanisms for polymeric waterborne thickeners are "hydrodynamic," "flocculative," and "associative." Each of these mechanisms may be further divided into subclasses, if desired, which have their own individual rheological and coating characteristics. Consequently, it is important to consider these mechanisms when making TRM selection for increasing coating consistency, for rheology modification, or for their effect on other coating properties.

Thickening is often a complex process. For example, the flocculation mechanism is frequently a byproduct of hydrodynamic thickening but may also occur in associative coating systems that are improperly formulated or in those systems where a controlled degree of flocculation is desired. Some associative thickeners (for example, alkali-swellable types) are sufficiently high in molecular weight that an appreciable hydrodynamic component of thickening is present. Depending on their chemical architecture, strength of the hydrophobic associations, and other formulation components present, some ATRMs actually function to varying degrees with both associative and non-associative mechanisms at the same time. Outlined in Table 3 are some possible thickening mechanisms for conventional and associative thickeners.

The Hydrodynamic Mechanism

Prior to the introduction of associative thickeners, nearly all organic thickeners used for aqueous coatings were water-soluble polymers of relatively high molecular weight (MW) or stiff backbones without hydrophobe modification. As previously defined, these are conventional TRMs as depicted in Fig. 3. The molecular weights of the conventional polymers that function as thickeners are generally greater than about 10^5 and can be as high as 10^6 or more. Polymers with stiff backbones (e.g., many cellulosics) at the lower end of the MW range are as effective in thickening ability as polymers in the high end of this range with flexible backbones (e.g., polyethylene oxide). When conventional thickeners dissolve in water, the polymer chains occupy a large hydrodynamic volume in solution and immobilize large volumes of water within the coils of their backbones. This increases viscosity of the continuous water phase dramatically. For a given polymer type, higher molecular weight molecules take up more space and produce higher viscosity. In fact, the solution viscosity of conventional polymers in water or nonaqueous solvents is one of the common methods used for determination of molecular weight when the Mark-Houwink constants ("K" and "a") are known. As previously stated, sufficiently low-molecular-weight polymer analogs (e.g., LMW HEC) can function more as true rheology modifiers since they do not contribute appreciably to consistency (MSV). However, these lower molecular weight conventional polymers have been mostly replaced or augmented with associative rheology modifiers in many coatings applications.

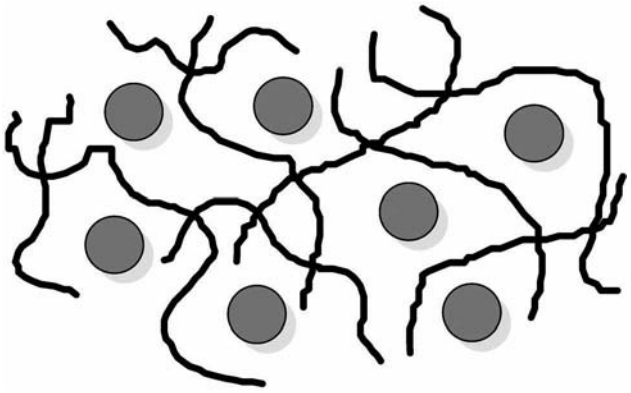

Fig. 3—Depiction of conventional (non-associative) polymer thickening in aqueous media.

Some conventional thickeners typically made by emulsion polymerization are addition copolymers that contain a substantial amount of carboxylic acid functionality. When neutralized, these polymers become water soluble and expand into the water phase providing thickening. Some of the copolymers are lightly cross-linked to make them water-swellable rather than water-soluble. On neutralization in aqueous media, these polymers may swell to many times their original particle diameter to produce viscosity by a hydrodynamic mechanism. Some of the neutralized copolymers contain both swellable (gel-fraction) and soluble polymer, but both contribute to thickening.

Examples of conventional water-soluble or water-swellable thickeners used extensively in coatings are hydroxyethyl cellulose, hydroxypropyl methyl cellulose, and alkali-swellable/soluble copolymer emulsions (ASEs). These and some other CTRMs are discussed later in this chapter under "Conventional TRMs (CTRMs)".

Flocculative Mechanisms

Because conventional thickener molecules take up significant volume in solution, they often induce flocculation in coatings, forming latex-rich, pigment-rich, and thickener-rich domains by a mechanism commonly referred to as "volume restriction," "volume exclusion," or "depletion" flocculation. This process is depicted in Fig. 4 and is now

TABLE 3—Thickening mechanisms for conventional and associative TRMs in aqueous media

Hydrodynamic—molecular size, chain entanglement, swelling, and chain stiffness
Depletion Flocculation—mostly conventional thickeners and promoted by hydrodynamic size
Bridging Flocculation—polymer bridging of particles
Structure Formation—moslty inorganic thickeners
Hydrophilic Interactions—ion dipole, and electrostatic interactions
Hydrophobe Association—associative thickeners only, intermolecular and with hydrophobic particle surfaces
Note: associative thickeners may also have one or more of the other mechanisms operating to some degree

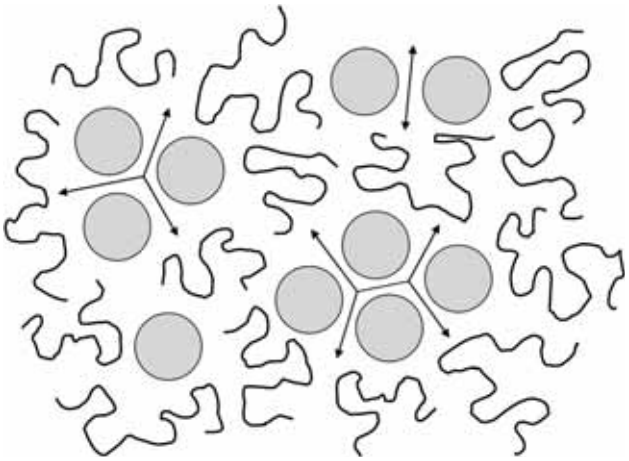

Fig. 4—Depletion flocculation—A conventional thickener occupies space, which results in flocculation of latex and pigment particles. This is facilitated by osmotic pumping of water from between particles interstices.

recognized as a primary mode of thickening for conventional polymeric thickeners in disperse phase systems such as in coatings with pigment or latex particles present. This flocculative mechanism has been examined in both experimental [33–36] and theoretical treatments [37–39], and also modeled by computer simulation [40,41]. The process begins when latex or pigment particles randomly approach each other. When they are close enough (on the order of a random-coil thickener molecular diameter), the thickener molecules in the coating are "excluded" from the interparticle region. The concentration gradient formed causes water to be osmotically "pumped" from between the latex or pigment particles driving the particles even closer together, which further concentrates the thickener molecules in the aqueous phase. Eventually, the latex or pigment particles touch, forming flocs that are readily observable on microscopic examination. This mechanism of thickening can adversely affect gloss and hiding and also may impart more shear thinning character and more viscoelasticity to the coating. Since these polymers are typically of high molecular weight, they also tend to impart high extensional viscosity to coatings and one consequence of that has already been identified (roll spatter and rib pattern in roll coatings).

Another flocculative mechanism that may occur particularly with conventional thickeners is "bridging" flocculation. In this mechanism, the polymer molecules partially adsorb onto latex or pigment particles. If the thickener molecules are sufficiently long and have a strong affinity for other particles, bridging can occur, forming flocs.

ASSOCIATIVE MECHANISMS

The primary thickening mechanism for ATRMs is via intermolecular hydrophobic association between thickener molecules, and more predominately by association of the thickener hydrophobes with disperse phase (colloidal phase) hydrophobic components in a coating formulation [42–47]. This mechanism is depicted in Fig. 5. When a water-soluble polymer contains both hydrophilic and hydrophobic moieties, the potential for associative interaction exists. Among the simplest associative molecular

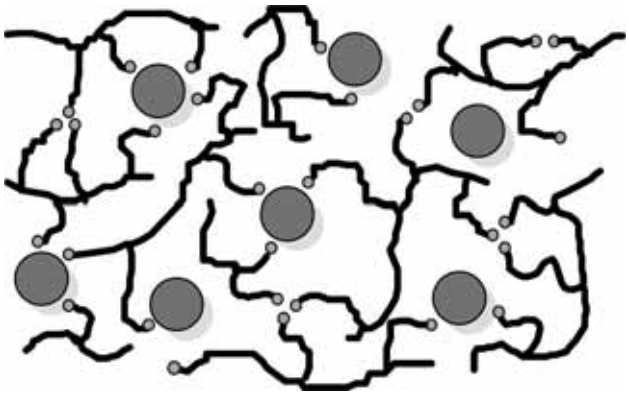

Fig. 5—Depiction of associative polymer thickening in aqueous media.

structures are nonionic surfactants. These molecules have a hydrophilic polymer segment (usually polyethylene oxide) on one end and a hydrophobic group (typically a long chain alkyl or alkyl aryl group) on the other end. At a sufficiently high concentration known as the critical micelle concentration (CMC), surfactants spontaneously form micelles in aqueous solution. At or above the CMC, the hydrophobes aggregate at the interior of the micelle, and the hydrophilic tails orient outward into the water phase. The key driving force for micellization is not the London Van der Waals attractive forces between hydrophobes, but rather the change in free energy on transfer of a hydrophobe in the aqueous phase to a more oil-like environment at the interior of the micelle. Water excludes the hydrophobes in the micellar process.

If a hydrophobe is chemically attached to the other end of a nonionic surfactant, a simple associative thickener is formed. However, because the thickener has a hydrophobe at each end, micelle formation is not a favorable process and is not observed except for certain chemical architectures at extremely low concentrations. Instead, the associative molecules aggregate into a more favorable three-dimensional structure of hydrophobes associating with other hydrophobes. The hydrophobe network structure that forms inhibits flow and raises the viscosity of the aqueous solution or coating. The driving force for association is similar to that for surfactant micelle formation—exclusion of the hydrophobes by water. To be viable in commerce, ATRMs usually have a few repeat hydrophile-hydrophobe units within the polymer backbone or in side chains to increase molecular weight, thereby increasing the hydrodynamic contribution and also the association efficiency. Although each associative polymer type has an optimum molecular weight, high molecular weight is not a requirement for associative thickeners, and most are significantly lower in molecular weight (typically <50,000) than conventional thickeners. Lower molecular weight has some advantages for supply of the thickener in aqueous solution, for the thickener's ease of incorporation, and for the rheology imparted to a coating. Another aspect of ATRMs is their interaction with colloidal components in a coating formulation. Whenever latex particles or hydrophobic pigments are present, the hydrophobes on the associative thickener can adsorb onto the hydrophobic particle surfaces. This results in a further increase in system viscosity and may result in coating rheology modification. The strength of the association is impor-

tant, and depending on the degree of association, a polymer can induce several types of equilibrium phase behavior including non-associative volume restriction flocculation and especially associative bridging flocculation [48–50]. Because associative thickeners are much lower in molecular weight than conventional thickeners, depletion flocculation is reduced or eliminated, resulting in advantages in coating gloss and more Newtonian rheology.

Although hydrophobe interaction is the predominate associative mechanism for ATRMs, some evidence suggests an additional associative mechanism, which is hydrophilic rather than hydrophobic in nature. Almost all latex particles possess carboxyl groups on their surfaces to impart stabilization. The proposed hydrophilic association is an ion-dipole interaction between the latex surface carboxyl groups and the polyethylene oxide (pEO) segments in the associative thickener present [51]. When the ATRMs contain both carboxyl and ethoxylate functionality in the same molecule (for example, associative alkali-swellable/soluble polymers), both intermolecular and intramolecular ion-dipole associations are theoretically possible.

TRM FUNCTIONS

Formulating for optimum performance with TRMs can be challenging, but the resources available are many [52–63]. The primary function of TRMs are the control of coating viscosity and rheology throughout the applicable shear rate spectrum: consistency is measured and adjusted in the medium-shear-rate range, application properties in the high-shear-rate range, and film formation and container storage properties in the low-shear-rate range. The viscosities associated with these ranges may be referred to as MSV, HSV, and LSV, respectively. ASTM Standard Practice for Rheological Characterization of Architectural Coatings Using Three Rotational Bench Viscometers (D7394) describes a procedure for obtaining a three-point rheology profile for prediction of performance properties. Background and discussion regarding this method are detailed in the following TRM function subsections. Several film properties are also affected and may be manipulated by the appropriate choice and amount of TRM in the coating. Two examples of architectural coatings formulated with TRMs to obtain very different rheology profiles are shown in Fig. 6. A clear understanding of the rheology profiles depicted in this illustration and their impact on application and film properties will become more apparent in the following subsections.

Coating Consistency MSV

The MSV is a measure of a paint's consistency (resistance to flow on mixing), and it is often determined on a viscometer operating in a shear rate range of 10–1000 s^{-1}. A common formulating practice is adjustment of coating viscosity in the medium-shear range by varying the amount of thickener in the coating. The "target" viscosity is normally based on prior experience or on a previously established specification range for a particular type of coating. For architectural coatings, the preferred instrument for determining coating consistency and for making thickener adjustments is a paddle type viscometer that measures viscosity in Krebs units (KU) as shown in Figs. 7 and 8. This instrument is sometimes referred to as a "Krebs viscometer" or more commonly a "Stormer

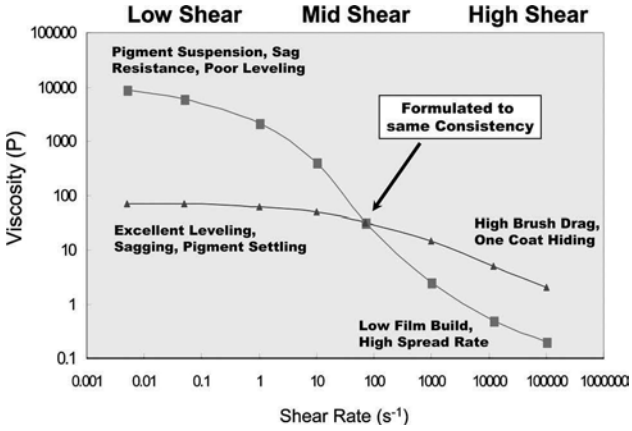

Fig. 6—Two examples of very different coating rheology in architectural paints.

Viscometer" (genericized trademark). Viscosity determination with this instrument is conducted in accordance with ASTM Test Method for Consistency of Paints Using the Stormer Viscometer (D562). The Krebs viscometer's rotor paddle geometry imparts mixing action during measurement similar to hand stirring or stirring on a lab mixer. The measurement range capability is 60–140 KU. Most architectural coatings fall within the range of 80–120 KU and more typically within 90–110 KU for coatings applied by roll or brush. A typical house paint might have a Krebs viscosity specification of 100±3 KU (±3% in this example). When a series of similar coatings are being compared for rheology, they ideally should have the same or similar KU viscosity. This is important for meaningful comparisons of their LSVs and HSVs because raising or lowering the consistency of a formulation will normally result in a corresponding increase or decrease in its LSV and HSV (i.e., the viscosity curve is shifted up or down). As some paints are thixotropic, it is a good practice to pre-stir the paint with a spatula or lab mixer to break up any structure prior to making a viscosity measurement.

The earliest and most well-known Krebs viscometer is the Stormer® Viscometer, and references on this instrument go back to the beginning of the 20th century [64–66]. The paddle spindle used on this viscometer is driven by mechanical coupling of suspended brass weights over a

Fig. 7—Manual Krebs type viscometer for measuring the MSV, otherwise known as the "consistency."

Fig. 8—Digital Krebs type viscometer for measuring the MSV, otherwise known as the "consistency."

pulley system (Fig. 7). The weights are adjusted until a constant paddle speed of 200 rpm is obtained, and from the weight required, the Krebs viscosity of the paint is computed. The latest version of the Stormer viscometer is the Thomas Stormer® Rotational Shear Viscometer (with Calibrated Paint Testing Outfit) from Thomas Scientific, as shown in Fig. 8. This instrument is calibrated by the Krebs Pigment and Color Corporation to give readings that will duplicate those obtained with other similarly standardized analog and digital instruments.

Today, modern digital Krebs viscometers are often used for obtaining Krebs viscosity. Three such digital instruments are the Thomas® ETS-2000 Digital Viscometer from Thomas Scientific, the Brookfield® KU-1 or updated KU-2 viscometer from Brookfield Engineering, and the Sheen 480 Krebs Viscometer from Sheen Instruments (Fig. 7). These viscometers provide digital readout in Krebs units, grams, or centipoise/poise. Like the Stormer and Thomas Stormer analog viscometers, the digital Krebs viscometers have the same paddle rotor geometry, obtain viscosity measurements at the same 200 rpm rotor speed, and also read out in Krebs units. Their main advantages are ease of use and easy-to-read LED display.

LSV and HSV for architectural coatings, as discussed in later sections of this chapter, are measured using instruments that typically provide viscosity in centipoise (cP) for LSV and poise (P) for HSV. The centipoise values are easily converted to poise by 100 cP = 1 P. However, consistency as measured in Krebs units is not directly convertible to poise for non-Newtonian fluids such as paints. To compare MSV with LSV and HSV in the same units, it would be advantageous to know the mid-shear viscosity of a paint in poise. It would also be desirable to know the shear rate of the Krebs viscometer for the paint tested, which would then allow the generation of a three-point flow curve of LSV, MSV, and HSV at the respective shear rates of each viscometer. A determination of this type has been made and reported previously for a semi-gloss latex coating. The determination was accomplished by first preparing a series of paints with different rheology modifiers to the same target viscosity of 95 KU. This was accomplished by adjusting the thickener concentration in each paint as measured on a Brookfield KU-1 Krebs viscometer. The coatings were then analyzed with a high-performance controlled shear rheometer over a wide shear-rate range. The average crossover point of the rheology spectra is the apparent mid-shear viscosity indicating that a Krebs viscosity of 95 KU was equivalent to ~20 P at a shear rate of ~ 70 s^{-1} (Fig. 8).

As an option to using a Krebs viscometer for determining coating consistency, a standard Brookeld® type spindle viscometer can be used when operated at the higher speed selections (20–100 rpm) to give the appropriate shear rate. However, the measurement readout is in cP rather than KU. As discussed later in the next section, this same instrument is also useful at lower speeds (0.3 or 0.5 rpm) for determination of low-shear viscosity and processes related to LSV.

The Rotothinner® is another viscometer that can be used to determine consistency. This instrument provides an even greater mixing action than a Krebs viscometer and is capable of stirring the entire container contents while the viscosity measurement is being made. While this instrument can be used for more conventional coatings, it is ideally suited for breaking down the structure of thixotropic coatings to obtain a sheared viscosity.

Leveling, Sag, Syneresis, Settling (LSV)

Besides MSV, there are also low-shear and high-shear process viscosities important in coatings that may also have target values when paints are formulated, and sometimes rheology modifiers are added to meet these targets. Once a paint's coating consistency (KU viscosity) has been appropriately adjusted or approached, a common next step for a paint formulator is to determine the LSV and HSV of the paint to make adjustments in these shear-rate regimes if needed. In this section, the low-shear coating processes are considered, and in a following section, the high-shear process are addressed.

Among the important low-shear processes for coatings are in-can pigment suspension [67], leveling [68–71], syneresis [72], and sag resistance [73]. The measurement of LSV can give an indication of performance for these processes. A properly formulated paint will typically have a sufficiently high LSV to prevent pigment settling on storage and to impart sag resistance on vertical surfaces when applied, but it will at the same time be low enough to provide leveling of brush and roller marks. Sometimes it can be difficult meeting all rheological requirements, and formulating becomes a compromise. The applicable shear rates for LSV processes are generally less than about 10 s^{-1} and more often in the range of 10^0 to 10^{-3} s^{-1}. The low shear applied in these processes is primarily due to the effects of gravity for container separation and sagging, and due to capillary pressure (generated by surface tension and surface curvature) for leveling. In architectural coatings, LSVs that are too high result in poor film leveling, and brush or roller

Fig. 9—Sag bars used for determining sag resistance of films in vertical orientation.

pattern can be very apparent. In contrast, LSVs that are too low may allow sagging on vertical surfaces and in-can settling or syneresis. Container settling can be assessed subjectively using ASTM Test Method for Evaluating the Degree of Settling of Paint (D869). Sag ratings are often conducted in accordance with ASTM Test Methods for Sag Resistance of Paints Using the Multinotch Applicator (D4400) as shown in Fig. 9. The degree of leveling is often determined by simple inspection of the brush marks or roller pattern, if any, after the applied film has dried. Optionally, a notched applicator on a horizontal surface may be used in accordance with ASTM Test Method for Leveling of Paints by Draw-Down Method (D4062).

A variety of viscometric techniques has shown some correlation with leveling. Among these is the Beeferman stress-relaxation procedure [68]. In this method, the coating is first sheared at a moderately high rate on a viscometer or rheometer to break down structure to simulate what would be accomplished during brushing or rolling. The shearing on the viscometer is then stopped to simulate secession of brushing or rolling, and the declining shear stress versus time for the paint is recorded. The area under the relaxation curve is then integrated to obtain a "leveling viscosity" that is the product of shear stress (dyne/cm^2) and time (s) with the dimensions of viscosity.

To obtain LSV in architectural coatings, a simple one-point viscometer technique is often used, which generally provides good correlation with leveling and other LSV processes. In this method, viscosity is measured at low rpm on a rotational bench spindle viscometer (e.g., at 0.3 rpm on analog or digital Brookfield® or similar viscometer) and can be conducted in accordance with ASTM Test Method for Rheological Properties of Non-Newtonian Materials by Rotational (Brookfield) Viscometer (D2196). Analog and digital instruments of this type are shown in Fig. 10.

With this spindle geometry and the instrument operating at its lowest speed, low-shear rate in the 10^0 to 10^{-3} s^{-1} range is imparted to the fluid being measured (Fig. 8). As with some other viscosity determinations, it is preferable to first stir the paint with a spatula or mixer. This is done to break up structure (e.g., thixotropy) if present and to obtain a uniform sample by redispersing any pigment that may have settled on storage. Ideally, the same viscometer spindle

Fig. 10—Digital spindle viscometers for determination of LSV conducted at lowest speed (0.3 rpm).

should be used for all paints being measured. However, this is not always possible as some coatings may be out of the preferred torque range of the viscometer. A recommended practice is to select the spindle that gives a torque reading between 10–100% of full scale for each coating tested. If that is not possible, a spindle change can be made, but the rotational speed should remain the same (0.3 rpm) to keep the shear rate relatively constant. The spindle should turn in the sample for about 60 s (or a longer fixed time period) before taking the reading, and the same time period should be used for all measurements. With this technique and assuming a pre-adjusted MSV of about 95 KU for each paint tested, the following guidelines provide low-shear performance predictions: excellent leveling for viscosities of less than about 250 P (25 Pa·s) as might be obtained with an associative thickener; too much flow for viscosities below about 100 P (10 Pa·s) and with sagging predicted on vertical surfaces; poor leveling at about 1000 P (100 Pa·s) as might be obtained from a moderately high MW conventional thickener; and little or no flow at 2000–3000 P (200–300 Pa·s) as might be obtained using some very high MW conventional thickeners or some unconventional associative thickeners. Another useful method that can be conducted on a Brookfield spindle type viscometer is the measure of "pseudoplastic index." This is a two-point determination that is the ratio of two viscosities a decade apart in shear rate (for example, 10/100 rpm). LSV is probed by extrapolation of viscosity to lower shear rates (lower rpm).

From the prior discussion, high LSV is a facilitator for pigment suspension and low flow coating characteristics, while a low LSV is desirable to promote flow and leveling. Some coatings have a prominent yield stress that can also be a factor in leveling. Due to their associative mechanism,

most, but not all, ATRMs provide low LSVs to impart excellent leveling characteristics. However, some alkali-swellable associative thickeners and even some nonionic associative thickeners impart uncharacteristically high LSVs, and like very high MW CTRMs, these thickeners have utility as antisag or antisettling agents for use in highly structured coatings (for example, texture paints). Their unusual behavior in coatings may be due to their ability to impart a degree of flocculation resulting from bridging or depletion mechanisms. Although gloss development is higher than most CTRMs with these thickeners, the gloss levels are not as high as most typical associative thickeners, which supports this conclusion. However, some alkali-swellable thickeners actually produce very high gloss levels, which suggests that aqueous phase networking has a larger influence on rheology than expected and/or that the dispersant character for these thickeners is greater than expected. Conventional thickeners, on the other hand, nearly always are highly shear thinning with high LSVs due to the hydrodynamic and flocculative mechanisms operating. Consequently, the gloss and hiding imparted from these thickeners tends to be lower.

Application Properties (HSV)

Most brush, spray, or blade coating operations are relatively high-shear processes. This is also true for roll coating applications when the circumferential velocity of the roll is significantly different than the linear velocity of the substrate. The shear on application for these operations is generally greater than about 10^3 s^{-1} and is typically about 10^4 s^{-1} for brushing and as high as 10^6 s^{-1} for some high-speed roll coating, blade coating, and spray operations. Many high-performance rotational rheometers are capable of measuring the HSV and most use cone/plate or plate/plate geometry. One general purpose instrument that is popular for laboratory and quality control of HSV measurement of architectural and other coatings is the ICI cone-plate viscometer as described in ASTM Test Method for High-Shear Viscosity Using the ICI Cone/Plate Viscometer (D4287-88). This instrument as shown in Fig. 11 has a fixed shear rate of 10^4 s^{-1} and the viscosity measured is a good predictor of film build when a coating is applied by brush and sometimes by paint roller [3,11–14]. The higher the ICI viscosity, the more resistance a brush encounters on application, which results in a thicker applied film. HSVs at this shear rate are typically from about 0.5–2.5 P (50–250 mPa s) for architectural coatings. If the HSV is too high, the coating will require too much effort to apply, will have a low spread rate, and may sag. If the HSV is too low, a second coat may be required to hide the substrate. Subjective brush drag by actual application is often conducted in accordance with ASTM Test Method for Comparison of Brush Drag in Latex Paints (D4958).

Conventional thickeners generally produce coatings with low HSV, while most associative thickeners and particularly associative rheology modifiers (lower efficiency associative thickeners) produce high HSV. Although less common, some associative thickeners produce low HSV and that may be advantageous depending on the application and film thickness desired. These thickeners tend to be very efficient in the medium-shear region, and the low HSV is primarily a consequence of less thickener being used. As a general rule for a given thickener type, the more thickener required to obtain desired consistency (MSV), the higher the HSV will be. Therefore, if an increase in HSV is desired, a less-efficient thickener or rheology modifier may be needed so that more thickener is incorporated. As an option with associative thickeners, efficiency in the medium-shear region can be suppressed or enhanced by adjustment of other components in the coating formulation. By proper TRM selection or TRM blending, the desired HSV can be obtained without adversely affecting MSV or LSV.

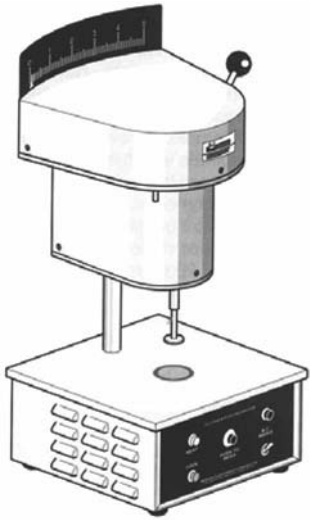

Fig. 11—Digital ICI cone/plate high-shear viscometer for determination of HSV.

Other TRM Test Methods

Although traditional viscometers and rheometers are very useful in providing coatings rheology, some nontraditional rheology characterization methods have been developed. Among these is a nondestructive technique for assessing rheology during film formation by measuring amplitude decay by optical two beam interference [74]. Surface tension was identified as an important factor for leveling by this method. Besides rheological characterization, other useful procedures have been developed for evaluation of some other properties for thickeners and rheology modifiers. Among these are a method for quantitative determination of thickener equilibration in coatings using a Krebs viscometer [75], and another for determining the relative water sensitivity of thickeners in neat form or in coatings by water vapor sorption [76]. Differences in water take-up between various classes of thickeners were revealed.

CONVENTIONAL TRMS (CTRMs)

In the broadest definition, CTRMs are non-associative water-soluble polymers, water-swellable polymers, or inorganic water dispersible materials that are capable of thickening or modifying the rheology of aqueous media. As defined, CTRMs are efficient thickeners or rheology modifiers without associative hydrophobe modification. For conventional polymeric viscosifiers, higher-molecular-weight polymer analogs within a given polymer type function primarily as thickeners, while lower-molecular-weight analogs function more as rheology modifiers. The primary thickening mechanisms of CTRMs are hydrodynamic and flocculative. Although there are many different chemical

types of these water-soluble polymers that could be used as TRMs in architectural, industrial, and other type of coatings, only a few have been accepted for use due to factors relating to economics, bio-stability, water sensitivity, compatibility, production quality, ease of handling, or the type of rheology imparted.

The CTRM polymers that are used in coatings are either synthetic or of biological origin. The synthetic polymers are derived from oil or natural gas feedstocks and are typically produced by addition or condensation polymerization. The biopolymers are either naturally occurring (rarely used in coatings), or are semi-synthetic including natural biopolymers that have been chemically modified, or biopolymers produced by a fermentation process. For classification herein, the polymeric CTRMs fall into three main categories: biopolymers (mostly modified polysaccharides), anionic synthetic ASEs, and nonionic synthetic polymers. The biopolymers may be further subdivided into modified cellulosics, guar derivatives, and fermentation biopolymers. The synthetic fermentation bipolymers, though less used in coatings, are of more recent vintage origin and employ microorganisms as a means of production. Several conventional polysaccharides are commonly used in architectural coatings (mainly house paints). ASEs are infrequently used in house paints but are often used to formulate adhesives and sealants. Conventional nonionic synthetics polymers are also seldom used in architectural coatings, but some polymer types are utilized in specialty applications such industrial roll coatings. Table 3 lists conventional water-soluble polymers used as thickeners in both coatings and noncoatings applications. As mentioned, nearly all of these thickener types have been tried in coatings, but only a few have found commercial acceptance. Table 4 details some important international suppliers of CTRMs and some of their respective products.

Cellulosic Polysaccharide Thickeners

Prior to the introduction of associative thickeners, conventional cellulosic thickeners were by far the most commonly used TRMs in aqueous coatings. Cellulosic thickeners for waterborne coatings were introduced in the 1950s, and they are still widely used today and are preferred as sole thickeners are in combination with associative thickeners in many formulations [77–81]. Some historical milestones during the development of cellulosic thickeners were enzyme-resistant grades in the 1970s, hydrophobe modified associative cellulosics in the 1980s, and fluidized (liquid) grades in the 1990s. Some of the conventional cellulosics are now being replaced or augmented in coatings by associative thickeners. Among these associative thickeners are hydrophobe modified cellulosic and galactomannan polymers, which are discussed later in this chapter. Cellulosic polymers are used in both interior and exterior architectural paints as thickeners and rheology modifiers, but they also are preferred for some other paint properties. One of these is the water-holding ability (water retention) of cellulosic polymers, which slows down evaporation and also retards penetration of water into the substrate. This property also helps to provide good "open time"—the time interval available for easily lapping back into a freshly coated architectural paint film with a brush or roller, and a new ASTM work item (WK13360), New Test Method for Open Time of Latex Paints, to measure this paint property is being developed.

Cellulose $(C_6H_{10}O_5)_n$ is a naturally occurring polysaccharide composed of repeating anhydroglucose units. Because of its relatively straight and stiff polymer chains and its strong intermolecular and intramolecular hydrogen bonding, cellulose is highly crystalline and consequently is insoluble in water. However, with appropriate chemical modifications, cellulose is readily converted to a variety of amorphous water-soluble polymers. The cellulose ether polymers are the most important for coatings and among those that have been used extensively are hydroxyethyl cellulose (HEC), methyhydroxypropyl cellulose (HPMC), sodium carboxymethyl cellulose CMC, and ethylhydroxyethyl cellulose (EHEC). Some standard terminology for cellulose and cellulosic polymers is provided in ASTM Standard Terminology of Cellulose and Cellulose Derivatives (D1695). The reactions used to produce water-soluble cellulose polymers are relatively uncomplicated. They typically involve treatment of cellulose with alkali to swell the polymer, followed by the chemical addition of the appropriate substituent. Each of the commercial cellulosic polymer types is available in a variety of grades that are differentiated by molecular weight, levels of chemical substitution, uniformity of substitution, and treatment for ease of dispersion. The chemical modifications are defined in two ways: the degree of substitution (DS), which is the average number of hydroxyl groups that have been substituted per anhydroglucose unit, and the moles of substitution (MS), which is the average number of moles of substituents per anhydroglucose unit for those substituents that generate repeating units (such as ethylene oxide in HEC).

In pure water, the more common cellulosics such as HEC, EHEC, HPMC, and HEMC at similar molecular weight have very similar rheology flow curves. The differences between these products become apparent in formulated products with respect to rheology and other properties. There are also regional preferences governed by production locations, cost, climate, formulating practices, and other factors.

In general, as molecular weight increases for conventional water polymers (e.g., polysaccharides thickeners), the amount of thickener required for constant MSV decreases (thickening efficiency improves). At the same time, LSV typically increases and HSV decreases, resulting in a more shear-thinning fluid. The effect on film build is predictably lower and with reduced leveling. However, some investigators have actually reported improved leveling with higher MW cellulosics, but this may be system dependent. Each type or grade of cellulosic thickener has a characteristic hydration time, which is defined as the onset of viscosity build. Some cellulosic grades (especially for coatings) also have surface treatments such as glyoxal to slow down the rate of hydration. This is called "retardation," and the result is improved incorporation of the thickener. The glyoxal reacts with hydroxyl methyl groups on the polymer to form hemi-acetal crosslinks. The dissolution time of the thickener is defined as the time to reach equilibrium viscosity (maximum viscosity).

One inherent liability with many cellulosic polysaccharide polymers is poor biostability [82–85]. Cellulase enzyme attacks the biopolymers, degrading them with resultant viscosity loss in coatings. Much research has been dedicated to finding reagents that would deactivate cellulase enzyme. Unfortunately there are dozens of different types of

TABLE 4—Commercial "conventional organic" thickeners for waterborne coatings: producers, product tradenames, product codes, and thickener type

Conventional Thickeners and Rheology Modifiers—for Coatings			
Company	**Trade Name**	**Thickener Type**	**Product Codes**
ADM	OPTIXAN™	Xanthan Gum	Dispersible, Dispersible T, 40, 40 (transparent)
Akzo Nobel	BERMOCOLL	EHEC	E (8 grades)
Akzo Nobel	BERMODOL	EHEC	EBS (9 grades)
Akzo Nobel	BERMODOL	MHEC	M
Akzo Nobel	BERMODOL	EMHEC	EM, EBM
Akzo Nobel/Alco	ALCOGUM®	ASE	L-11, L-12, L-15, L-52, L-68, L-72
Arkema/Coatex	VISCOATEX™	ASE	46, 53 L, 730
Arkema/Coatex	ULCAR THICKENER	ASE	146
Ashland/Aqualon	AQUALON®	CMC	CMC
Ashland/Aqualon	BLANOSE TM	refined CMC	CMC
Ashland/Aqualon	CULMINAL®	HPMC (MHPC)	MHPC 400, MHPC 3000 P1R, MHPC 6000 R, MHPC 20000 R
Ashland/Aqualon	CULMINAL®	HEMC (MHEC)	MHCE 35000 R
Ashland/Aqualon	KLUCEL®	HPC	HPC
Ashland/Aqualon	NATROSOL®	HEC	250 HHR, 250 H4R, 250 HR, 250 MHR, 250 MR, 250 KR, 250 GR
Ashland/Aqualon	NATROSOL® B	HEC	250 HHBR, 250H4BR, 250HBR, 250MHBR, 250MBR
Ashland/Aqualon	NATROSOL FPS®	HEC Fluidized	H4B, HB, MB
BASF	LATEKOLL	na	D
BASF/Ciba	Ciba® VISCALEX®	PNASE-NH4	HV30, HV100, HV300, VG2, VM
DOW Chemical	CELLOSIZE™	HEC	EP 09, EP 300, ER4400, ER 15M, ER 30M, ER 37M, ER 52M, ER 100M, DCS LV, DCS HV
DOW Chemical	METHOCEL™	HPMC	J5MS, J12MS, J20MS, J40MS, J75MS, K4MS, K15MS
DOW Chemical	WALOCEL™	HEMC	MTX, MW, MKX
DOW Chemical	WALOCEL™	HPMC	MK/MKS
DOW Chemical	WALOCEL™	CMC	CRT A, Clear+stableTM, C, CRT
DOW Chemical	ACRYSOL®	ASE	ASE-60, ASE-75, ASE-95NP, G-111 (NH4 salt)
Elementis	RHEOLATE®	na	CVS-2, CVS-3
FMC Corporation	FMC Biopolymer	MCC	Lattice NTC 80, AVICEL
Huber/Kelco	CELFLOW®	CMC	S-50, S-100, S-150, S-200
Huber/Kelco	K1C626	Diutan Gum	K1C626
Huber/Kelco	KELCOGEL®	Gellan Gum	AFT, AF
Huber/Kelco	KELZAN®	Xanthan Gum	AR, ASX, ASX T, BT, CC, HP, HP-T, RD, S, ST, T
Huber/Kelco	WHELAN GUM	Welan Gum	K1A96
ISP	STABILEZE™	MVE/Mah	O6, QM
King Industries	DISPARLON®	Polyamide for WB	AQ-600, AQ-607, AQ-610, AQ-630, AQ-870
Lamberti SPA	ESACOL™	Guar Derivative	ED 5, ED 10, ED 15, ED 20 W, ED 30 W
Lamberti SPA	CARBOCEL™	CMC	MM 15, MM 75C, MM 500, MA 100, MA 200, MA 300, UBM 25, PASL 2000, ED 20000
Lamberti SPA	VISCOLAM™	ASE	330
OMG/Borchers	BORCHI® GEL	PN ASE	A LA
Shin-Etsu	METOLOSE™	MC	SM
Shin-Etsu	METOLOSE™	HPMC	SH, SE
Shin-Etsu/SE Tylose	TYLOSE®	HEC	H300 - H100000 (7 grades), HS6000 - HS100000 (5 grades)
Shin-Etsu/SE Tylose	TYLOSE®	MHEC (HEMC)	MH200 - MH300000 (9 grades)
Shin-Etsu/SE Tylose	TYLOSE®	MHPC (HPMC)	MO 60009 P4, MO 30023 P4, MO 60016 PA

naturally occurring cellulase enzyme, and a deactivator that is effective for one enzyme is often ineffective for another. A cocktail of deactivators would be required, and to date, this has been an impractical solution because of cost, toxicity, interaction with other components in a coating formulation, and issues with persistence in the coating over time. However, in another approach, chemical modification of the cellulosic polymers has resulted in the development and commercialization of bioresistant grades of HEC and some other cellulosics. The chemical modification that imparts enzyme resistance (for at least on a major producer of HEC) is the DS and uniformity of ethylene oxide substitution. To achieve the enzyme resistance, the glucose repeat units in HEC are substituted with pendent ethylene oxide on at least every other alternating anhydroglucose unit. The uniformity of substitution effectively blocks the attachment of the enzyme to the polymer backbone. Cellulosic polymer may also be subject to degradation by oxidant/reductant impurities that are carried over from the emulsion polymerization of latexes used in the coatings formulations [86]. This has mostly been solved on the latex side by ensuring that only low levels of those impurities remain in the latex products.

HEC

Of the cellulose ether polymers available, HEC has been by far the most popular cellulosic thickener used in waterborne coatings, and it is also the most popular coatings thickener regardless of chemical type [81]. HEC is a semi-synthetic nonionic polysaccharide manufactured by reacting ethylene oxide with the reactive hydroxyls on the anhydroglucose units of cellulose. The ethylene oxide also reacts with previously substituted hydroxyls resulting in short pEO side chains of usually two or three units in length. The ratio of molar substitution (MS) to DS defines the number of EO groups per side chain. The most popular products have MS values in the range of 1.5–3.0 and DS values of about 0.85–1.35. Optimizing reaction conditions results in a more uniform distribution of substitution to produce bio-resistant polymer grades. Commercial products are available in several regular and enzyme-resistant grades. Microrganisms such as bacteria, molds, and fungi can produce enzymes that degrade cellulosic thickeners. These microorganisms are often introduced into paint through contaminated raw materials or poor in-plant housekeeping. Although in-can preservatives will kill the microorganisms present, there are no additives effective against the enzymes that might have been produced in the paint. Consequently, bioresistant grades of HEC with unique structures were developed that have resistance to cellulose enzyme. Of the various grades of HEC available, the medium- and high-molecular-weight bio-resistant grades have been of greatest utility in coatings as thickeners. Low-molecular-weight grades are occasionally used as secondary TRMs to modify rheology (improve flow or film build).

Some cellulosic grades also have surface treatments to slow down the rate of hydration, thereby reducing the tendency for lumping. HEC is most often used in solid powder form, but moderately viscous "fluidized dispersions" are also available, which improve handling and may also improve the rate of incorporation. To minimize the dispersion viscosity of the supplied product, proprietary salts are incorporated. Various test methods for HEC are found in ASTM Test Methods for Hydroxyethylcellulose (D2364).

EHEC AND EMHEC

EHEC and ethymethylhydroxyethy cellulose (EMHEC) are two related cellulosic thickeners used in coatings with regional preferences [78–80]. In this more common naming convention, these cellulosic polymers are considered derivatives of HEC. Of the two, EHEC is more widely used in coatings, and mostly because of its favorable economics, EHEC has become competitive with HEC in North America and is the dominant cellulosic thickener in some other geographies. EHEC and EMHEC are inherently somewhat more bioresistant than HEC, but the respective bioresistant grades tend to be similar in enzyme resistance. To avoid lumping on addition of the powder to aqueous media, all paint grades of EHEC and EMHEC are treated with glyoxal for ease of incorporation. Increasing hydroxyethyl substitution along the cellulose backbone increases water solubility, improves salt tolerance, and decreases the tendency for gellation on heating. EHEC is used in several architectural coatings applications including textured paint, chemical plaster, flat paint, satin paint, and semi-gloss paint. The general performance in paint is typically somewhere between HPMC/HEMC and HEC. As is typical with other cellulosic thickeners, lower molecular grades impart less spatter and impart better leveling, while higher MW grades are more efficient with more pseudoplastic rheology.

EMHEC was developed to impart the combined properties of both HEC and HPMC. This high-efficiency thickener has particular application in flat paints where it provides good color acceptance and water resistance. Another attribute of enzyme resistance EMHEC is its low surface activity resulting in low foaming relative to HEC and HPMC.

HPMC AND HEMC

Another water-soluble nonionic cellulose polymer is methyl cellulose (MC). This polymer is mainly used in food and cosmetic applications but also has major industrial application in construction materials, where it is used in cement or gypsum-based mortars to control workability, slump, open time, water retention, substrate adhesion, and viscosity. The industrial construction grade is modified with glyoxal for increased dispersibility Although MC is not typically used as a thickener in coatings, some water-soluble derivatives of MC with hydroxyethyl or hydroxypropyl substituents have found acceptance in coatings. Two of the principal derivatives are hydroxypropylmethylcellulose (HPMC) and, used to a lesser extent, hydroxyethylmethylcellulose (HEMC) [87,88]. An alternative naming for these polymers in some literature is based on their being derivatives of HPC and HEC. In this convention they are MHPC and MHEC. These polymers have a modest degree of surface activity, which is advantageous in cementitious compositions, but this characteristic can be problematic in coatings for color development and color acceptance. For coatings, HPMC and HEMC are mainly in Europe and particularly in Northern European formulations. They are used as viscosifiers in interior and exterior emulsion paints to control in-can consistency, rheology, and storage stability. Some binder systems that seem to work well with these thickeners are styrene-acrylics and VA/VEOVA emulsions. Standard grades of HPMC and HEMC are more bioresistant to enzymatic degradation than standard grades of HEC or EHEC; however, the bioresistant grades of HEC and EHEC are considerably more resistant than HPMC and HEMC. There

is some controversy regarding the relative performance of these products for spatter resistance. HPMC has some niche applications and is especially recommended for Italian Tempera type paints because of its compatibility with certain types of calcium carbonate used in those formulations. HPMC tends to impart less pseudoplastic character than similar grades of HEC in some formulations.

Grades of HPMC vary in molecular weight, the ratio of methyl to hydroxypropyl substitution on the cellulose backbone, and the degree of substitution. Commercial grades of HPMC have average DS for the methyl groups in the range of 0.9–1.8 and MS for hydroxypropyl groups in the range of 0.1–1.0. Variations in these parameters affect solubility, thermal properties, and resistance to enzymes. Both MC and HPMC exhibit lower critical solution temperatures (i.e., they possess the somewhat unusual property of being soluble in cold water and insoluble in hot water). Solutions of these polymers form gel structures on heating. With modifications in processing, the DS, MS, gel temperature, and gel texture are altered. Because of its structure, HPMC is also inherently more resistant to bio-organisms compared to some other polysaccharides. Various test methods for the characterization of HPMC may be found in ASTM Test Methods for Hydroxypropyl Methylcellulose (D2363).

HEMC is another MC derivative, but it is used to a lesser degree in coatings than HPMC. For reasons of economics and product line extension, the same producers that make MC also conveniently make HPMC and HEMC. The HEMC grades are generally fewer for HEMC than HPMC, but they are prepared in a similar fashion regarding variation of DS for methyl groups and MS for the hydroxyethyl groups on the polymer backbone.

CMC

CMC is an anionic water-soluble polymer that has been of limited use in coatings because the modification constituent (sodium carboxylate) leaves the dried films more water-sensitive than most non-ionic polysaccharides [78–80]. However, in some lesser-developed countries and where lowest cost is a primary consideration, this polymer as a thickener in coatings is quite popular. CMC is prepared by reaction of cellulose with monochloroacetic acid after treatment with alkali. Commercial grades have DS for carboxylate substitution ranging from 0.4–1.4, and the most popular products are with MS 0.7 to 0.8. As with most other conventional polysaccharides, the viscosity is primarily controlled by varying the molecular weight of the cellulosic chain. Some technical grades of CMC contain by-product salts (primarily sodium chloride and sodium glycolate) that further limits their use in coatings applications. One application of utility for CMC is in dry-mix paints where the CMC functions to control viscosity and wet edge. A purified grade of CMC referred to as cellulose gum is preferred for use in latex paints. Various procedures for characterization of CMC may be found in ASTM Test Methods for Sodium Carboxymethyl-cellulose (D1439).

MCC

Microcrystaline cellulose (MCC) is a nonionic form of cellulose that is typically coprocessed with carboxymethyl cellulose and supplied in powder form for use in paints and coatings [89,90]. MCC forms a three-dimensional stabilizing network after high shear dispersion in water resulting in millions of insoluble microcrystals. The viscosifying network is shear thinning and forms very stable thixotropic gels. This provides stability at low shear rates for improved pigment suspension and reduced color float in tinted gloss paints co-thickened with nonionic associative thickeners. For proper incorporation, it is recommended that the MCC be the first component dispersed in water with high shear.

Galactomannan Polysaccharide Thickeners

GUAR GUM AND LOCUST BEAN GUM

Guar gum (GG) and locust bean gum (LBG) are two galactomannan polysaccharides with different mannose/galactose ratios [91,92]. These polymers are widely used in many industrial sectors including food, textiles, paper, paint, adhesives, cosmetics, mineral processing, and pharmaceuticals. Of these two polymers, guar, and especially modified guar, is more important in paints and coatings though used less than many other polysaccharides. Guar (guaran) is a naturally occurring, high-molecular-weight galactomannan polymer obtained from the guar plant *(Cyamopsis Tetragonalobus)*. Also known as clusterbean, guar is a drought-tolerant annual legume with major crop production and processing in India, Pakistan, and the United States (mainly Texas and Oklahoma). The polymer backbone of guar is a linear chain of β1,4-linked mannose residues to which galactose residues are 1,6-linked at every second mannose, forming short side-chain branches. The polymer, with molecular weight of over 1×10^6, takes on a rigid rod-like conformation because of the beta linkage between the monomer units. Guar gum is sometimes used as a thickener for coatings in its natural unmodified form, but more often it is derivitized for industrial applications. The primary derivative is hydroxypropyl guar.

HYDROXYPROPYL GUAR (HPG)

Guar is often chemically modified similar to cellulosics with akly and hydroxylakyl ether substituents. The most common derivitized product is hydroxyproply guar (HPG). Although natural and derivitized guar are sometimes used in coatings, they are more commonly employed as efficient viscosifiers in food and in non-cementicious construction products [93–95]. Solutions of galactomannan polymers exhibit strongly pseudoplastic behavior, excellent heat stability, good cold water solubility, high salt tolerance, and lubricity. Of the non-cellulosic polysaccharides thickeners available in commerce, only hydroxypropyl guar has found any significant application in coatings. Like the synthetic biopolymers described below, HPG produces coating rheology that is more shear thinning (more pseudoplastic) than most of the cellulosic polymers previously described. Consequently, HPG tends to have better suspension and antisag characteristics than some cellulosics but produces more roll spatter and is less bio-resistant. Another limitation for HPG is that it is available in only a few grades for coatings. Compared with its parent (guar gum), solutions of HPG are more bioresistant, less electrolyte sensitive, and have improved solubility and clarity. The biostability is typically less than enzyme-resistant cellulosics. Utility of HPG is primarily as a secondary thickener for sag and suspension control in flat, texture, and dripless paints such as spray ceiling paints

Fermentation Biopolymer Polysaccharide Thickeners

The cellulosic thickeners previously described are all semi-synthetic biopolymers. However, the terms "semi-synthetic biopolymer" or "synthetic biopolymer" sometimes imply biopolymers produced by a non-traditional chemical method—fermentation. However, fermentation is a mostly natural process; therefore, it is more appropriate to refer to these polymers as biopolymers by fermentation or simply fermentation biopolymers [26,96]. These polymers are often referred to as gums or biogums. The use of fermentation biopolymers in paints and coatings has been quite limited; nonetheless, at least two products are being used as either primary or secondary thickeners, some to provide suspension characteristics. Like commercial cellulosic thickeners, commercial fermentation biopolymers are also polysaccharides; however, they are enzymatically produced rather than being made by chemical modification. The biopolymer synthesis is typically conducted in a fermentation broth with naturally occurring bacterium or yeast. Some common traits of biopolymers are their superior ability to suspend or gel, their inherent salt tolerance, and their stable viscosities over a wide temperature range. Biogums also tend to have better enzyme resistance than non-enzyme resistance grades of cellulosic thickeners. As with HPG, a limitation is that there are only a few grades available from suppliers. Among the commercial biopolymer products which are available for use in coatings are xanthan gum, rhamsan gum, welan gum, gellan gum, and diutin gum. Biogums have a naturally occurring cellulose enzyme that must be controlled for paint applications. Because of that factor and cost, most biogums find little use in coatings.

XANTHAN GUM

The most well known and commercially important synthetic biopolymer is Xanthomonas campestris polysaccharide (XCPS), better known as xanthan gum [97,98]. This "cultured" biopolymer was initially discovered in USDA laboratories in 1959 by fermentation of glucose with the bacterium *Xanthomonas campestris* [30], a microorganism found in nature mainly on the leaf surfaces of green vegetables. The discovery of Xanthan gum was brought into first commercial production by the Kelco Company under the trade name Keltrol in the early 1960s. In the optimal fermentation process, aeration, temperature, pH, and agitation are carefully controlled, resulting in a tan-colored, free-flowing powder on drying. Though xanthan is produced by fermentation, this polymer is made up of β-1,4-linked D-glucose residues producing a backbone that is identical to the cellulose molecule. A trisaccharide branch with one glucuronic acid unit between two mannose units is linked to every other glucose unit in the main chain. This high-molecular-weight (approximately 2×10^6), branched polysaccharide is characterized as having high yield stress values and a high degree of pseudoplasticity (high LSV and low HSV). The rigid structure of the Xanthan polymer matrix immediately dissociates on shear and instantly recovers to the original viscosity when the shear is removed. This immediate recovery of viscosity after shearing is a key characteristic for pigment suspension and sag resistance in coatings, but it does inhibit leveling. Other features of xanthan gum are its relative insensitivity to *p*H, temperature, enzyme attack, the presence of most salts, and good compatibility with other coatings ingredients. Applications for Xanthan are similar to those for HPG but with somewhat better thickening efficiency and even more shear thinning rheology (higher LSV). Grades of xanthan gum are available to provide a range of dispersibility and hydration.

OTHER FERMENTATION BIOPOLYMERS

There are several other biopolymers produced by fermentation that have gained commercial importance in some industries such as food, pharmaceuticals, and personal care, but these polymers currently have very limited use in coatings [26,96]. However, they do have potential in certain types of coatings and for some specific properties. Cost is often a deterring factor though, as there are more cost-effective options with cellulosics and other thickeners. Among these fermentation biogums are rhamsan gum, gellan gum, welan gum, and diutin gum.

Rhamsan gum has some very minor application in coatings. One of the more outstanding characteristics of this polymer is its exceptional suspending power (produces very high LSV in coatings). In approximate order of decreasing suspending ability are Rhamsan gum > Xanthan gum > HP guar > CMC > HEC. Rhamsan gum also is reported to have good salt tolerance and improved stability to high-shear mixing.

Gellan gum is a water-soluble anionic polysaccharide produced by microbial fermentation of the *Sphingomonas elodea* bacterium. This gum is a very efficient thickener and forms gels with even minor levels of mono or divalent cations. Its principal application is in food. The repeating unit of the gellan polymer is a tetrasaccharide with repeating units of glucose, L-rhamnose, and D-glucuronic acid. The polymer is available with both low- and high-acyl content to provide hard non-elastic and soft elastic gels, respectively. The high-acyl polymer has ester side groups, and the low-acyl polymer is produced by alkali treatment of the high-acyl polymer.

Welan gum is an anionic polysaccharide with excellent thermal stability and retention of viscosity at elevated temperatures (greater than 90°C) in aqueous media. This microbial polysaccharide is produced by fermentation with *Alcaligenes* sp. bacterium resulting in a tetrasaccharide repeating unit backbone with single sugar branches of either L-mannose or L-rhamnose. Welan gum is considered a first-generation thickener for cementitious systems (cements and concrete). It is also recommended for oilfield, foundry coatings, pigment suspensions, and paint.

Diutan gum is considered a second-generation product to welan gum and was designed specifically for cementitious systems. This polymer imparts pseudoplastic rheology with virtually instantaneous response to either the application or removal of shear. Consequently the fluid is easy to pump or process but then provides instant suspension. Some applications include grouts and mortars with limited use in coatings.

Alkali-Swellable/Soluble Emulsions (ASEs)

Alkali-soluble and alkali-swellable emulsions (ASEs collectively) are among the few conventional synthetic hydrocarbon thickeners used in coatings [99–102]. Conventional ASEs are carboxyl functional copolymers produced by the free-radical emulsion polymerization of ethylenically

unsaturated monomers [31]. They are low-viscosity water-insoluble latexes at low *p*H as produced and commercially supplied, but they exhibit thickening on dissolution or swelling of the latex particles when the *p*H is raised (generally above *p*H 5.5) with full viscosity development on the alkaline side of *p*H. Copolymers of methacrylic acid and ethyl acrylate are by far the most common pair of primary monomers used, and they often include a small amount (generally less than 1 %) of a polyfunctional monomer to lightly cross-link the polymer to enhance swellability. Since most coating formulations are finished on the basic side of *p*H, the ASE polymers are fully neutralized in most applications. They achieve their maximum viscosities above about *p*H 7, and ideally, the maximum viscosity should be relatively constant from about *p*H 8–10 so that slight changes in *p*H on storage will have little or no effect on coating consistency. Although ASEs impart viscosity and pseudoplastic rheology similar to some other conventional thickeners, their primary advantages compared to the powder form polysaccharides and fermentation biopolymers are in ease of handling and bio-stability ASEs may be more water sensitive than most nonionic polysaccharides; however, unlike CMC, which is supplied as a water-soluble sodium salt, neutralization of ASEs is normally conducted with ammonia or volatile aminoalcohols, which eventually leave the film on drying. The ASE polymer is insoluble before neutralization, soluble after neutralization, and again insoluble after the volatile base leaves the paint film thus producing a film with relatively low water sensitivity. Hydrophobe modification of conventional ASEs to produce associative products (HASEs) has greatly increased the popularity of alkali-responsive emulsion thickeners. The HASE associative thickeners are discussed later in this chapter under "Hydrophobe Modified ASEs (HASE)."

A current list of conventional commercial thickeners suppliers and their products are compiled in Table 4.

ASSOCIATIVE TRMS (ATRMS)

Because of the increasing importance of rheology modification in coatings, the use of ATRMs continues to grow with many product offerings now available. The study of associative thickeners, their performance, and formulating with these products has been examined extensively over the past 20 years [103–124]. Presently, three broad classes of commercial ATRMs represent many older and newer products: hydrophobe-modified nonionic synthetics (HMNS), hydrophobe-modified cellulosics (HMC), and HASE. Contained within these major classes are important subclasses, all of which are discussed in detail hereafter. Table 5 summarizes the commercial product classification scheme for CTRMs and ATRMs used in coatings. Included in this table are the principal thickener classes, subclasses, conventional/associative analogs, and the designated acronyms. Those acronyms that are prominent in the literature as well as those which are assigned here are indicated.

Coating components and coating formulation variables are known to affect the rheological performance of associative thickeners [125,126]. Some specific parameters that have been examined are volume solids [127], type of latex binder [128–130], latex binder particle size [131], particle surface acid groups [132], surfactants and cosolvents [133–135], coalescing aids [136], and some clay pigments [137,138]. The steady shear, linear viscoelastic, and extensional rheological properties of associative thickener solutions have also been characterized. The classes of associative thickeners will be discussed below in no particular order. However, the three most significant products commercially have been hydrophobe modified nonionic synthetics (mainly HEUR), hydrophobe modified alkali-swellable emulsions (HASE), and hydrophobe modified polysaccharides (mainly HMHEC).

Hydrophobe Modified Nonionic Synthetics (HMNS)

The HMNS ATRMs are nonionic condensation polymers of synthetic origin. Most of these polymers are amphiphilic and therefore contain distinct polar (hydrophilic) and non-polar (hydrophobic) regions in the molecules that can promote micelle formation in very dilute solution. The hydrophilic regions are usually pEO segments that alternate with hydrophobic (usually alkyl, cycloacyl, or aromatic hydrocarbon) groups. The ends of main chains and any side chains of these polymers are also typically terminated with hydrophobic groups.

The HMNS polymers tend to be much lower in molecular weight than conventional thickeners, and the repeat units (pEO segment plus hydrophobe) are generally less than about 20 units. The most well-known HMNS subclass of which there are many commercial representative examples are the hydrophobe-modified ethoxylate urethane (HEURs). You will note that the M (for Modified) is dropped in this accepted acronym and in several other commonly accepted associative acronyms to follow. Another prominent HMNS subclass includes the hydrophobe-modified ethoxylate ethers (HEET) that are sometimes designated in literature as hydrophobe modified nonionic non-urethanes (HENN), or hydrophobe modified ethoxylate ethers (HEET). Other sub-classes include hydrophobe modified ethoxylate aminoplast thickeners (HEAT), and hydrophobe-modified urea/urethanes (HEUUR), which are sometimes designated PEUPU (polyether urea polyurethane). On examination, differentiation between HMNS subclasses mainly reflects the linkages between the hydrophobes. However, the size of the polymer, the macro structure of the polymer (linear, comb, branched), and the length of pEO segments are important elements for relative performance. Among the attributes of HMNS thickeners are excellent flow and leveling in coatings and high film build for increased coating thickness or one-coat coverage. These thickeners also tend to give better corrosion resistance in coatings. However, the low-shear viscosity that gives excellent leveling can be a liability for sag resistance on vertical surfaces. One issue with these thickeners has been viscosity loss on tinting due to the disruption of the associative thickening network by surfactants present in the tinting material. This is a research area where there as been much recent development to correct this problem [139–141]. Another area of recent activity for improvement is color acceptance with associative thickeners [142–144]. The subclasses of associative thickeners are discussed below.

HEUR (SUBCLASS OF HMNS)

As mentioned, the HEUR polymers are the major subclass of the nonionic synthetics (HMNS) [145–153]. They were the first HMNS polymers commercialized and are still among the most popular ATRM products with several

TABLE 5—Organic TRMs for waterborne coatings with conventional and associative analogs and their acronyms

Organic TRMs for Waterborne Coatings—Conventional/Associative Analogs and Acronyms				
		CTRMs		**ATRMs**
Cellulosics	HEC	hydroxyethyl cellulose	HMHEC	hydrophobe modifed HEC
	EHEC	ethylhydroxyethyl cellulose	HMEHEC	hydrophobe modifed EHEC
	EMHEC	ethylmethylhydroxyethyl cellulose	—	—
	HEPC	hydroxyethylpropyl cellulose	—	—
	HEMC	hydroxyethylmethyl cellulose	—	—
	HPMC	hydroxypropylmethyl cellulose	—	—
	CMC	carboxymethyl cellulose	—	—
	MCC	microcrystalline cellulose	—	—
Galactomannans	GG	guar gum	—	—
	HPG	hydroxypropyl guar gum	HMHPG	hydrophobe modified HPG
	HEG	hydroxyethyl guar gum	—	—
	LBG	locust bean gum	—	—
Fermentation Biopolymers	XCPS	xanthan gum	—	—
	Other	welan, gellan, and diutin gums	—	—
Alkali-Swellable/Soluble Emulsions	ASE	several products—most are EA/MMA copolymers	HASE[a] HEURASE[b]	hydrophobe modified ASE hydrophobe modified urethane ASE
Nonionic Synthetics	—	—	HEUR[c]	hydrophobe modified ethoxylate urethane
	—	—	HEUUR[d]	hydrophobe modified ethoxylate urea urethane
	—	—	HEAT	hydrophobe modified ethoxylate aminoplast
	—	—	HEET[e]	hydrophobe modified ethoxylate ether
	—	—	HPAPE[f]	hydrophobe modified polyacetal polyether
	PVP	Polyvinyl pyrolidone	—	—
	PVOH	Polyvinyl alcohol	—	—
	PAM	Polyacrylamide	HMPAM[g]	hydrophoben modified polyacrylamide

[a] HASE usually contain ester linkages to associative side chains.
[b] HEURASE contain urethane linkages to associative side chains—they are sometimes considered a subclass of HASE.
[C] HEUR are sometimes designated PEPU (polyether polyurethane) or simply PU Thickener (polyurethane thickener).
[d] HEUUR are sometimes designated PEUPU (polyetherurea polyurethane).
[e] HEET are sometimes designated HMPE (hydrophobically modified polyether) or PEPO (polyetherpolyol).
[f] HPAPE is designated HMPAPE by supplier with same text description.
[g] HMPAM is used mainly in oilfield applciations.

domestic and international suppliers. Common to all HEUR polymers are the presence of three chemical components: hydrophobes within and at the ends of side or main chains, hydrophilic pEO segments, and urethane linkages that join the pEO segments to the hydrophobes. Most HEUR polymers are formed by the reaction of mono- and di- or tri-isocyanates with the hydroxyl groups on the pEO segments—the reaction of an isocyanate with a hydroxyl group is a urethane group. The HEUR and some other HMNS subclass polymers are generally considered to be among the most effective of the associative products with respect to rheology modification. Being low in molecular weight and highly associative, they tend to provide the most Newtonian rheology (low LSVs and high HSVs) for superior flow/leveling and film build. They also impart low extensional viscosity and low viscoelasticity for superior spatter resistance.

Many HEUR polymers are supplied as moderately viscous solutions in a combination of water and cosolvent such as Butyl Carbitol® or propylene glycol. The cosolvent is present to suppress viscosity for ease of handling. Like conventional surfactants, these cosolvents have polar surfactant-like character that can disrupt the intermolecular association of the HEUR hydrophobes thereby reducing viscosity. Without the cosolvent, the viscosity of the HEUR thickener in water alone would be too high for practical

use. HEURs are now available that are 100 % aqueous (without cosolvent). Ordinarily these polymers would be extremely viscous in solution, but low viscosity is achieved with the addition of cycloextrin that effectively traps the HEUR hydrophobes to minimize their association. Since HEURs are non-ionic, they should have inherently low water sensitivity. However, they are generally less efficient than cellulosics or ASEs and they are also much lower in molecular weight, which may limit their use in some exterior applications. Because the HEUR products have very low LSVs for superior flow, they may permit sagging, syneresis, or pigment settling, particularly when used as the sole thickener. They are also very sensitive to other coating components, and proper formulation balance is necessary for optimum performance.

Other Nonionic Synthetics

As mentioned, one of the key differentiating features of the associative nonionic synthetic thickeners is the linking functionality joining the internal and terminal hydrophobe groups to the polyethylene oxide segments. In HEUR polymers, the linkage is urethane. In some other similar associative polymers the linkage can be ether, urea, or a combination of linkages, and some of the other commercial HMNS subclasses are discussed below [154,155].

HEET (SUBCLASS OF HMNS)

Synthetic nonionic associative thickeners with hydrophobe-pEO linking groups other than urethane are among the newer products in the HMNS arena. These polymers as a group are sometimes referred to as HENN thickeners. One of the subclasses in this group are the HEET. One major difference that defines the HEET subclass compared to HEURs is that urethane linkages are replaced with ether linkages. Another difference is that polyether segments may not be limited to ethylene oxide alone (that is, EO-PO blocks may be present).

HEUUR (SUBCLASS OF HMNS)

Another recent HMNS subclass is the HEUUR. In literature, the acronym PEUPU is sometimes used. As the names imply, these associative polymers are similar to HEUR except that some urea segments are present. That would suggest that at least some of the ethoxylate segments initially contained amine functional end groups—the reaction of an amine with an isocyanate results in the formation of a urea group. The HEUUR would be expected to have rheological properties similar to the HEUR and HEE polymers.

HEAT (SUBCLASS OF HMNS)

Another HMNS subclass is HEAT. This thickener subclass contains the usual hydrophobes and pEO segments, but it uses an aminoplast linkage to join the components. At this time there is only one commercial supplier of these products. Like the HEUR polymers, HENN thickeners contain cosolvent and are supplied as moderately viscous aqueous solutions. Little information is currently available; however, based on advertising claims for chemical composition and performance, the rheological characteristics of these products are expected to be similar to HEUR ATRMs. The chemical composition and physical form would also suggest that the handling and performance limitations are similar to those of HEURs. Improved color acceptance, color stability, and block resistance are claimed for the commercial product, and improved shear stability due to lower molecular weight is claimed for the developmental products but at the expense of thickening efficiency.

Hydrophobe Modified ASEs (HASE)

The HASE polymers were among the first ATRMs to be developed and their commercial significance dates back to the late 1960s, and since then, these polymers have been extensively studied in both academic and industrial settings [102,156–159]. The popularity of these products continues due to their relatively good economics, bio-stability, rapid viscosity equilibration, lack of cosolvents (0 or low VOC), and low-viscosity liquid form as supplied. Like ASEs, the HASE products are synthetic addition polymers produced by emulsion polymerization of carboxyl functional monomers. Consequently, they are of relatively high molecular weight (higher than HMNS but lower than conventional thickeners) and thicken by a hydrodynamic mechanism in addition to the associative mechanism. The predominate mechanism operating depends on several factors, including the molecular weight and the amount and type of associative functionality.

Typically, HASE products are terpolymers of ethyl acrylate, methacrylic acid or itaconic acid, and an associative macromonomer. The effects of monomer types, monomer ratios, and the types of associative side chains have been examined [160–165]. The macromonomer usually contains pEO units (typically 10–100 mol ethylene oxide) terminated with a hydrophobe (typically alkyl or alkylaryl). The associative side chain linkage to the main chain backbone is pre-dominately either ester (HEEASE) or urethane (HEURASE) per the classification scheme of Table 5. The patent literature does describe other linkages and although some have been used in the past, they are not commercial today (for example, products with ether linkages and products with anhydride ester linkages were marketed in the 1960s, but they were later discontinued). Like ASEs, the HASE polymers may also be cross-linked to varying degrees with small amounts (typically less than 1 %) of a polyfunctional monomer to increase swellability. Although HASE polymers are anionic and, therefore, predicted to be more water sensitive than non-ionic ATRMs, many HASE products are more efficient (less thickener is required for consistency), which minimizes the effect of the anionic character. Additionally, performance of HASEs in exterior coatings can be improved with ZnO or zinc complexes, which cross-link the carboxyl functionality present [157], which is lacking in the HMNS polymers. Being polyanionic, the HASE polymers also have dispersant character that contributes to hiding and gloss. The carboxyl groups in HASE polymers can also covalently cross-link with melamine, urea, and epoxy resins in thermoset coatings, and being acidic, they catalyze the cross-linking process. Some structural depictions of the three most polular associative thickeners are shown in Fig. 12.

HEEASE (SUBCLASS OF HASE)

Hydrophobe modified ethoxylate ester alkali-swellable/soluble emulsions (HEEASE) are one of two major HASE subclasses [166–168]. Although the HEEASE acronym is not often used, it helps to differentiate between associative ASEs that contain ester linkages and those that contain

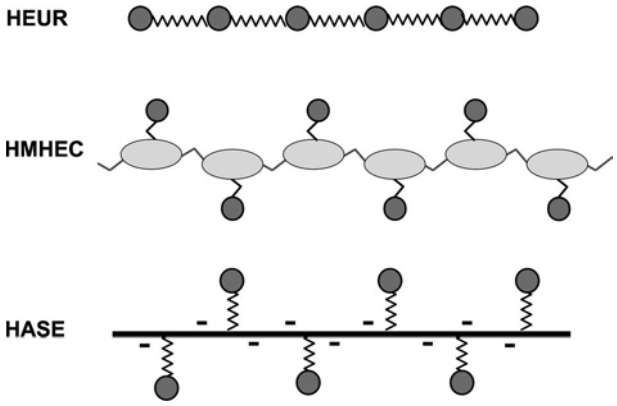

Fig. 12—Relative polymer architecture of three popular associative thickeners used in waterborne coatings.

urethane linkages. Prior to the introduction of HASEs containing urethane linkages, the HEEASE polymers were the only lasting commercial representatives of the HASE class. Consequently, HASE often implied HEEASE in the literature. Since there are now several commercial urethane functional HASE polymers, subclassification was needed, and like the HEUR and HENN polymers, differentiation here relates to the presence or lack of urethane linking functionality. The associative side chains of HEEASE polymers contain ester linkages, and like most other ATRMs, some HEEASE polymers function more as rheology modifiers and are often lower in molecular weight while others function as primarily thickeners to produce efficient mid-shear viscosity. Because of the dual thickening mechanisms, the molecular weight and type and amount of associative functionality are among the processing variables that can be altered to effect change in performance. With respect to rheology, the HEEASE thickener rheological performance is generally similar to the associative cellulosics.

HEURASE (SUBCLASS OF HASE)

The second major subclass of HASE thickeners are the hydrophobe modified ethoxylate urethane alkali-swellable/soluble emulsions (HEURASE) [169–173]. These ATRMs are of more recent vintage and were designed to combine some of the chemical architecture and performance attributes of anionic ASEs with the chemical architecture and performance attributes of nonionic HEUR thickeners. Like conventional ASEs, HEURASE polymers are prepared by emulsion polymerization and supplied as low-viscosity, low-*p*H latexes. However, the associative side chains in HEURASE contain the same three functional components found in HEUR thickeners (terminal hydrophobes, pEO segments, and urethane linkages). Because of this and the relatively high level of associative monomer present in these terpolymers, rheology modification approaching that of the premium HEUR thickeners is claimed without many of the HEUR and HENN limitations. Although most HEURASE thickeners provide the expected Newtonian rheology, some atypically impart suspension characteristics (high LSV) for use in antisag, antisettling, or texture paint applications. The extensional viscosity imparted by HEURASE products is low and comparable to some HEUR thickeners.

Hydrophobe Modified Cellulosics (HMC)

Like the HMNS polymers, hydrophobe-modified cellulosics (HMC) are nonionic condensation polymers but of biological origin. These polymers are prepared by modifying standard or special grades of conventional cellulosics such as HEC or EHEC with hydrophobes, and like the other ATRMs described above, the hydrophobes are typically alkyl or alkylaryl, but the pEO chains are comparatively very short. Presently there are two commercial subclasses of HMC: HMHEC and HMEHEC. Although the acronyms for associative thickeners are usually unhyphenated, the hyphen is included in the sections for polysaccharides to avoid confusion where H often means hydroxyl (rather than hydrophobe) and M means methyl (rather than modified). These HMC are non-ionic; however, the potential exists for other cellulosic associative products, which may be either nonionic [for example, hydrophobe-modified hydroxypropyl methyl cellulose (HMHPMC) and the like] or anionic [for example, hydrophobe-modified carboxymethyl cellulose (HMCMC) and the like]. One non-cellulosic hydrophobe modified polysaccharide recently commercialized is based on hydroxypropl guar gum, discussed later.

HMHEC (SUBCLASS OF HMC)

The first commercial associative cellulosic thickener on the market in the late 1980s was a HMHEC introduced by Hercules/Aqualon. At least three grades of this product are still available at this writing under new umbrella ownership. Another competitive HMHEC product was introduced later from Dow Chemical. HMHEC thickeners have overcome many of the limitations of conventional HEC, including improved film build, improved leveling, and better spatter resistance [174–180]. The associative behavior (adsorption onto latex and pigment particles) and the rheology of this polymer have been characterized along with various solution properties. The improvement in rheology (more Newtonian for better leveling and increased film build) over HEC is generally similar to the HASE type thickeners, but since HMHEC is nonionic, the early water sensitivity of coatings made with it tends to be better. The methods of preparation and solution properties of HMHEC have also been described. HMHEC is prepared by attaching hydrophobes to conventional HEC via the hydroxyl groups along the polymer backbone. The degrees of substitution and molecular weight grade of HEC chosen for this modification are important. Unlike other classes of ATRMs, the ethoxylate content between hydrophobe and HEC backbone is small (generally one to a few units). Because HMHEC is a solid, the handling limitations are similar to those of HEC and other solid thickeners. To improve on this, developmental fluidized aqueous dispersions of HMHEC were introduced but with limited success. The viscosity of the fluidized products as supplied is still moderately high and similar to that of the HEUR and HENN products.

HMEHEC (SUBCLASS OF HMC)

Associative EHEC polymers were introduced in 1992 and are among the most recent commercial HMC products [181,182]. Their chemical construction and performance is somewhat similar to HMHEC but based on EHEC. As with the unmodified cellulosic analogs, use is often geographically driven. At this writing, there is currently only one supplier of HMEHEC products.

HMHPG (SUBCLASS OF HMC)

A relatively recent entry into the polysaccharide associative thickener category is hydrophobe modified hydroxypropyl guar gum (HMHPG) [183–185]. This polymer is somewhat similar to the hydrophobe modified cellulosics but is of course a galactomannan derivative. Like HMEHEC, this thickener is used primarily in certain geographies and the success in coatings is somewhat limited. Anti-spatter properties with improved flow and film build are expected.

In Table 6 a current list of principal associative thickener suppliers, their products, and the thickener classification for each is compiled.

INORGANIC THICKENERS FOR AQUEOUS AND SOLVENT-BORNE COATINGS

Most inorganic thickeners and rheology modifiers (ITRMs) are supplied as powders and are mainly either modified clays or fumed silicas. When they are properly dispersed into a coating, they usually function as suspending or gelling agents and some may have secondary utility as extender pigments. Rheologically, ITRMs tend to have high yield values and are characterized as "thixotropes." The viscosity of the coating decreases with time under constant shear as its gel structure is broken down. When the shear is removed, the coating gradually recovers to its original viscosity. The rate of recovery can be very rapid (complete within seconds) or can take several minutes or even hours depending on the degree of thixotropy and prior shear history. Certain grades or mineral types of ITRMs are useful for thickening aqueous systems and others for solvent-borne coatings. Utility in one media or the other is mostly a function of the thickener. Table 7 lists and catagorizes the various types of inorganic thickeners used in waterborne and/or solvent-borne coatings. Included are synonyms, chemical type, and the type of thickening mechanism.

Particle surface is often modified with organic treatments to render it hydrophilic (usually for waterborne coatings) or hydrophobic (usually for solvent-borne coatings). ITRMs are also sometimes added to aqueous formulations as secondary thickeners to impart some degree of antisag, antisettling, or antisyneresis to coatings containing primary conventional or associative thickeners. The most common types of modified and unmodified ITRMs are attapulgite clays, bentonite clays, organoclays, and treated and untreated synthetic silicas.

Clay Thickeners

The term "clay" or "silicate clay" refers to minerals that are rich in alumina, silica, and water. The main building blocks of silicate clays are layers of silica tetrahedron and aluminum octahedron. Many clays also contain magnesium in their crystal lattice (magnesium aluminum silicates), and some also contain one or more other cations including iron, zinc, sodium, calcium, or lithium. The five primary silicate clay mineral groups are kaolinite, illite, vermiculite, smectite, and chlorite, which are differentiated by their layer type, layer charge, and by chemical formula [186]. Of these five main clay groups, only smectite clay (and some related clays) are commercially significant as thickeners in waterborne and/or solvent-borne coatings [186–188]. Smectite means "expanding lattice," and refers to a family of thickeners that undergo an increase in effective volume (swelling) during incorporation into coatings. This is also the only clay group that swells with water. Two important types of swelling smectite clays are bentonite and hectorite. Also commercially important as thickeners are the non-swelling organoclays derived from bentonite and hectorite. Another non-swelling clay containing some smectite is attapulgite. This clay and the organoclays thicken by structuring rather than by swelling. The other four main clay groups (kaolinite, illite, vermiculite and chlorite) do not function as thickeners, but they are important in commerce as pigment extenders, insulation materials, fillers, and the like. Although smectites and attapulgite clays work very well as viscosifiers, they can be challenging to incorporate into coatings. They typically must be predispersed under high shear, may require some time for full equilibration, and their water demand sometimes limits formulating latitude. However, some dispersible grades are available for ease of incorporation. Each of these clay thickeners is discussed in more detail below and they are identified as being either swelling or structuring clays.

BENTONITE/MONTMORILLONITE CLAY—SWELLING

As mentioned, the two main commercial classes of smectite clay for swellable coatings thickeners are bentonite and hectorite. Bentonite is by far the most abundant of these two minerals in nature, and the term bentonite is commonly used generically to mean smectite. The principal bentonites are sodium bentonite and calcium bentonite. Although bentonite and hectorite are similar in their mechanism of swelling behavior, they differ in their crystal lattice composition. Bentonite is an absorbent, naturally occurring hydrated aluminum silicate originally deposited by volcanic ash and metamorphosed into rock over time [189,190]. This clay consists mainly of the mineral montmorillonite, which is named after its discovery location in Montmorillon, France.

There are actually several types of bentonites, and their names depend on the dominant elements present, such as K, Na, Ca, and Al. Bentonite is typically described as colloidal hydrated aluminum silicate with varying degrees of aluminum replacement with magnesium, calcium, and sodium. The crystal lattice of montmorillonite contains mainly aluminum with the chemical formula $(Na,Ca)_0$, 3(Al, $Mg)_2Si_4O_{10}(OH)_2 \cdot n(H_2O)$. Wyoming bentonite is considered a relatively pure form of montmorillonite, and often montmorillonite means Wyoming bentonite. The vast majority of natural bentonite is calcium bentonite. When sodium ions are substituted for calcium ions, sodium bentonite is obtained and the swelling ability is enhanced. Natural sodium bentonite has a very high swelling ability, and this bentonite gets its name from its discovery near Fort Benton, Montana.

The crystal structure of bentonite is a three-layer sheet that forms flake-like colloidal particles of less than 0.5 μm. In aqueous media, bentonite is naturally hydrophilic and readily dispersible. The water is taken up between the mineral laminae, causing the lattice structure to stretch and swell. Thickening is due to a combination of swelling and particle network interaction, and purified forms of un-modified bentonite are highly effective as thickeners in aqueous coatings. Although the thickening mechanism is rather different than attapulgite clays, most bentonite clays also require wetting, high-shear for dispersion, and time for complete hydration. Some modified grades are,

TABLE 6—"Associative" thickeners for waterborne coatings: producers, product tradenames, product codes, and thickener type

Associative Thickeners and Rheology Modifiers—for Coatings			
Company	**Trade Name**	**Thickener Type**	**Product Codes**
Akzo Nobel	BERMOCOLL	HMEHEC	EHM-200
Akzo Nobel	BERMOCOLL	HEUR	PUR 2101, PUR 2110, PUR 2130, PUR 2150
Akzo Nobel/AIco	ALCOGUM	PN HASE	HPT
Akzo Nobel/AIco	ALCOGUM	HASE	L-251, L-265, L-283, L-289, L-501, SL-70, SL-78, SL-117, SL-920
Arkema/Coatex	COAPUR™	HEUR	817 W, 830 W, 2025, 3025, 4435, 6050, XS22, XS 71, XS 73
Arkema/Coatex	RHEOTECH™	HASE	2000, 2100, 2800, 3000, 3800, 4200, 4800
Arkema/Coatex	UCAR POLYPHOBE	HASE	102, 106HE, TR-115, TR-116, TR-117, T-900, T-901
ASHLAND/Aqualon	AQUALON®	HMPAPE	NLS-200, NLS-205, NLS-210, NHS-300, NHS-310
ASHLAND/Aqualon	NATROSOL™ *Plus*	HMHEC	100, 330
BASF/Ciba	COLLACRAL	HEUR	LR 8989, LR 8990, PU 75, PU 85
BASF/Ciba	Ciba®RHEOVIS®	HASE	112, 132, 152
BASF/Ciba	Ciba®RHEOVIS®	HEUR	PU10, PU20
BYK	BYK	Mod Urea	BYK 420, BYK E 420
Cognis	DSX®	HEUR	1514, 1516, 1525, 1550, 3100, 3220, 3256, 3290, 3291, 3515, 3800
Cognis	DSX®	HEET	2000, 3000, 3075
Dow Chemical	CELLOSIZE	HMHEC	HMHEC 500
Dow Chemical	WALOCEL™	HEMC	XM 6000, XM 20000, XM 40000
Dow Chemical	ACRYSOL®	HASE	DR-1, DR-72, DR-73, DR-110, DR-130, DR-300, DR-5500, RM-5, RM-6, RM-7, RM-55, TT-615, TT-935, TT-935ER
Dow Chemical	ACRYSOL®	HEUR	RM-8, RM-8W, RM-12W, RM-825, RM-895, RM-1020, RM-2020, RM-2020NPR, RM 3000, RM-5000, RM-6000, SCT-275
Elementis	RHEOLATE®	HASE	1, 420, 450
Elementis	RHEOLATE®	HEUUR	212, 244, 255, 266, 278, 644, 655, 666
Elementis	RHEOLATE®	HEET	310, 350
Elementis	RHEOLATE®	HEUR	FX 1010, FX 1070
Evonik/Degussa	TEGO® ViscoPlus	HEUR	3000, 3010, 3030, 3060
Hankuck/Nae Wol	HISOL	HASE	D65, D85, D105, D108, D160, D180, D201, D203, D206
Hankuck/Nae Wol	HIRESOL	HEUR	80, 180, 182, 200, 350
King Industries	K-STAY®	HEUR	501, 720, 730, 731, 740
Lamberti SPA	ESACOL	HMHPG	ED Special, EH Special 446
Lamberti SPA	VISCOLAM	HASE	330, 600
Lamberti SPA	VISCOLAM	HEUR	PS-166, PS-167, PS-202
Lubrizol/Langer	LANCO™	HEUR	PUR 21
Lubrizol/Langer	SOLTHIX	HASE	A100
Munzing	TAFIGEL®	HEUR	PUR 40, PUR 41, PUR 45, PUR 50, PUR 55, PUR 60, PUR 61, PUR 80
Munzing	TAFIGEL®	HASE	AP 10, AP 15, AP 16, AP 20, AP 30
OMG/Borchers	BORCHI® GEL	HEUR	013, 0024, 0434, 0435, 0620, 0621, 0622, 0625, 0626, L 75 N, L76, LW 44, PW 25, WN 50 S
Shinetsu/SE Tylose	TYLOSE	HMHEC	HX 4000 YP2, HX 8000 YP2
Rockwood/SCP	OPTIFLO®	HEAT	H370, H370-VF, H400, H500, H600, H600-VF, TVS, TVS-VF
Rockwood/SCP	OPTIFLO®	HEUR	H3300, H3300-VF, L1400, M2600, M2600-VF
Rockwood/SCP	OPTIFLO®	HASE	HV80

TABLE 7—Inorganic thickeners for waterborne and solvent-borne coatings: their classification, synonyms, composition, type of thickening, and where they are used

Inorganic Thickeners for Waterborne (WB) and Solvent-borne (SB) Coatings					
Class	**Clay or Silica**	**Synonyms**	**Chemical Composition**	**Type**	**Primary Use**
Smectite clays	Bentonite	Montmorillonite[a]	aluminum phyllosilicate	Swelling	WB
	Hectorite	—	magnesium lithium phyllosilicate	Swelling	WB
Organoclays	modified bentonite and hectorite	—	smectite clays modified with quaternary ammonium hydrophobes	Structuring	SB/WB
	mixed mineral thixotropes	MMT	composite of several different types of clays and modified with QAH	Structuring	SB/WB
Other clays	Attapulgite	Palygorskite[b]	magnesium aluminum phyllosilicate	Structuring	WB
	Sepiolite	Meerschaumc[c]	hydrated magnesium silicate	Structuring	WB
Synthetic silicas	Precipitated Silica	—	hydroxylated sodium silicate	Structuring	WB
	Fumed Silica	Pyrogentic Silica	silicon dioxide	Structuring	WB
Hydrophobic silicas	organo modified silica	—	made from organo treatment of precipitated or fumed silica	Structuring	SB/WB

[a] Depending on the reference, montmorillonite is the principal mineral in bentonite, or bentonite is the principal mineral in montmorillonite.
[b] Palygorskite is the principal mineral in attapulgite—also some smectite present.
[c] Meershaum (meaning sea foam) was the previous name for sepiolite.

however, readily dispersible with conventional agitators. For effective incorporation, *p*H must be carefully regulated. If it is too high, excessively rapid hydration occurs, and if it is too low, hydration times are long with loss in thickening efficiency. The presence of salts (electrolytes) may cause flocculation, rendering bentonite ineffective in highly ionic environments. The bentonite and hectorite clays are often organically treated with hydrophobic quaternary amines to produce "organoclay" thickeners as discussed later.

HECTORITE CLAY—SWELLING (NATURAL AND SYNTHETIC)

Hectorite is a rare soft, greasy smectite clay mineral that occurs with bentonite. Like bentonite, hectorite is derived from volcanic ash and tuff but with relatively high glass content. Hectorite is often associated with hot spring activity and is an alteration of the mineral clinoptilolite. This smectite group mineral gets its name from a mining location near Hector, California, and it is one of the two primary swelling smectite clay thickeners, the other being bentonite, Na_0, $3(Mg,Li)_3Si_4O_{10}(OH)_2$. Hectorite differs from bentonite in that it contains lithium in its crystal lattice with absence of aluminum. Of these two similar clays, natural hectorite is a relatively more scarce mineral in nature. When it is mined and purified it is an effective swelling thickener similar to bentonite but is somewhat more efficient. To compensate for its natural lack of abundance, synthetic hectorite was commercially developed. This synthetic hectorite produces relatively clear solutions in water, is a more efficient thickener for suspension than natural purified hectorite, and is also significantly more efficient than bentonite as determined by measuring yield stress values [191–193].

ATTAPULGITE CLAY—STRUCTURING

Attapulgite clay is the most commonly used inorganic thickener in latex paints because it is economical and can also function as an extender pigment [194–196]. Attapulgite is a magnesium aluminum phyllosilicate with formula $(Mg,Al)_2Si_4O_{10}(OH)\cdot4(H_2O)$ which occurs in a type of clay soil common to the Southeastern United States. Attapulgite was named after the town Attapulgus in Georgia where it is very abundant, but the primary mineral in this clay is palygorskite, which was originally discovered in the Ural mountains and is given its name for the mining location there. Attapulgite is not a single mineral, but is actually a composite of smectite and predominately palygorskite. Attapulgite clays found in the Meigs–Quincy district of Georgia are bundles of palygorskite clay particles surrounded by a matrix of smectite clay, which is slightly swellable. Georgian attapulgite clay particles consist of a palygorskite core surrounded by smectite. Unlike pure smectite, the palygorskite component is an acicular bristle-like crystalline form that does not swell or expand. Attapulgite in its natural form consists of lathe-shaped colloidal particles called "spicules," which are typically less than 0.5 μm in diameter. These particles form a crystal chain-like structure in which the spicules attract each other, become entangled, and result in entrapment and suspension of solids. It does this by establishing a lattice structure of particles connected through hydrogen bonds.

In an aqueous environment, attapulgite is nonswelling and essentially inert. Unlike bentonite, which is sensitive to the presence of salts, attapulgite will form gel structures in both fresh water and salt water systems. Taking advantage of this characteristic, attapulgite is widely used in special salt water drilling muds that are used for drilling through brine formations. Coatings containing attapulgite clay thicken not by swelling, but instead by the structured reflocculation of the pigment particles into a colloidal interaction network after shearing. In coating preparation, attapulgite clays can be added as powders or as pregelled dispersions throughout the formulation process. However, they are normally added

in the grind using high-speed mixers for dispersion and hydration. The thickening power of these clays is high, and salts have little or no effect on viscosity. However, like many other ITRMs, the amount of attapulgite clay required for thickening is generally higher than for organic TRMs, and the water demand is high (water is pulled from the aqueous phase to wet the particle surface, thereby increasing effective coating solids). Attapulgite can be used for solvent-borne systems with a cationic surfactant. Some advantages of attapulgite clay are compatibility with a wide range of formulations, use over a broad *p*H range, insensitivity to presence of salt, and resistance to attack by microorganisms.

SEPIOLITE CLAY—STRUCTURING

There are many specialty clays in nature, but only a few have commercial significance for coatings. Sepiolite is a light, porous, high-surface-area clay that was formerly known as Meerschaum (sea froth) [197]. This is an unusual form of non-swelling clay that functions as a thickener in a manner similar to attapulgite. Sepiolite is relatively rare with few commercial deposits, mostly located near Madrid, Spain. This mineral is unique in that it has the highest surface area of all the clay minerals. Chemically, it is a hydrated magnesium silicate with chemical formula $(Si_{12}Mg_8O_{30}(OH_2)_4 \cdot 8H_2O)$ or $Mg_4Si_6O_{15}(OH)_2 \cdot 6(H_2O)$. Unlike smectites, sepiolite is not a layered phyllosilicate but instead is described as a quincunx of five talc sheets separated by parallel open channels within its crystal structure. It has a chain-like structure of needle particles rather than the plate-like particles of many other clays. Although sepiolite is a non-swelling clay, the needle particles have an exceptionally large surface area. This provides a high degree of hydrogen bonding to produce structure in fluids including waterborne and solvent-borne coatings. This structure entraps the mobile phase liquid, thereby increasing viscosity and suspension of the fluid. The structure is stable even in high salt-content fluids.

ORGANOCLAYS—STRUCTURING

Many different grades of organoclays are available for both solvent-borne and aqueous coatings [198–202]. Although these products differ in their chemical modification, the mechanism for thickening and rheology control is substantially the same. Bentonite and hectorite clays are the principal minerals used to prepare organoclays. Because these clays initially are both hydrophilic and oleophobic in their natural form, they must be modified for dispersion in organic solvents. Only after a sophisticated purification process followed by cation exchange with organic ammonium bases is the surface rendered sufficiently organophilic for use in nonaqueous media. As supplied, organoclay thickeners are in the form of agglomerated platelet stacks. Conventional organoclays require wetting and shear for deagglomeration and the addition of a chemical polar activator for full rheological development. The chemical activator serves to disperse the organoclay and also carries water into the hydrophobic organic solvent to insure full hydrogen bonding. Some newer products still require wetting and shear but are functional without the chemical polar activator. Although not essential, elevated temperatures are preferred for efficient processing. High-performance organoclays have recently been developed with greater thixotropy and improved sag resistance. Special grades of organoclays (organophilic clays) have also been designed for aqueous coatings. Some of these depend on shear, wetting, and hydration for full rheological performance, while others are available in readily activated slurry form. The efficiency of these products is generally independent of *p*H.

MIXED MINERAL THIXOTROPES (MMT)

Mixed mineral thixotropes (MMTs) are essentially non-conventional organoclays [203]. The most widely used thixotropes (mainly for solvent-borne systems) are organoclays, fumed silicas, and castor waxes. Although the base materials for MMTs and organoclays are both clays, the particle structure is significantly different than the laminar organoclays that are based on the smectites (bentonite and hectorite). MMTs differ by being made up of many different types of clay minerals that are condensed to give particles with multi-shaped architecture, including platelet-shaped, ribbon-shaped, and pipe-shaped clays. This allows them to be separated more easily than conventional organoclays. Like organoclays, the surface of MMTs is covered with quaternary ammonium compounds to render it hydrophobic. In organic media, the platelets of MMTs interact with each other by hydrogen bonding to form a three-dimensional network producing thixotropy in coatings that is similar to that of fumed silica. Two advantages of MMTs are the possibility to produce pregels at higher concentrations and the reduced shear required for their dispersion.

Synthetic Silicas

Another class of inorganic thickeners are certain types of synthetic amorphous hydrophilic and hydrophobic silicas [204]. Both are widely used in solvent-borne coatings; however, excessive hydration generally limits the utility of the hydrophilic silicas to aqueous media. Two forms of amorphous hydrophilic silica are commercially available and get their names, "precipitated silica" and "fumed silica," from the respective manufacturing processes. A proposed thickening mechanism for these silicas is based on hydrogen bonding between the silica particles and with other coating components to form a three-dimensional structure. High water demand may also contribute to thickening with these products.

PRECIPITATED SILICA

Precipitated silica is obtained in a wet process by the neutralization of sodium silicate solution [205]. This results in a polar, fully hydroxylated surface. Consequently, hydrogen bonding is strong, and excellent thickening comparable to that of fumed silica is obtained especially in nonpolar media. However, because of the competition between hydroxyls on the silica and those in the continuous phase, precipitated silica tends to be less efficient than fumed silica in polar media.

FUMED SILICA

Fumed silica (pyrogenic silica) is amorphous, non-porous, low-density, high surface area silicon dioxide prepared by vapor phase hydrolysis of silicon tetrachloride in a hydrogen-oxygen flame [206,207]. An optional process is the vaporization of quartz sand in an electric arc. Particle size of fumed silica is on the order of 5–50 nm with surface area of 50–600 m^2/g. First discovered in a Degussa laboratory in 1941, this synthetic product gets its name from the smoke-

TABLE 8—Commercial inorganic-based thickeners and rheology modifiers for WB and SB coatings

Company	Trade Name	Thickener Type	Thickener Product Codes
Active Minerals Int.	MIN-U-GEL®	400, 500	Attapulgite clay for waterborne
BASF/Engelhard	ATTAGEL	40, 50	Attapulgite clay for waterborne
Cabot Corp.	CAB-O-SIL	M-5	untreated Fumed Silica
Cabot Corp.	NANOCEL®	Aerogel Silica	Aerogel silica
Elementis/Rheox	BENAQUA®	4000	OM hectorite clay
Elementis/Rheox	BENTONE®	DE, DY, CE	Hectorites or Smectite clays
Evonik/Degussa	AEROSIL®	many grades	Fumed Silica
Rockwood/SCP	CLAYTONE®	40, HT, AF, HY, APA, P53	Organoclay for solvent-borne
Rockwood/SCP	TIXOGEL®	VZ, VP, EZ100, MP100	Organoclay for solvent-borne
Rockwood/SCP	GARAMITE®	1210, 1958, 2578	Mixed mineral thixotropes for solvent-borne
Rockwood/SCP	OPTIGEL®	CG, CK, LX, WA, WX, WH	Smectites, mod. Smectites or Bentonites
Rockwood/SCP	BENTOLITE®	L 10	Smectite/Ca Bentonite
Rockwood/SCP	GELWHITE®	GP, H	High bright Smectite
Rockwood/SCP	LAPONITE®	RD, RDS, S482, SL25, RD	Synthetic Smectite/Hectorite
Rockwood/SCP	MINERAL COLLOID®	BP, MO	Purified montmorillonite
Rockwood/SCP	PERMONT	SX 10A, SC 20	Synthetic Smectite
Wacker	WACKER HDK®	H15, H18, H20, H30	Hydrophobic fumed silica for Polar Systems
Wacker	WACKER HDK®	N20, N20P, T30, T30P, T40	Hydrophylic fumed silica for Non-Polar Systems

like appearance as it forms in the flame. In the fuming process, the particles formed have a partially hydroxylated surface containing hydroxyl, silanol, and siloxane groups. The resulting particle surface is somewhat less polar than that of precipitated silica. Fumed silicas primarily provide thickening through the formation extensive network structures generated by hydrogen bonding via the silanol groups, which can interact with a number of functionalities including hydroxyl, carboxylic acids, carboxylic esters, and other silanol groups. The structuring is accomplished by the creation of relatively large silica particle chains, which associate via interparticle hydrogen bonding. Because fumed silicas have both hydrophilic (hydroxyl and silanol) and hydrophobic (siloxane) functionality, they are effective in producing thickening in both polar and non-polar media. To take full advantage of their thickening potential, the proper incorporation of the silica is very important. Like some clay thickeners, suboptimal dispersion can impact coating gloss. *p*H does have a significant effect on the thickening efficiency of fumed silica in aqueous systems. To be effective, *p*H must be below about *p*H 7.5. Above this *p*H, electrostatic repulsion keeps the particles far enough apart to inhibit hydrogen bonding. Some fumed silicas have very small surface area, which results in very high thickening efficiency even in non-polar media. Some performance properties claimed for fumed silica are improved sag resistance, crack resistance, film hardness, and dirt pick-up resistance. To improve on incorporation into coatings, aqueous fumed silica dispersions have been developed. This liquid form provides advantages in handling, health, ease of dispersion and speed of thickening equilibration. The liquid form also has the potential to reduce VOCs since the dispersions are solvent free and surfactant free.

HYDROPHOBIC SILICA

In less-polar environments, the silica hydroxyls of precipitated silica or the silanol groups of fumed silica are encouraged to interact with each other through hydrogen bonding for development of the thickening network. To make precipitated silica and fumed silica particles more hydrophobic, they are often reacted with organophilic groups on the silica surface to produce hydrophobic silica grades [208,209]. The reactants are typically either organosilane or organosiloxane compounds, which replace many of the surface hydroxyl groups with the organic functionality. Various patented processes are used and the following are representative. Fumed silica can be reacted with chlorosilanes in a fluidized bed reactor to produce hydrophobic fumed silica. Precipitated silica can be hydrophobized with alkylchlorosilanes or trimethylsilanol in precipitated solution to produce hydrophobic precipitated silica. After treatment, these products have few surface silanol groups left for hydrogen bonding, and the amount of carbon incorporated onto the surface is typically on the order of 1–5 %. Hydrophobic silicas are generally superior to hydrophilic silicas in water-reducible systems.

Compiled in Table 8 is a current list of commercial suppliers of inorganic thickeners and rheology modifiers used in waterborne and solvent-borne coatings. Some close-up photomicrographs showing the diversity of particle shapes for four different inorganic thickeners are shown in Fig. 13.

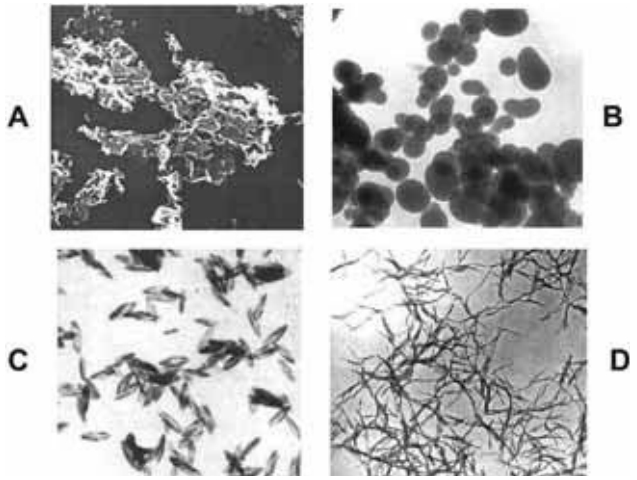

Fig. 13—Photomicrographs of various dispersed thickeners particles: A=clay, B=fumed silica, C=polyolefin, D=polyamide.

Thickener Blends

Often, one or more different thickener types are used in coatings formulation to obtain a desired combination of performance properties. This is usually not an issue when conventional type thickeners are combined with other conventional types. However, care must be taken when combining thickeners with thickening mechanisms that may compete with each other [210–214]. One such combination is a high molecular conventional hydrodynamic thickening polymer with a highly associative polymer which can, on occasion, result in syneresis, loss of hiding, and loss of gloss. However, the thickeners can often be made compatible with the appropriate addition of surfactants and/or optimum dispersant selection.

ORGANIC TRMs FOR SOLVENT-BORNE COATINGS

Besides the inorganic products described above, a variety of organic additives also function as thickeners, rheology modifiers, and mainly thixotropes in solvent-borne systems [215–217]. These products are available in liquid paste and powder form. Many require some dispersion and activation for thickening, and the recommended process temperatures often depend on the strength of the solvent present in the coating formulation. Careful formulation procedures are required to avoid seeding, "false body," or loss in thickening efficiency. Among the many types of organic products available for use as thickeners and flow control agents for solvent-borne systems are castor oil derivatives, polyethylene glycol, polyamides, polymerized oil derivatives, organic esters, complex polyolefins, and aramid pulp fibers, overbased calcium sulfonate. Some of the materials that are very effective are waxes with melting points. Among these are the polyamides and polyethylene glycols. The waxes are favored for their performance in many formulations. Because of the number of products, their diverse nature, and the fact that little information is available on many due to their proprietary status, only a few of the principal TRM types for solvent-borne will be discussed—castor oil derivatives, polyamides, and overbased calcium sulfonate. In Table 9, a list of commercial suppliers of organic thickeners for solvent-borne coatings, the products of each, and the chemical class type is compiled.

CASTOR OIL DERIVATIVES (CASTOR WAXES)—STRUCTURING

One of the main classes of thickeners for solvent-borne systems are castor oil wax derivatives [218,219]. As the name implies, these products are produced by modification of castor oil, including their sulfonation, hydrogenation, and esterification with polyols. These materials provide thickening by structure formation due to hydrogen bonding of the pendent hydroxyl groups in the castor derivatives with each other and also with the hydrophilic entities within the solvent-borne binders. Often heat activation is recommended for effective incorporation.

POLYAMIDES—STRUCTURING

Polyamides are another widely used TRM class for solvent-borne coatings [220,221]. Polyamides are high molecular weight polymeric waxy solids typically produced by the reaction of diamines with dicarboxylic acids. The internal segments of these polymers contain amide functionality while the terminal ends usually do not. These polymers create structure viscosity in coatings by swelling in the coating solvents, which increases the effective volume and provides chain entanglement. The structure formed is weakly associated and thus easily disrupted (shear thins) by mixing and also for high-shear application processes such as spraying and roll coating. Like some of the clays and silicas used as thickeners, polyamides require high shear for incorporation. One issue with polyamides is migration to interfaces in the coating films that can result in a blotchy appearance on the surface or intercoat adhesion at the substrate.

OVERBASED CALCIUM SULFONATE—STRUCTURING

Overbased calcium sulfonate gels are a complex matrix of calcium carbonate in its calcite crystalline form stabilized by sulfonate dispersants [222,223]. The dispersants typically used are alkyl benzene sulfonates. In the overbasing process, calcium hydroxide is formed *in situ* to provide colloidal stability. In the preparation of this thickening component, the calcium carbonate undergoes a change to its calcite crystalline form, and the alkali-metal portion of the sulfonate dispersant adsorbs onto the hydrophilic carbonate particles with the hydrophobes extending into the continuous solution phase. The carbonate crystals interact with the polar heads of the dispersant, producing ionic crystal flocs to provide structure and colloidal stability. Additional structure is generated through Van der Waals interactions of dispersant hydrophobe tails with the nonpolar phase components in the coating. Good suspension and anti-sag properties are conferred to the coatings, and since they are supplied in pre-gel form, they do not reduce coating gloss. The structure is easily broken down with shear and reforms rapidly after shear is removed. These thickeners do not require heat for activation and are typically incorporated at the pigment dispersion stage.

MODIFIED POLYUREA—STRUCTURING

Modified ureas function by their selective insolubility, which results in a controlled separation of fine needle-like particles [224,225]. The mechanism of thickening is by strong cohesive hydrogen bonding interactions of these particles to form a three-dimensional network and by association with binder molecules producing gel structure and rheology modification. Solvent-borne coatings with

TABLE 9—Other commercial thickeners for solvent-borne coatings: producers, product trade names, product codes, and thickener type

Company	Trade Name	Thickener Type
OMG Borchers	Borchi® Gel	Aluminum Soaps
BYK-Chemi	BYK®	Polyamide, Modified Urea
Chattem (Elcat)	Cyco-Gel®	Aluminum Compounds & Soaps
Chattem (Elcat)	Gel-Wei®	Aluminum Compounds & Soaps
Chattem (Elcat)	ViscoMaster®	Aluminum Compounds & Soaps
Cognis	Dehysol®	Polyamide
Cognis	Rilanit®	Polyamide, Hydrogenated Castor, Mod HCO
Cray Valley	Antisettle	Castor Waxes
Cray Valley	Flowtone®	Castor Waxes/Inorg. Mod. Castor Wax
Cray Valley	Crayvallac®	Oxidized Polyethylene
Cray Valley	Crayvallac®	Pure Amide/Polyamide Blends/Amide Castor Waxes
Cray Valley	Crayvallac®	Modified Urea
Evonik/Degussa	Aerosil®	Hydrophilic & Hydrophobic Fumed Silica
Elementis	M-P-A®	Oxidized Polyolefin
Elementis	Post 4®	Sulfonated Castor Oil
Elementis	Suspend-Ayd®	Not Specified
Elementis	Thixatrol®	Polyamide
Elementis	Thixin®	Hydrogenated Castor Oil
Elementis	Nuvis®	Surfactant, Polyamide
Ferro	Synpro®	Aluminum Stearate
King Industries	Disparlon®	Polyamide, Oxidized Polyethylene
King Industries	Kstay®	Overbased Sulfonate
Lubrizol	Ircothix®	Overbased Calcium Sulfonate
Lubrizol	Ircogel®	Overbased Calcium Sulfonate
Lubrizol	SOLTHIX®	Undefined RM for Solvent-Borne
Lubrizol	SOLPLUS	Undefined Two-Pack RM for Solvent-Borne
Poly-Resyn	Suspeno®	Oxidized Polyolefin
Poly-Resyn	Polythix®	Hydrogenated Castor Oil
Poly Resyn	Polytrol®	Hydrogenated Castor/Amide Co-melt
Rockwood	Rheocin®	Hydrogenated Castor Oil
Rockwood	Advitrol®	Hydrogenated Castor/Amide Co-melt
Rockwood	Rheotix®	Hydrogenated Castor Oil Based
Rockwood	Adjust®	Sulfonated Castor Oil
Rockwood	Y-Type	Oxidized Polyolefin
Troy Corporation	Troythix®	Polyamide, Polyester, Hydrogenated Castor Oil

1) Chattem Chemicals is an ELCAT Company.
2) Cognis was formerly Henkel.
3) Elements acquired Rheox & Servo Deldin.
4) Lubrizol acquired Avecia Additives.
5) Rockwood acquired Southern Clay Products and Sud Chemie.
6) Borchers was acquired from Bayer by OMG.
7) Lubrizol acquired Langer & Co.

these thickeners form very shear thinning flow and thixotropy The effective typical concentration is about 0.5 % using high-speed dispersion for incorporation. However, the modified ureas are not recommended for dispersion in the grind as it breaks down the polymer, resulting in lower efficiency.

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List of Producers and Suppliers

* Company Reference Numbers for Tables 3, 5, and 6.

[1] Active Minerals International, LLC
[2] Akzo Nobel N. V.—includes recent acquisitions and thickener products from Berol Nobel and ICI/Alco Chemical
[3] Archer Daniels Midland (ADM)
[4] Arkema—includes recent acquisitions and thickener products of Coatex and Dow UCAR Emulsion Systems & Monomers
[5] Ashland—includes recent acquisitions and thickener products of Hercules/Aqualon
[6] BASF—includes recent acquisitions and thickener products of Ciba Specialty Chemicals Corporation, Engelhard Corporation, and Allied Colloids
[7] BYK Chemie
[8] Cabot Corporation
[9] Chattem Chemicals—an Elcat company
[10] Cognis—was formerly part of Henkel
[11] Cray Valley
[12] The Dow Chemical Company (includes acquisition of Wolff Wolrode acquisition—now DowWolff Cellulosics BU, and the acquisition of Rohm & Haas Co.
[13] Elementis Specialties—formed from Rheox, Daniel Products, and Hardman—includes recent aquisition and thickener products of Condea Servo
[14] Evonik—was previously Degussa—includes recent acquisition and thickener products of Tego
[15] Ferro
[16] FMC Corporation
[17] Hankuck/NaeWoi Korea
[18] J. M. Huber Corporation—includes recent aquisitions and thickener products of C. P. Kelco and Noviant
[19] International Specialty Products (ISP)
[20] King Industries
[21] Lamberti SPA Chemical Specialties
[22] Lubrizol—includes recent acquisition and thickener products of Langer & Co.
[23] Munzing—includes recent acquisition and thickener products of Ultra Additives
[24] OMB Borchers GmbH—includes recent aquisition and thickener products of Borchers GmbH
[25] Poly-Resyn
[26] Rockwood—includes acquisitions and thickener products of Southern Clay Products (a Rockwood Specialties Inc. Company), Sud Chemie, and Sud-Chemie's prior acquisition United Catalyst
[27] ShinEtsu—includes acquisitions SE Tylose GmbH & Co. KG and Clariant
[28] Scott Bader
[29] Troy Chemical Corp.
[30] Wacker Chemie A. G.

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Part 8: Physical Characteristics of Liquid Paints and Coatings

34

Density and Specific Gravity

Raymond D. Brockhaus[1] and Ben J. Carlozzo[2]

INTRODUCTION

Why Concern Ourselves with Density? The World of the Producer and the Customer

MATERIALS ARE EXCHANGED FOR AN AGREED upon value based upon a "cost per unit material." The "unit of material" is in terms of what the user wants to do with the material expressed in physically measurable units such as volume or weight. The customer does not want to be shorted, and the provider does not want to give away material. Accurate measurements are expected to keep both parties happy. When a customer wants a gallon of paint, the manufacturer blends the component materials together by weight and fills out by weight. Balances are easy devices to place and use with filling lines. Delivery of constant volumes, on the other hand, is not an easy task, as will be explained later. Measurement of the weight of a known volume of the paint generates a relationship defined as density. With this relationship, the producer can fill by weight and then sell to the customer on a by-volume basis. The customer wants volume; the producer wants to work in weights. The relationship—density—enables the transformation to make life easier for both groups.

MEASURE OF QUALITY

In the open marketplace, the business person and the customer have this rule of thumb—let the buyer beware. Testing for quality of the shipment is best done on-the-spot, quickly, and in a way that is highly reliable. If you are in charge of the wine and ale stocks of a restaurant, one method of determining the quality of the goods obtained would be verification of the density with flotation probes called hydrometers. Similarly, the purchasers of metals such as gold, lead, silver, and copper could use various methods of determining density to keep from being cheated and assuring quality.

In our more modern world, with instruments capable of assaying individual chemical compounds in complex mixtures, verification of density has become a manufacturing tool for in-process control. Density measurement becomes an indirect assurance that the ingredient(s) of interest exists in the material of exchange at the proper concentration. For paint, ingredients such as solvents, polymers for binders, and pigments have a different range of density typical of that material. Partial omission of a major component, for example, a solvent, can make the paint density change from the formula loading target. Quick approximate determinations of density can be done with an inexpensive piece of equipment that acts as a screening tool, catching special-case errors like wrong material shipped. Common errors of minor contamination are usually not caught this way.

While the use of density measurements as the sole or major measure of quality is declining in favor of testing designed to provide ingredient concentrations and chemical functionality, it still remains as a typical, routinely performed quality control test method and is almost always found in tests run to certify contents (Certificates of Analysis). There is often a balance between spending time, money, and manpower on testing and risking the liability of inadequate product performance.

REGULATORY CONCERNS

In addition to customers and producers, government can express concerns in the exchange of materials. Government's concern is for regulation. Paints or other similar heterogeneous materials are mixtures in which only the nonvolatile portion of the bulk material being exchanged is of true value to the customer. The "carrier" portion of the bulk material must be accounted for because it is a discarded material and thus a "pollutant." The carrier portion, solvents, and viscosity reducers are used to aid in transporting the solids to the work surface to form a thin film. These can pose disposal problems and have a significant impact on landfills, air, and water quality, which are all regulated by federal, state, and local governments. Paint volume solids and critical pigment volumes are two significant concepts which require the use of raw material and finished product densities for their determinations and must be understood and accounted for when dealing with modern government regulations [1].

Definitions: Density—Static and Dynamic Mathematical Models

STATIC MODEL

ASTM D16 Standard Terminology for Paint, Related Coatings, Materials, and Applications defines density as the mass per unit volume of a substrate at a specified temperature and pressure, usually expressed in g/ml, kg/L, g/cm^3, g/L, kg/m^3, or lb/gal [2]. In other texts, "in vacuo" is specified because measurement of weights in gaseous or liquid environments may require a buoyancy correction. If the volume of the mass being weighed is large, a correction must be made for displacement of the environmental media (air or a liquid).

For some samples, however, vacuum conditions will cause vaporization of the sample. Therefore, "in vacuo"

[1] *E. I. Du Pont, Automotive Products, Mt. Clemens, MI 48043.*
[2] *DCA Coatings, Cleveland, OH 44139.*

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is usually a theoretical condition rather than a normally experienced one and deals with the surrounding environment. The balance used to weigh the sample must also be in vacuo.

The Greek letter ρ (rho) is used to denote density.

$$\rho = (m/V) \tag{1}$$

where m is mass, and V is volume expressed in units consistent with the mass units.

$$\rho = (W/V) \tag{2}$$

where W is weight (a function of mass), and V is volume expressed in units consistent with the mass units.

DYNAMIC MODEL

Density is a mathematical value describing a balance of physical forces acting on a material called mass occupying a known volume of space under known temperature conditions. This equation is identical to that given in the static model. Density is expressed as a single value, but is really an average value of forces dynamically fluctuating, both internal to the material and external as the surrounding environment.

The first model (static) is the traditional model. It has changed only slightly over the ages, being upgraded with the terms "mass" in place of weight and "in vacuo" after vacuum bell jars were developed. The second model (dynamic) is a more fundamental model, dealing with materials on a molecular level, where the concepts of chemical functionality, kinetic and potential energy, and interfacial boundaries come into play. With the second model, we can understand and deal with mixtures of chemicals and mathematically deal with how a single component's densities interact when mixed. For most practical determinations the static model will suffice. However, in some cases, the need for truly accurate determinations of density in situations where molecular interactions of chemical ingredients can create errors, the dynamic model is a must.

The attractive forces exerted on a primary mass or collection of particles by a second mass much larger than the first mass is called weight. This is an attractive action, resulting in compression and increasing the density of the primary mass. The dispersing forces are caused by thermal energy absorption, resulting in particles of increasing motion or kinetic energy. This manifests itself as temperature of the material.

The volume of space occupied by a mass of particles that exists at an average kinetic energy level expressed as the temperature of the physical material is defined as the volume. This total quantity includes the voids of space between the particles on a molecular level.

The average kinetic energy level of the material is expressed in the motion of the particles of the material. That is, the material is made up of many small particles that are independent in their motion. These motions are random, such that the overall motion in the X, Y, and Z directions cancel each other and the net motion of the total mass is zero. As the kinetic energy level, expressed as temperature, increases, the distances between particles increase and the material is identified as expanding.

TABLE 1—Density of water (g/cm³) at various temperatures (°C) [15]

Temperature, °C	Density, g/cm³
15	0.999 127
16	0.998 971
17	0.998 772
18	0.998 623
19	0.998 433
20	0.998 231
21	0.998 020
22	0.997 798
23	0.997 566
24	0.997 324
25	0.997 072
26	0.996 811
27	0.996 540
28	0.996 260
29	0.995 972
30	0.995 684

Special cases used as standard measurement reference points:

- One cubic centimeter (cm^3) of pure water (H_2O) at 4.0°C is defined to weigh 1.0000 g.
- $Density_{water}$ = 1.000 g/1.000 cm^3
- 1.000 mole of a gaseous compound occupies 22.4 L of volume at 0°C (273 °K) at 1.000 atmosphere pressure (a molar volume).

For air, whose composition is 22 % by weight oxygen and 78 % by weight nitrogen (ignoring other gases), 1 mole weight = (32 g × 0.22) + (28 g × 0.78) = 28.88 g. Density = 28.88 g/22 400 cm^3 = 0.001 29 g/(cm^3) or 1.29 g/L [3].

Relative density, also referred to as specific gravity, is the ratio of a density determined for Material A at Temperature T_1 divided by the density of a reference material at some temperature, T_2. For solids and liquids, and of particular concern to us, for paints and coatings, the reference material is pure water. For gases, the reference material is air.

$$\text{Density}_{\text{Relative } A} = \frac{\text{Measured Density } A \text{ at } T_1}{\text{Measured Density at 0°C}} \tag{3}$$

If a Liquid A has the same density as water at T_1 when determined by a buoyancy device, then the density can be determined from a table of known density values established for pure water over a range of temperatures.

When T_2 equals 4.0°C, the relative density for pure water equals the measured density. As temperature increases, water expands. For a constant volume, the mass of water must be decreased to fit into a given volume. Thus, water's density value, Table 1, must decrease with increasing temperature. Relative density is a ratio of two values carrying the same units. Therefore, relative density is a dimensionless number.

Specific gravity is an old term but still widely used today, particularly when the density determination is of a liquid such as paint; the term *relative density* is identical and may be less misleading [4].

Apparent density—This term refers to a density value widely used for powders and macroscopic particulate solids, which are compacted by vibration, such as pigments and extenders. Air is still present in the voids between the particles and in pockets or voids at the irregular surface of the macroscopic particles. This means the volume is greater than just for the solids, and the density is smaller in value than if the material was a liquid or compacted such that no voids existed. Pigments used in paint are mechanically worked with solvents and resins to fill in these voids. The true density of the pigment, which is needed in paint calculations, is that obtained without any of the air (void) contribution.

Fundamental Concepts—Material, Objects, Volumes, Masses, and Weights—What Really is Density?

Density is more than just the mathematical numerical value identified above. It also incorporates units of measure which are, in turn, based upon more general and fundamental concepts. These units of measure assume a set of definitions that will be explored in very general terms. These units are crucial to understanding the dynamic model of density and in allowing microscopic concepts to be explored.

Material—Anything (a physical entity) that exists for a period of time, occupies space, and has mass. Mass is a stable configuration of atoms individually loosely organized as elemental atoms or joined together chemically to form molecules.

Object—A collection of materials, homogeneous or heterogeneous, localized to a portion of volume (space). The material can be in any one of three states: solid, liquid, or gaseous. The shape of the volume of space occupied by the object plays a role in dealing with density but does not define the object itself.

Volume is based upon measurement of distance in three directions at right angles to each other as in Fig. 1. The physical universe in which we live is often described in three dimensions in terms of distance, which is a scalar property. When dealing with three dimensions, the term distance is described as length, width, and depth.

An object having all three is described as having volume. The mathematical value for volume is the product of multiplication of the three scalar values. Volume can exist without objects occupying that space. This condition is called a vacuum. Vacuum's volume and object's volume can both be of very irregular and non-matching shapes, yet they can equal in the scalar value of the volumes. Examples are shown in Fig. 2.

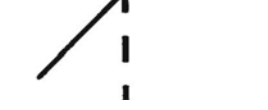


Fig. 1—Coordinated in three dimensions.

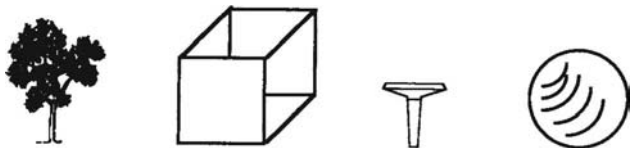


Fig. 2—Examples of physical objects.

PROBLEMS WITH VOLUME MEASUREMENTS

Customers often make use of material based on volume as applied and want to purchase these products in containers recognized to hold standard volumes. Materials have the property of responding to temperature changes with expansion or contraction of their volume. Products that experience wide temperature ranges during filling, shipping, storage, or in use must also have extra unfilled volume to accommodate expansion or the material forces leak and material is lost. This problem is most severe with liquid materials. Material suppliers use containers with larger than exact volume required to allow for expansion. These vessels must be marked in some way to indicate the volume increments if they are to be used for filling by volume. Producers seldom can or want to control temperature during packaging. Temperature control devices will add expense without making a difference in the material's performance. Without temperature control, filling at a constant volume will produce units of varying amounts of material. Use of density overcomes these problems and permits correct volumes to be filled out.

Weight and Mass

A fundamental attribute of a physical entity is mass. This is one of the indefinable mechanics [4]. Two physical objects exhibit an attraction for each other in proportion to the quantity of mass in each object. The greater the mass, the greater the attractive force. When the ratio of two masses is grossly unequal, such as the planet Earth and an object on

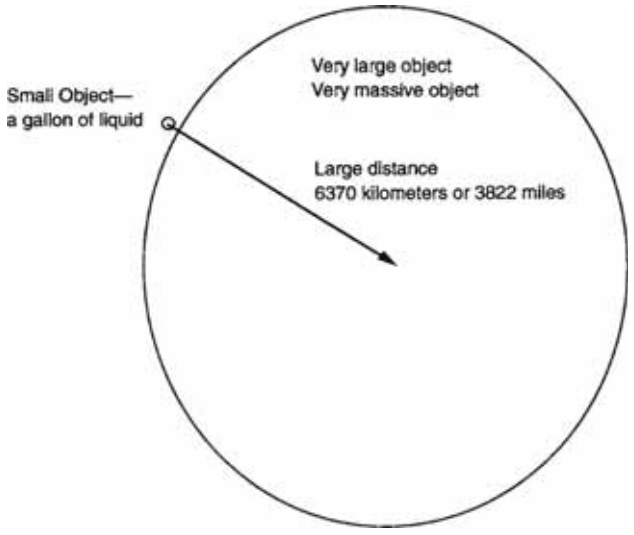


Fig. 3—Moderate distance to large body center.

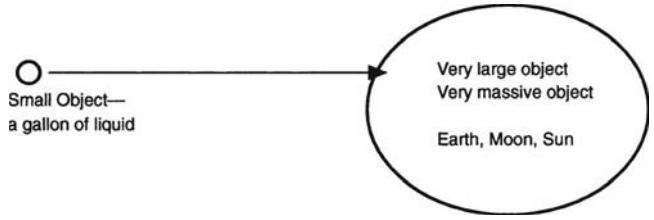


Fig. 4—Vast distance to large body center.

its surface, the larger mass is assumed to be constant and the second object is described to have a "weight" relative to this larger object. The mass of the planet is effectively unchanging and thus constant. Our moon is also a very large object, but smaller than Earth, thus its attraction to a second object would be weaker than for Earth. Mass is the unchanging, fundamental property.

But we are human, and we deal in the measurement of weight, which is a force. While weight is a vector quantity having both scale and direction, the direction portion is taken for granted and weight is usually treated as only a scalar value. Fig. 3 and 4 graphically depict this issue.

Weight, *w,* is defined as a force of gravity, F_g, [4].

$$w = F_g = G\frac{mm_E}{R^2} = mg \tag{4}$$

where:

G = a gravitational constant for Earth
= 6.670×10^{-11} N·m²/kg·m²,
m_E = mass of the Earth = 5.98×10^{27} g,
R = the radius of the Earth = 6370 km,
m = mass of a second body (Newton's law) [5],
g_E = 9.80 m/s² or 32.0 ft/s²,
g_{Moon} = 5.333 ft/s² or 1 /6 that for Earth,
$g_{Distance\ from\ Earth}$ = 1.0×10^6 km= $g_E/[(1.0064 \times 10^6\ km)^2/(6370\ km)^2] = 0.004g_E$

These values are given as constants in physics calculations but actually represent average values. In the real world, the value of *g* varies from location to location for a variety of reasons. Table 2 shows that variation present in the value of *g*, the acceleration due to gravity, is greatly influenced by the distance that point on the earth is to the center of gravity of the earth. Mountains many miles above sea level and deserts below sea level have an effect, not to mention the varying densities of the composite materials which make up earth itself [5].

Example 1: A gallon of paint produced in Galveston, Texas, has a weight of 10.000 lb/gal. The product then finds its way to Eagle City, Alaska. Here it has a gallon weight of 10.03 lb/gal. The difference is minor but real.

If the paint specification is a density in the range of 9.90 to 10.10 lb/gal, the +0.03 lb leaves only 0.07 lb for testing errors before the material is identified as out of specification. As environmental regulations on the volatile organic content (VOC) increase in importance, these minor differences will play a larger role and should not be overlooked for their contributions to relationships such as density.

The pull of gravity is not as strong at a mountaintop as it is on the plain. The reason is because the mountaintop is at a greater distance from the center of gravity than the plain. A plumb line might not point exactly to the Earth's center of gravity, however, if it is attracted to a large deposit of denser material beneath the earth's crust that is not in line with the Earth's center of gravity [5].

TABLE 2—Values of *g*, the acceleration due to gravity [5]

Place	Value[a]	Place	Value[a]
Cambridge, Massachusetts	980.398	Denver, Colorado	979.609
Eagle City, Alaska	982.183	Galveston, Texas	979.272
Greenwich, England	981.188	Honolulu, Hawaii	978.946
Madras, India	978.281	New Orleans, Louisiana	979.324
Punta Delgada, Azores	980.143	Reykjavik, Iceland	982.273

[a] Centimeters per second per second. Use of centimeters emphasizes the differences that are occurring in the second through sixth numerical place.

Example 2: The weight of a gallon of paint in New York City is recorded at 9.5 lb. The distance from the center of the Earth is 6370 km at this location. At a distance of one million kilometers from the earth, the same gallon of paint would weigh 0.003 78 lb.

Has the amount of mass changed? No. Has the weight changed? Yes, because of distance. Has the volume of the material changed? Possibly. If the gallon container is surrounded by air at 1 atm, the container shape is retained and the material in it will not overflow. But, in the new location, the fluid does not want to remain together. It forms droplets and wants to float off in all directions. It has lost the cohesiveness provided by gravity. Has the density of the material changed? By definition, yes, drastically! By fact, little. The same physics rules apply in both locations, but the environment has changed and with it our appreciation for the term mass.

Example 3: A 1.00 m³ Styrofoam cube of material is created on Earth in our atmosphere (air) at 20°C and 1.0 atm. This is a heterogeneous material because it has trapped air in the foam. Let us say it weighs 900 g on a balance on an open desktop.

$$Density_{earth} = 900\ g \div 1.00\ m^3 = 900\ g/m^3$$

Next, this cube is taken to the moon (gravitational factor = 1/6 Earth) and kept inside a building with 1.0 atm at 20°C:

$$Density_{moon} = (900 \times 1/6 \div 1.00\ m^3 = 500\ g \div 1.00\ m^3 = 500\ g/m^3$$

Next, the cube is taken out onto the moon's open surface, where there is no atmosphere (vacuum conditions). Now, two things happen to this cube.

1. There is no air to displace when weighing the cube. It can thus exhibit a heavier weight since there is no buoyancy correction: 1 m³ of air weighs 1.29 g on Earth and 0.215 g on the Moon. So the weight would be 150.215 g.

2. The material can also lose the air entrapped in the foam. This may be a slow process, but it can happen. Now the cube will appear to lose weight. Let us say it loses 0.050 g by moon weight and now weighs 150.215–0.050 g.

$$\text{Density}_{\text{vacuo,moon}} = 150.165 \text{ g} \div 1.00 \text{ m}^3 = 150.165 \text{ g/m}^3$$

Return the cube back into the building on the moon with 1.0 atm and the weight might now be 149.95 g if the foam structure is strong enough to retain the cubic shape without crushing from the external pressure. Its density is now 149.95 g/m^3.

Density is a very simple, straightforward concept and relationship. Still, as noted before, physical reality can and does impact on it, adding subtle perturbations that should be understood. What appears to be homogeneous may not be. Physical reality is a source of variability, and affects must be taken into consideration when arriving at results we will share with one another.

Solids, Liquids, and Gases—As Concepts, Under Ideal Conditions

Materials exist in one of three states: solids, liquids, or gases. For an equal amount of weight, solids usually occupy less volume than liquids, which occupy much less volume than a gas. Solids also retain a shape and flow or distort very slowly. Liquids take on the form of a containing vessel. Gases have no shape and are bounded and shaped by their container. Techniques exist to determine densities for all three states.

Solids—Fig. 5 is a depiction of a solid in which the particles are atomic or molecular in scale. The distance between particles is a regular, repeatable distance. Most kinetic energy is gone. Only external pressure can shorten the distance between particles. This shortening is called compression and affects the ratio of weight present and the actual volume occupied by that mass of material. If the solid remains compressed after the external pressure is released, the material is called inelastic. If it returns to the original volume, it is elastic. Density of solids can depend on the processing history.

Liquids—In a liquid as depicted in Fig. 6, the particles are molecular or atomic in scale. Distances between particles are not constant. Kinetic energy is greater than in solids. External pressure can shorten the distance between particles. Each material has a characteristic compressibility factor. All liquids behave elastically, flowing back and filling in. The population of particles has a distribution of kinetic energy values, with some being greater than the surface energy. The portion of the population that has a kinetic energy greater than the surface energy escapes, and is called vapor.

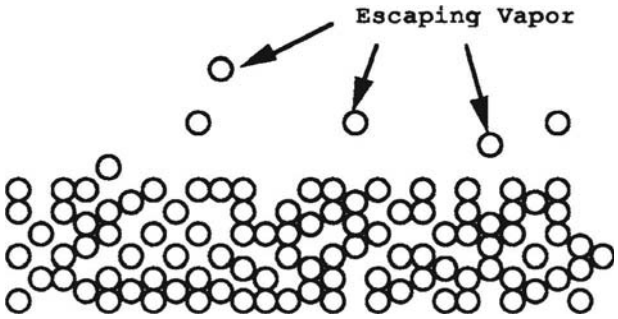


Fig. 6—Simple model of particles of matter in liquid state.

For ideal conditions and "conceptual" materials, no interactions occur between the materials, the testing containers, and the surrounding environment. The material investigated is well behaved. When such materials are mixed together, the weight of each material times the individual material's density will add together as a linear sum. For a majority of coatings this is a good approximation and allows formulating programs to give useful density values for the finished products. These include older solvent-borne technologies, as well as waterborne latex formulations. Exceptions to this rule are two component systems where the separate ingredients begin to react with each other forming various intermediates. Some of these will eventually be lost as VOCs. Densities measured of the different parts can be useful for filling operations, but determining the density of the mixed materials may not give reliable numbers. Other exceptions involve highly ionic mixtures in waterborne formulations. (Salts of amines, and acids designed to improve water solubility as well as anionic and cationic surfactants, are usually nonlinear additions, although the small amounts used of the later can still allow for close approximations to actual density.)

Gases—In a gas, as depicted in Fig. 7, the particles are molecular or atomic in scale but more widely separated. Distance between particles is irregular. Kinetic energy is even higher than in liquids. External pressure can shorten the distance between particles. Each material has a characteristic compressibility factor.

Weighing solid or liquid material in a container or as a solid object is an easy task. Instruments for this task keep improving in accuracy, precision, ease of use, and lower cost. For gas-phase material, vessels of accurately determined volume can be purchased and used. Materials of

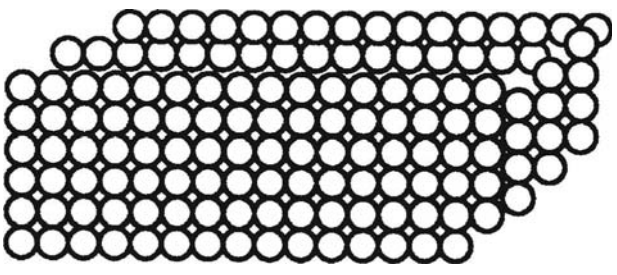


Fig. 5—Simple model of particles of matter in solid state.

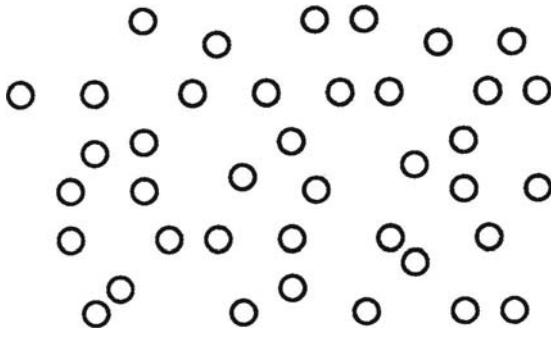


Fig. 7—Simple model of particles of matter in gas state.

construction for durability and reuse are of concern. If the temperature of testing is controlled within the tolerance of the calibration of these vessels, expansion is not a concern. Since gases are seldom incorporated into a paint system (on purpose, although entrapped air manifested as foam can throw off measurements and in most cases is removed before the material is deemed finished), this topic will be skipped.

Further Discussion of Liquids and Solids

For liquids, containers can be constructed to hold a known volume. These vessels can be mass produced with adequate accuracy to allow large numbers of users to have access. These are called liquid pycnometers. Some are also called Weight per Gallon Cups. Within the temperature range of 1°C and 99°C, the density of water can be determined. More detail will be given in the section entitled "Liquids." Devices that can float in water can be calibrated to show a scale calibrated directly in density. When these floats are used along with a scale for weighing, the volume of material can be determined [6,7].

Fig. 8 contains drawings of several pycnometers as seen in a commercial scientific supplies catalog. The catalog text descriptions for two pycnometers have been included to inform you as to sizes, capacities, materials of construction, etc. The features discussed identify attributes of importance to the end user.

Liquids have other properties that can be used to test for density. One of these is sound transmission. Replacement of air with a liquid in a container will cause that container to shift a tone impulse to higher frequencies. The extent of the shift is related to the liquid's density and can provide a direct measurement with different degrees of accuracy depending on the sophistication of the instrument.

For solids, the task is more complex. Two paths are available. Either shape the solid into a known geometric figure and calculate the volume or use the solid to displace a material, such as a liquid or a gas, which has a known density. The solid can be shaped by mechanical, thermal, or chemical means. Mechanical means can be employed to cut, carve, and shape, then weigh. Thermal shaping is changing the solid into a liquid using heat to melt the solid, pouring the liquid into a mold, cooling to form a solid, and then weighing. Chemical shaping is dissolving the solid in a "carrier" liquid (solvent), pouring the solution into an open mold, and evaporating the solvent, leaving behind a solid properly shaped to accommodate testing. The drawbacks of this technique are:

- Complete solvent removal is often difficult.
- Chemical reshaping of solids can cause problems if the original solid had small air pockets or if the solvent used is trapped in these voids, thus actually changing the solid and affecting its apparent density. Solids which demonstrate the latter behavior have a bulk density different than their skeletal density.

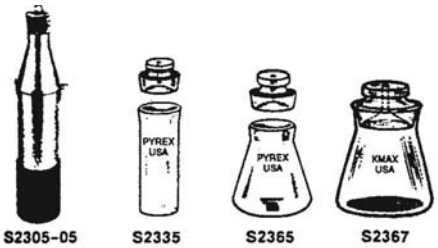
The principle of buoyancy, discovered in the third century by Archimedes, provides a means to determine volume [5]. Determination of volume by displacement requires acquiring a weight in air and a weight in a liquid of known density at the testing temperature. Complete submersion of the solid object or a representative portion of the material in a liquid of known density is required while determining the material's apparent weight. The weight difference is equal to the weight of the volume of liquid displaced. Knowing the liquid's density and the weight difference, the volume for the tested portion can be calculated. The practical application of Archimedes' Principle is used in the following discussions to describe the determination of specific gravity of pigments and other solid ingredients in paint.

Solids, Liquids, and Gases as Concrete Materials in a Physical World—A Practical Guide to Density

A vast variety of materials exist, and interactions are possible between any of the different types of materials. When an attribute, like density, can be directly measured, it is possible to identify two types of these interactions.

The first is ideal behavior with respect to the attribute under investigation and the amount of mass used. These interactions are well behaved and produce predictable attribute changes. The second type is non-ideal and means that other interactions are taking place than just that of mass-to-mass attraction. Materials are ideal if when mixed together the sum of the weight fraction of each material multiplied by the material's density equals the density determined for the entire mixture. Materials are non-ideal if when mixed together the sum of the weight fraction of each material multiplied by the material's density does not equal the density determined for the entire mixture.

Some solids can exist with varying degrees of crystalline domains incorporated into their solid form. As temperatures cycle up and down in the surrounding environment of



ASTM Crude and Fuel Oil Sampler

As specified in ASTM D270 for sampling light lubricating and crude oils, nontransparent gas oils, and fuel oils in sewage tanks. Copper with 19 mm (0.75 in.) diam neck opening and 430 cm (17 in.) brass handle; body ODxH, 95x356 mm (3.75x14 in.); capacity, 950 mL (1 qt).

S2305-05 .....

PYREX® Hubbard-Carmick Specific Gravity Bottle (Corning No. 1620)

■ ⅗ **Stopper, ASTM**

For use in place of S2335 in accordance with ASTM D70; especially for viscous fluids and semisolid samples. Conical shape with wide bottom for increased stability and ground solid stopper, concave on bottom. Capacity, 25 mL; bottom diameter, 40 mm; diameter of mouth, 25 mm; height without stopper, 45 mm; weight empty, less than 40 grams. With 24/12 short length ⅗ grinding and 1.6 mm hole in stopper to allow air to escape.

S2365 .....

Fig. 8—Specific gravity testing pycnometers. (Courtesy of Sargent-Welch.)

these solids, the solids will change density as these domains increase or decrease and they move toward a thermodynamically stable form of the solid.

Finally, as we alluded to earlier, materials can chemically interact when mixed, producing or absorbing heat and generating an entirely new material with its own unique attributes. These actions are not bad or good, but they basically exist and must sometimes be taken into consideration when dealing with mixtures such as liquid paints and solid coatings.

When a material (A) is homogeneous, the density is a fixed value for a fixed temperature. When a material (B) is heterogeneous, the density is also a fixed value for a fixed temperature. When two different materials, homogeneous or heterogeneous, are mixed together, they become a new, heterogeneous material, and the resultant density is a new fixed value for a fixed temperature. Depending on whether the interactions are ideal or non-ideal, the density can be predicted by calculation or a deviation in the density will result. Paints are formulated as ideal mixtures, but they don't always follow this assumption. The relationships between these values are given below [8].

$$\text{A + A has A's density which is } \frac{W_{A\rho A} + W_{A\rho A}}{W_A + W_A} \tag{5}$$

$$\text{B + B has B's density which is } \frac{W_{B\rho B} + W_{B\rho B}}{W_B + W_B} \tag{6}$$

A + B has a new density which may be =, >, or < that of A or B and is:

$$\frac{W_{A\rho A} + W_{B\rho B}}{W_A + W_B} \tag{7}$$

where:

W = weight of component,
ρ = density of the component.

Many important materials are available as complex mixtures in today's world. These mixtures can be heterogeneous in terms of phase. Gasoline for the car and lawn mower can contain butane dissolved into the heavier hydrocarbons. Paints, inks, and cements contain liquids and solids, with the liquid phase either neutral or reactive. If the liquid's role is neutral, it can be a solvent or carrier or plasticizer. If the liquid's role is reactive, it is called a binder, reactive diluent, or catalyst.

Modern paints contain chemically reactive, low-molecular-weight polymers that, when heated, produce a crossed-linked solid and usually volatile by-products. When chemical changes occur, the linear density addition model is correct only by chance. Usually the volume is reduced from chemical bonds forming, and as a result, the density goes up.

Theoretical volume solids have been calculated for years in the coating industry using the linear model. This model has worked well for lacquers, varnishes, and other systems where chemical reactions took place at low levels and were of the oxygen uptake type, making the final film heavier from oxygen addition. Modern paints react internally, generate by-products of low molecular weight, and actually lose weight during cross-linking and film formation. But, because there has been no good way to determine the volume of paint films that is repeatable and reproducible, the practice of calculating volume solids is still used in 2010. (Repeatable means in the same lab, with the same instrument, time after time, and reproducible means between different sites or labs using similar but physically different instruments like balances, ovens, etc.)

Definitions Related to Density and Specific Gravity

BULK DENSITY

$$= \frac{\text{Total weight of object including air or water}}{\text{Total volume occupied including air or water}} \tag{8}$$

SKELETAL DENSITY

$$= \frac{\text{Total weight of object less air or water}}{\text{Total volume of actual material less air or water}} \tag{9}$$

Surface interactions—These interactions involve wetting of solid surfaces by liquids during liquid displacement testing. In determining the volume of a material due to displacement of a liquid, the liquid must come in close contact with the material surface. When the liquid meets or wets the surface without penetration into the bulk of the material, the volume of liquid displaced is equal to the bulk volume of the material being tested. When the liquid does not contact and wet the surface, a thin layer of air exists between solid and liquid. This also displaces liquid, making the apparent volume of the material larger. In tests like ASTM D2965, where the volume of paint film being tested is very low, this error can be significant. Materials called surfactants can be added to increase wetting, but they affect the density of the liquid. Where surfactants cannot be used, another liquid must be used.

Permeation—When the liquid meets or wets the surface with total penetration into the bulk of the material, the volume of liquid displaced is equal to the skeletal volume of the material being tested. If there are molecules with low molecular weight left inside the bulk of the solid, these can migrate out, leaving the testing liquid in its place. These will change the bulk testing liquid's density as they accumulate.

MEASUREMENT SYSTEM UNITS, CONVERSIONS, DENSITY, AND RELATIVE DENSITY

Today's world uses three systems of measurement [4]:

1. International System of Units (SI), previously referred to as the metric system, based upon powers often. This was called the MKS system, standing for meters (distance), kilograms (force), and seconds (time). A common form of this system uses millimeters, grams, and seconds as the units. By universally accepted definition, 1.0000 g of distilled water occupies 1.0000 cm^3 (or 1.0000 ml) at 4.00°C.
2. The British system uses the British yard (distance), pound (force), and second (time).
3. The United States (U.S.) system uses the U.S. yard (distance), pound (force), and second (time).

The British and U.S. systems use the same basic linear distance and force units, but, when measuring volumes, the systems do not have equivalency. A British gallon of water

Precision Hydrometers for Light and Heavy Liquids—175 mm

A series of short range hydrometers with an accuracy of 0.001, calibrated 60° /60°F. Design corresponds with ASTM specification E100 for plain hydrometers. With smooth, easily cleaned shapes, solid metal ballist, and cemented paper scales. Subdivisions, 0.001.

Cat. No.	Range		
S41885-F	1.000	to	1.070
S41885-G	1.060	to	1.130
S41885-H	1.120	to	1.190
S41885-I	1.180	to	1.250
S41885-K	1.240	to	1.310
S41885-L	1.300	to	1.370
S41885-M	1.360	to	1.430

Fig. 9—Hydrometers—specific gravity scale—plain design [6].

(volume) weighs 9.993 lb at 77°F (25°C), while a U.S. gallon of water weighs 8.321 lb at 77°F (25°C) [7]. Conversion between the three systems can be accomplished using the following relationships:

$$2.54 \text{ cm} = 1.00 \text{ in.}$$
$$231 \text{ in.}^3 = 1.00 \text{ U.S gallon}$$
$$453.6 \text{ g} = 1.00 \text{ lb}$$

or

$$277.4 \text{ in.}^3 = 1.00 \text{ British (Imperial) gallon}$$

From SI to U.S.:

$$(2.54 \text{ cm/in.})^3 \times (231 \text{ in.}^3/\text{U.S. gal})/453.6 \text{ g/lb} = 8.345 \text{ cm}^3\text{lb/U.S. gal. g} \quad (10)$$

$$(2.54 \text{ cm/in.})^3 \times (277.4 \text{ in.}^3/\text{British gal})/453.6 \text{ g/lb} = 10.02 \text{ cm}^3 \cdot \text{lb/British gal} \cdot \text{g} \quad (11)$$

These are conversion factors, which carry particular units. They are used to convert density values for a material at any temperature into a second set of units at that same temperature. The 8.345 factor for converting to U.S. lb/gal is sometimes confused with the 8.321 value for a U.S. gallon of water at 25°C (77°F) [9].

Density (in the SI system) at any temperature = density (in the U.S. system) × 8.345 at the same temperature.

Example for pure water at 4°C (39.2°F):

$$\frac{1.000 \text{ g}}{1.000 \text{ cm}^3}(\text{SI}) = 1.000 \times 8.345(\text{conversion}) = 8.345 \frac{\text{lb}}{\text{U.S. gallon}} \text{ at } 4°\text{C} \quad (12)$$

For pure water at 25°C (77°F):

$$\frac{0.997\,04 \text{ g}}{1.000 \text{ cm}^3}(\text{SI}) = 0.997\,04 \times 8.345(\text{conversion}) = 8.321 \frac{\text{lb}}{\text{U.S. gallon}} \text{ at } 25°\text{C} \quad (13)$$

Note in these examples that the volume of space (container internal volume) has not changed with temperature. But, the amount of material which can fit into that volume has changed with temperature! Using known volume devices provides only density values. Temperature must be stated as a significant variable.

LIQUIDS

Densities of Liquids—Methods of Determination

BUOYANCY-HYDROMETERS

Hydrometers are flotation devices that are calibrated using water at various temperatures. When placed in clear liquids, the relative density is read directly from the scale on the hydrometer. The hydrometers range from low-cost, low-precision versions, to expensive, high-precision devices. Higher-grade hydrometers also have thermometers incorporated for temperature correction and greater independence of reading liquids in an as-is condition. A balance or a known volume device is not needed with this technique. Simplicity is the advantage of this technique. Shown in Figs. 9 and 10 are two types of hydrometers. The catalog text has been included to explain ranges and features unique to these devices.

ASTM methods using hydrometers are [10,11] Standard Test Method for Density, Relative Density (Specific Gravity), or API Gravity of Crude Petroleum and Liquid Petroleum Products by Hydrometer Method (D1298) and Standard Test Method for Calculation of Volume and Weight of Industrial Aromatic Hydrocarbons (D1555).

DISPLACEMENT-SUBMERSION—SPECIFIC GRAVITY BALANCES

A specific gravity balance is similar to the hydrometer. It is actually a balance that measures the counterweight applied to balance a plummet submerged in the liquid sample. The weight and volume of a mercury-filled elongated glass bulb (plummet) is determined by comparison with standards established by regulatory agencies and traceable back to well-characterized standards, referred to as primary standards, established by national scientific bureaus. The plummet is attached to a balance and submerged into a liquid to displace some of the liquid's volume. The change in weight is attributed to the weight of the displaced liquid. The plummet's volume is known, and it is related to

Sugar Hydrometers with Brix Scale and Enclosed Thermometers—380 mm

Hydrometers are similar to S42436, but provided with a thermometer, range 0° to 50°C in 1° subdivisions, and with scale of correction values in red.

Cat. No.	Range
S42440-B	0 to 12
S42440-C	9 to 21

Fig. 10—Hydrometer–Sugar with Brix scale and enclosed thermometer [6].

displacement of water. These are related back to water as a calibration liquid, so they provide a relative density rather than a true density. With this device, the sample does not need to be clear because there are no markings on the plummet. The devices also allow the liquid to be at temperatures other than 4.0°C. This type of device is good for solvents and low-volatility materials. Two balances are shown in Fig. 11 and are from recent scientific lab supplier catalogs [12]. The catalog descriptions have been included because they are concise statements about the devices, their operating principles, ranges, and other relevant information.

ASTM method using submersion [13], Standard Test Method for Specific Gravity (Relative Density) and Density of Plastics by Displacement (D792).

Displacement—Fluid External Media

This is a device where the sample-holding chamber is not of a known, calibrated volume. A helium gas pycnometer can be used to determine the volume of a liquid in a metal or glass container. The pycnometer's test chamber volume is first established by determination of gas pressure differences in a sample chamber and after expansion into a connecting expansion chamber. Then an independent, empty sample container is introduced into the gas pycnometer test chamber and tested. The reduction in volume is allocated to the empty sample container. The independent sample container's weight is measured on an analytical balance. The sample is added to the sample container and weighed. The container and sample are tested again to establish a new volume. The sample volume is (sample + container volume) – (container volume). The sample weight is (sample + container weight) – (container weight). Density is (sample weight/sample volume). The test is fairly fast. Containers of predetermined volume can be kept available to help shorten testing time. Precision and accuracy are good.

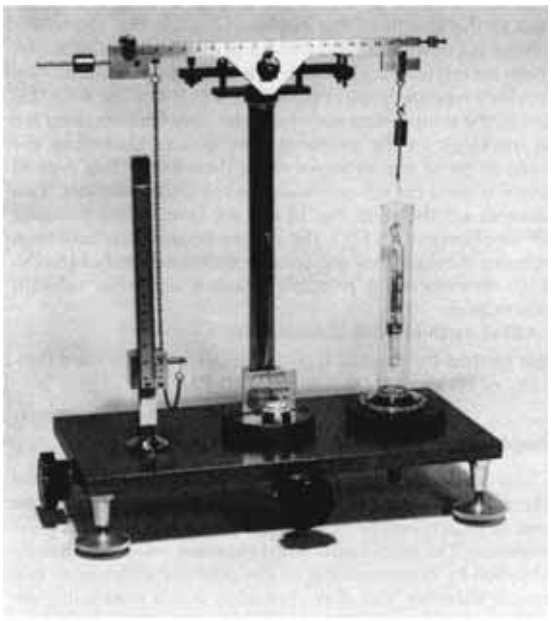
The ASTM method for using a helium gas pycnometer [14] is Standard Test Method for Percent Volume Nonvolatile Matter in Clear or Pigmented Coatings Using a Helium Gas Pycnometer (D6093).

Displacement-Known Volume Devices-Fluid Internal Media

These are devices of known, internal volume. They have many names such as liquid pycnometers, U.S. standard weight-per-gallon cups, U.S. mini weight-per-gallon cups, British standard weight-per-gallon cups, "featherweight" type weight cups, and Monk cup [7,9,15]. Liquid pycnometers come in a variety of sizes, shapes, volumes, and materials of construction. For precision, glass (inert, light weight, and transparent) is usually used. For testing conditions that require demanding repeated use, other materials with reasonable inertness or resistance to chemical attack, such as stainless steel, are used. To combine both the lighter weight of glass and the ruggedness of metal, a "featherweight" construction of anodized, high-tensile aircraft alloy is employed at a cost consistent with the use of specialized materials of construction. The Monk cup is a special design (Fig. 12) and discussed under the topic of handling entrapped air in samples.

Liquid pycnometers or weight-per-gallon cups are built with a main body or container volume, a cap or lid with a vent hole, and sometimes a tare weight object. The tare weight is used as a counterweight for dual pan balances. The weight read after correcting for the tare weight is attributed to the material contained in the vessel at a level which reaches the top of the vent hole in the cap (see Fig. 13).

Both the vessel and a sample of the material to be tested are equilibrated to room temperature or a constant temperature bath temperature. Common temperatures for



Chain Balance

For liquid densities from 0.0001 to 2.110

Chain gravitometer balance determines specific gravity of liquid with high degree of accuracy. Uses both plummet displacement principle and chain weight system for weighings. No calculations or riders are needed.

Instrument is prebalanced at zero reading by adjusting counterbalance weights. Plummet is immersed in liquid sample. Balance is zeroed again. Single roller-type weight is moved to notch on beam where equilibrium is approached; final adjustment is accomplished by raising or lowering one end of rhodium-plated bronze chain. Specific gravity is determined by adding rider and chain-support readings.

Fig. 11—Specific gravity balances—chain balance and Mohr Westphal balance with catalog text instruction and comments [11]. (Courtesy of Fisher Scientific.)

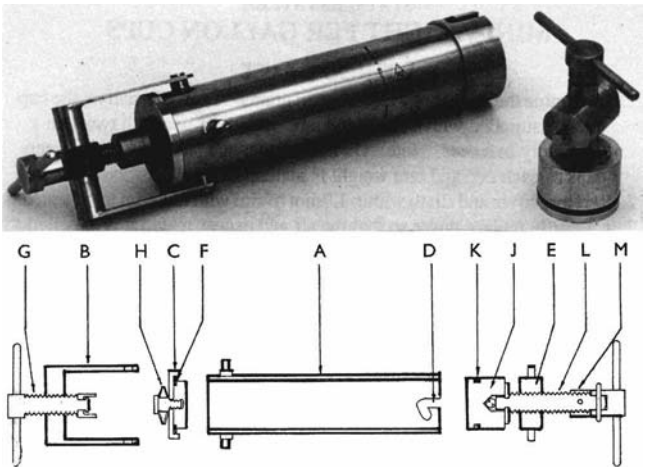


Fig. 12—Monk cup (weight per gallon cup) (courtesy of C. J. Monk and Journal of Oil and Color Chemists' Association) [5]. See reference for a discussion of Parts A to M.

STAINLESS STEEL

MINI WEIGHT PER GALLON CUPS

METHOD OF USE

1. Determine the weight of a clean cup in grams. As an alternative, the cup may be supplied with an accurate tare weight for use with two-pan laboratory balances. Note: Do not interchange tare weights between cups as each cup and tare weight is matched.
2. Remove cover and fill to within 1.7mm of rim with material to be tested.
3. Carefully replace cover so that the air and excess material is expelled through vent.
4. Wipe over cover to remove surplus and reweigh. By subtracting the original weight of the cup, the weight of the contents will be found. If a tare weight was used at the start, the balance will show the weight of the contents. Clean thoroughly immediately after use.

TEMPERATURE		WEIGHT
C.	F.	Grams
21	69.8	8.329
22	71.6	8.327
23	73.4	8.325
24	75.2	8.323
25	77.0	8.321
26	78.8	8.319
27	80.6	8.316

DETERMINING ACCURATE CUP FACTOR

Comparative results on different materials measured in the same cup are accurate to within the limits of sensitivity of the balances used. Comparative results between cups may be improved by determining a cup factor as follows: Divide 99.925 by the gram weight of distilled water held by the cup at 25°C to determine the cup factor. For example, if the weight of water held by the cup is 99.800 grams, divide 99.925 by 99.800 which is 1.0013. Multiply all cup readings by this factor. In the same manner, if the cup holds 100.200 grams, divide 99.925 by 100.200 which is 0.9973 and all cup readings should be multiplied by this factor.

Fig. 13—Mini weight per gallon cups [7].

paint and solvent testing are 20°C (68°F) and 25°C (77°F) because these are temperatures in the human comfort range. Using temperatures greater than these would drive off solvents. Moisture is not likely to condense out on surfaces from being too cool (weight gain drift during weighing), and volatile materials will not evaporate at a rate that significantly affects the weight readings taken (weight loss drift during weighing). Temperatures colder than these are easily obtained, but are less comfortable for the tester. However, any temperature can be used if the temperature is noted and the vessel volume is corrected for that temperature. If the bath is used, the vessel exterior must be dried off. This has to be done with minimum handling to prevent temperature changes from heat exchange by hands or drying materials.

Next, a portion of the tempered sample is poured into the vessel up to the top rim. The lid is carefully placed on the vessel so that the excess liquid is forced up through the vent hole in the lid without coming out around the lid lip. The excess is carefully cleaned off the surface of the lid and from around the lid lip. This is a cleaning, not merely a wiping off. Wiping leaves residues, which affect the results obtained. The sample-containing vessel is then carefully weighed.

Afterwards, the vessel and lid are cleaned as soon as possible and as well as possible to prevent buildup of residues, which will change the vessel's volume. A verification test should be performed at frequent intervals with distilled water to catch inaccuracies from poor cleaning or damage to the vessel surfaces. For improved accuracy, the vessel can be calibrated using pure water at normal reading temperatures. Divide the gram weight of water by the weight determined by direct testing. This produces a correction factor. This factor number is multiplied by the weight of the gallon weight found for an unknown liquid or mixture. If the determined density of water was less than expected, a factor greater than 1.000 is generated. As a result, the vessel's volume is less than expected. Tracking the factor value will alert the tester to problems arising from poor cleaning or rough handling that can damage and alter the testing vessel.

Sample sizes range from 10 to 84 ml. The combined weight of the vessel, lid, and sample affect the type of balance that can be used to provide good repeatability and reproducibility. The larger the size, the easier it is to get a sample representative of the bulk material. But the larger the size, the harder it is to remove entrapped air bubbles from the sample introduced during sample collection or preparation. For very volatile solvents, use of larger size vessels offsets the weight drift seen during weighing.

The problem of entrapped air can be countered in two ways:

1. The Monk cup is designed to pressurize the sample to 150 lb/in.^{2} in a known volume of space. This pressure compresses the entrapped air in the sample to such an extent that occluded air bubbles are reduced to a negligible volume. Entrapped air of up to 10 vol % can be dealt with by this technique. The volume produced is still larger than the true volume, and a density error is still present. Entrapped air should not be accounted for if the air escapes before use or the air is an artifact of sample mixing before testing. The Monk cup is large and heavy and requires use of non-analytical balances. Fig. 12 is a schematic diagram and picture of a Monk pressure weight-per-gallon cup.
2. An alternative technique is to mix a measured weight of the unknown density material with the weight of a known diluent from a full weight per gallon cup. The blend is then placed back into the cup and weighed. The following, enclosed in quotes, is copied directly from the GARDCO mini catalog Number 9, including the diagrams, with permission from GARDCO [7].

$$X = \frac{W_{unknown} B_{lend\ wt\ per\ gallon}}{(W_{unknown} + W_{diluent\ cup\ weight} - 10 B_{lend\ wt\ per\ gallon})} = \frac{WB}{(W + A - 10B)} \quad (14)$$

where $A = W_{\text{diluent cup weight}}$.

"Heavy-bodied materials which entrap air present a problem in true weight per gallon (density) measurements. Air entrapment causes the apparent volume of a material to be greater than actual and density or weight-per-gallon calculations are low and erroneous. The practice of measurement under pressure does reduce the error but the error is far from eliminated as the entrapped air is normally not removed, but only compressed, as shown in Figs. 14 and 15.

Most materials that are difficult to evaluate can be simply and accurately measured by the following depicted procedure.

"A measured weight of the unknown material is thoroughly blended with the weight of a known diluent from a full weight per gallon cup. The blend is then placed in the cup and the weight per gallon is determined. The value of

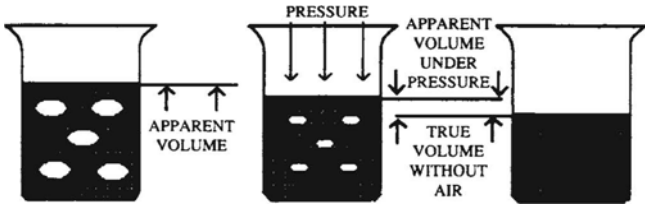


Fig. 14—Liquid with entrapped air [7]. Figure provided by Paul N. Gardner Co., Inc.

the unknown material is calculated from the formula given above. The diluent liquid must be compatible with the material containing the entrapped air and it must be thin enough in viscosity to allow entrapped air to rise to the blend's surface and escape. In the case of particulate, such as pigment, the liquid must be able to wet the particle surfaces and displace air in pockets or depressions on the surface."

ASTM methods using known volume devices are [15,16] Standard Test Method for Density or Relative Density of Pure Liquid Chemicals (D3505) and Standard Test Method for Density of Paint, Varnish, Lacquer, and Related Products (D1475).

Sonic Frequency Shifts

Waves of air reaching a human ear are recognized as sound. The pitch of a sound is related to how many waves reach our ear per unit of time. This unit of time is referred to as frequency. Waves are made by an object moving in the media: air or liquids or even solids. The media touched by the wave can pass this movement through itself. When a boundary between two media of different densities is encountered by the wave, two actions occur: (1) some waves are reflected back; (2) a portion of the waves are passed into the new media but with their frequency changed.

Changes in density also lead to changes in frequency. This can be demonstrated by filling a matched set of water glasses to different levels with water, then striking each glass lightly to produce a sound. The higher the water level is in the glass, the higher the tone. Just as the frequency changes from an empty glass (air, less dense) to a high frequency tone when filled with water (more dense), the replacement of liquids of differing densities also shifts the frequency for glasses filled to the same level. This is the principle for several digital density meters commercially available today.

Measuring devices have been devised using a glass tube, an oscillator, and a sensor. The oscillating frequency

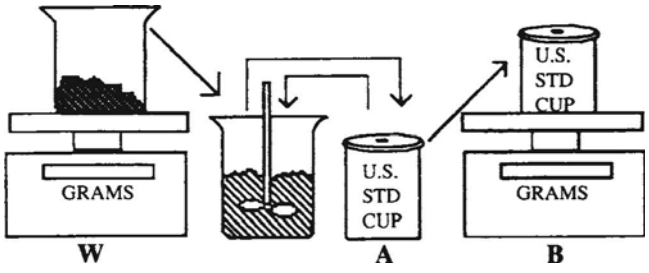


Fig. 15—Diagram for mixing known- and unknown-density materials [7]. Figure provided by Paul N. Gardner Co., Inc.

of the tube changes when air is replaced with a liquid. The instrument can use air and water to establish a set of constants, called *A* and *B*, for the following relationships [17]:

$$A = (T_w^2 - T_a^2) \div (d_w - d_a) \tag{15}$$

$$B = T_a^2 - (A \cdot d_a) \tag{16}$$

where

T_w = observed period of oscillation for cell containing water,
T_a = observed period of oscillation for cell containing air,
d_w = density of water at test temperature,
d_a = density of air at test temperature,
t = test temperature expressed in degrees Kelvin,
p = test barometric pressure expressed in Torr,
d_a (g/ml) = 0.001 293 × (273 ÷ t) × (p ÷ 760)
d_w (g/ml) = 0.997 04 at 25°C (273°+ 25° = 298°K)

Constant A is used by the instrument's computer to calculate constants K_c and K_{cr}. Constant *B* is used by the instrument's computer to return the reading for air density.

Modern digital density instruments are equipped with heating and cooling devices internal to the instrument, such that the sample can be equilibrated within the instrument in a matter of seconds. This leaves the pressure term, *P*, as a visible variable. Pressure changes can occur over a period of time due to weather changes.

The sample tube must be cleaned after each use. The tube's condition needs monitoring to verify that it is at original condition. Frequent calculation of the instrument cell constant K_c overcomes both of these problems.

For density values

$$K_c = \frac{1}{A} = \frac{d_w - d_a}{T_w^2 - T_a^2} \tag{17}$$

$$d_{\text{material}} = d_w + K_c \cdot (T_a^2 - T_w^2) \tag{18}$$

For relative density values

$$K_{cr} = \frac{1.0000 - d_a}{T_w^2 - T_a^2} \tag{19}$$

$$d_{\text{material}} = 1.0000 + K_{cr} \cdot (T_s^2 - T_w^2) \tag{20}$$

where:

T_w = observed period of oscillation for cell containing water,
T_s = observed period of oscillation for cell containing sample,
K_c = instrument constant for density,
K_{cr} = instrument constant for density,
d_w (g/ml) = 0.997 04 at 25°C (273 + 25 =298°K) density of water at test temperature, and
t = test temperature expressed in degrees Kelvin.

Small process computer chips built into commercially available instruments handle all the necessary calculations. Small sample volumes (1.0 to 2.0 ml) are used so heterogeneous samples like paint must be well mixed. The samples

must be free of entrapped air. Small amounts of air cause fluctuations in the readings. Use of dilution with a compatible solvent (of known density) to thin the sample can be used if the thinning does not cause pigment dropout. The contribution of the thinner solvent can be calculated and backed out.

The ASTM method using the digital density meter is [17] Standard Test Method for Density and Relative Density of Liquids by Digital Density Meter (D4052).

SOLIDS

Densities of Solids—Methods of Determination

With solids, determining the volume for a known weight of the material is a challenge for several reasons. First, the form is fixed and direct, accurately known volumes are the exception rather than the rule. Second, solids are seldom homogeneous in their density. Processing often introduces voids or regions of differing degrees of crystallinity, both of which affect density. For large objects, displacement techniques as well as sonic shifts are useful. For powders and small particles, displacement and density by mixing with liquid diluent are the most common techniques. For thin films, only displacement techniques are useful.

Direct Volume Measurement by Pycnometer

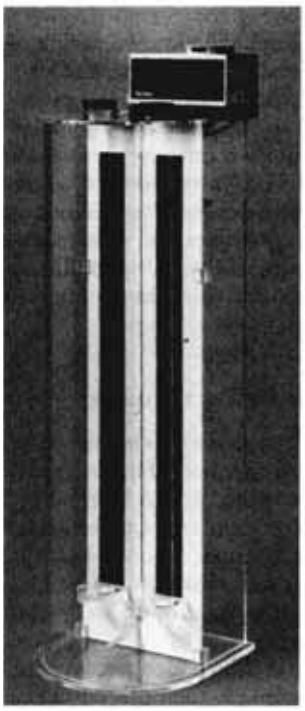
Pigments are insoluble, solid particles used to impart color or light reflectance in paints. To provide more than an apparent density, special steps must be taken. ASTM Method for Specific Gravity of Pigments (D153) is a set of three variations on the diluent pycnometer technique described in Fig. 15. It uses a vacuum pump and vacuum dessicator or bell jar to reduce the pressure on a sample of solid pigment. Variation A places a weighed sample of pigment in a dry, weighed glass pycnometer. White kerosene is then added to cover the pigment. The pycnometer and sample is then placed in the dessicator or bell jar and slowly evacuated to remove air entrapped on the irregular surfaces of the pigment. This is a method to wet the pigment surface and remove the contribution of entrapped air in the pigment. After all bubbling stops, air is let back into the jar and the pycnometer is filled to the top with kerosene and weighed. Variation B evacuates the pycnometer before the kerosene is added. Most of the kerosene is added to the pycnometer while it is under vacuum. The pycnometer is topped off with kerosene after returning to normal pressure. Variation C uses a measuring burette to add the kerosene so that volume of kerosene added is known [9,18].

ASTM methods using a pycnometer are [18,19] Standard Test Methods for Specific Gravity of Pigments (D153) and Standard Test Method for Density (Specific Gravity) of Solid Pitch (D2320).

Displacement of Liquids

This was discussed in the section "Solids, Liquids, and Gases—as Concepts" Under Ideal Conditions.

Density gradient column systems (Fig. 16) are another form of submersion test methodology, inverted from the plummets of the density balances. Here the fluid is the calibrated, known test media, and the solid is the unknown. A vertical column tank with black background is carefully filled with a mixture of liquids in a very strict order to establish a heavy-to-light liquid density gradient. Measurements



For accurate density determination of small solid samples to 0.001g/mL. Conform to ASTM D1505-68 for testing plastics. Measurements are made with reference to standard glass floats calibrated within ±0.0001g/mL. Fibers, irregular fragments, pieces of film, powders and glass are suitable. Several determinations can be made at same time.

In wide use for testing polyolefins, fluorocarbon polymers, nylons, PVC. Can separate natural and synthetic fibers. Can assay factors affecting density such as degree of crystallinity of plastics, concentration of isotopic content, presence of trace amounts of boron in silicon.

Fig. 16—Density gradient column systems with text from supplier catalog [6]. (Courtesy of Fisher Scientific.)

are made by adding in both unknown solid materials such as fibers, film pieces, powders, and glass particles and reference materials of known density. The particles will sink to the level of their own density. Using the proper reference materials, exact matches can be established within 0.0001 g/ml. There is a problem when the sample interacts with the fluids and absorbs them or interacts in other chemical ways that perturb the normal test action as with inert materials such as glass or plastics. Powders with irregular surfaces can also experience surface wetting problems and air pocket entrapment. Densities can be determined from 0.79 to 2.89 g/ml with this technique [26].

The test is of long duration, requiring a settling time of usually several hours. Several caution notes are included concerning thin film samples and their handling, which could change the density. Potential users should review ASTM D1505 to assess the applicability of this technique to their own personal needs and use.

ASTM methods using displacement of liquid and gases are [13,20,21] Standard Test Method for Specific Gravity (Relative Density) and Density of Plastics by Displacement (D792), Standard Test Method for Volume Nonvolatile Matter in Clear or Pigmented Coatings (D2697), and Standard Test Method for Density of Plastics by the Density-Gradient Technique (D1505).

Displacement—Gases

Helium pycnometers have been available for a number of years with many people expressing interest in using these devices to determine the volume of solids of known weight. These instruments are usually relatively expensive and only recently have become sufficiently automated to reduce the

intense manual labor required to do a good job. The main problem is to provide a sufficient amount of free paint film to test at a valid film thickness. Films that are too thick can retain solvents. Films that are too thin are very hard to handle. Free films develop static charge buildups, which further complicate the testing procedure.

Dry powders are a second candidate for this technique. Helium gas displacement eliminates the need for the vacuum pump and the kerosene used in ASTM Method D153, Test Methods for Specific Gravity of Pigments, to replace the air in the voids and available surface cavities. The drawback is that the fine powder is easily blown around. The instrument must be designed to eliminate powder travel and to keep the fine particles from the valves and seals. Hopefully most of these drawbacks have been addressed [14].

ASTM methods using Helium Pycnometry are [14,22] Standard Test Method for Percent Volume Nonvolatile Matter in Clear or Pigmented Coatings Using a Helium Gas Pycnometer (D6093) and Standard Test Method for Density of Solid Pitch (Helium Pycnometer Method) (D4892).

Sonic Frequency Shifts

The sonic frequency shift, principle and equations, has been discussed previously. Use of the sonic technique is limited to continuous objects that can be cut and shaped. Powders and small particles can be suspended in liquids and tested using the equipment discussed previously and using the equations noted earlier under Sonic Frequency Shifts. When the instrument uses solids instead of liquids, several considerations change. A glass tube is no longer used. The solid specimen must be cut into a rectangle with a smooth surface. Surface flaws will introduce errors in the readings.

A sonic sensing head is attached to the solid specimen (approximately 75 mm in thickness), and measures the velocity of sound transmitted through the specimen. Solid specimens require a minimum conditioning time period under controlled temperature and humidity conditions before testing. A calibration curve can be established using materials of known density. The published use is limited to polyethylene plastics. Alternative methods are probably cheaper or less time/labor consuming.

ASTM method using ultrasound [23] The Standard Method for Density of Polyethylene by the Ultrasound Technique (D4883).

Apparent Density

Many pigments or powders are tested without regard to the air entrapment on the particle surfaces or in the voids between where the particles touch. These materials are placed in a graduated transparent container, and a vibrator is touched to the container wall. The particles pack down and a weight is taken. This is referred to as apparent density.

ASTM methods based on apparent density include [24–26] Test Methods for Methylcellulose (D1347), Standard Test Methods for Sodium Carboxymethylcellulose (D1439), and Standard Test Methods for Hydroxypropyl Methylcellulose (D2363).

PAINT VOLUME SOLIDS

Paint is a mixture of materials that is designed to protect and beautify a substrate. When paint is sold, it is sold by volume as gallons or liters. What the consumer wants is the most coverage for the money. Commercial painters and original equipment manufacturers paint surfaces to a minimum thickness called "hiding." They know the square footage or square meter surface area they need to cover. With the thickness for hiding known, a volume of solids needed for painting a house or an automobile can be calculated. Government regulators would like to know the volume of volatile organic material included in a gallon of paint. A ratio of volume volatiles to volume solids would be a measure to compare paint products in terms of pollution contribution.

Theoretical Calculations of Paint Volume Solids

For many paint systems in commercial use today, a straight calculation of solids content can be performed with good results using the densities and weight percent content of materials that contribute solids to the final product. For many other systems, however, this calculated answer does not account for additional reaction by-products or provide information about how the density of the material has changed when cross-linking occurs. For these systems an analytically tested answer is needed. For the last revision of this book, the major document in force by the U.S. Environmental Protection Agency (EPA) was Reference Method 24: Guidelines of Testing for VOCs at 110°C for 1.00 Hour Bake [1]. This was the document to which all methods development related to VOCs relied. In the last 15–20 years, several ASTM test methods have been developed to address the concerns associated with how and when a VOC is occurring, be it the slight amount of solvent introduced via a minor additive, or a reaction product of a catalyzed system. All of the methods referenced in this manual that deal with paint and coatings raw materials and finished products reference EPA Method 24. These analytical methods are appropriate regardless of whether the composition of the coating is a known or an unknown.

Analytical Determination of Paint Volume Solids

Standard Test Method for Volume Nonvolatile Matter in Clear or Pigmented Coatings (D2697) [20] is commonly used. The test is based on displacement of liquids, usually water or kerosene. Perhaps a more reliable test is Standard Test Method for Percent Volume Nonvolatile Matter in Clear or Pigmented Coatings Using a Helium Gas Pycnometer (D6093) based on volume determination by gas (helium) displacement [14]. The helium is a pervasive gas that behaves closely to an ideal gas. Where paint surfaces are hard to wet with water, the helium has no problem getting very close to the paint surface and displacing air residing at the surface. The test chambers are usually from 5.0 to 30 cm^3 in volume. The paint sample is introduced as a free film or attached to a carrier such as a metal disk or aluminum foil. When the film is a free film, static charges can build up and cause sample loading and handling problems. The test instrument is not inexpensive, but it is highly automated and minimizes the human labor required to about 5 min per test. The fact that the test specimen is a solid film is very beneficial in the case of reactive systems, which are not chemically the same before and after cure. This may be the only means to ascertain the reactive elements (by difference), which should be included in VOC determinations.

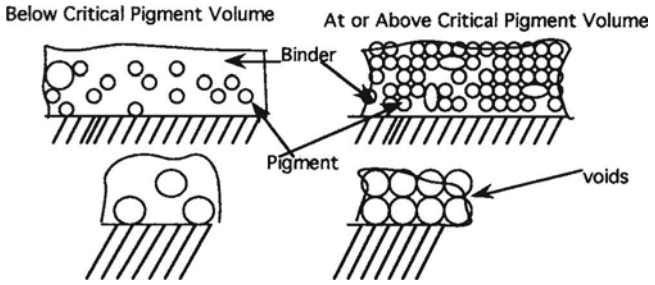


Fig. 17—Pigment volume relationships.

CRITICAL PIGMENT VOLUMES

The pigment volume concentration is a physical property of paint that can help indicate its performance. The definition of Pigment Volume Concentration (PVC) is the ratio of the pigment volume divided by the pigment volume plus resin solids (and sometimes additive solids) volumes. The reader is directed to chapter 28 of this book where this concept is discussed in greater detail.

Pertinent to our discussion is a volume concentration of pigment known as the Critical Pigment Volume Concentration (the CPVC or cPVC). At this ratio, several things happen to the properties of the paint. At this point, there is just enough resin or binder to completely fill the spaces between all the pigment particles. As the PVC increases past the cPVC, the dried paint film will contain voids. The porosity will increase, the moisture vapor transmission will increase, the stain resistance will decrease, the wet hiding will decrease, but the dry hiding will increase. As the paint dries, a condition will exist where the paint has too much pigment and too little polymer such that the internal voids created will entrap air or solvent in the vapor phase [1]. Paint companies actually take advantage of one of these properties to make inexpensive paints that can still hide in the dry state. By formulating above the cPVC, the coating can contain much less pigment, while still performing sufficiently well enough for noncritical applications (ceiling paints and the interior low-performance application). For our discussion it is enough to say that a solid is created that has a higher apparent volume than really exists (see Fig. 17).

If a volume solids test is used that uses strictly liquids to determine displacement solids, they may be unable to penetrate into the void areas. A larger volume of water will be displaced and the apparent weight loss will be greater in water. The bottom line is that all the tests that rely on an accurate determination of specific gravity will be in error. It is exactly in this situation where the ability to accurately determine the volume solids of a paint film, such as the Standard Test Method for Percent Volume Nonvolatile Matter in Clear or Pigmented Coatings Using a Helium Gas Pycnometer (D6093), really shows its worth.

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Characterizing Particle Size and Size Distribution

George D. Mills[1]

INTRODUCTION

CHARACTERIZING THE SHAPE, SIZE AND SIZE-distribution of particles that go into liquid paint or coating formulations as well as dry formulated powdered coatings are very important. These materials may vary from being ground mineral fillers to crystalline epoxy cross-linkers and catalysists used in finished powdered paint products. There is a significant effect on the coating's density, mechanical strength, electrical, thermal as well as sound and small molecule transmission properties as a function of the included average particle size and shape.

An example of the importance of particle size is the inclusion of crystalline dicyandiamide (dicy) as a cross-linker in fusion bonded epoxy (FBE) powder coatings or the blowing agent in "fire resistive" paints. Dicy is not stable after melting and decomposes to gaseous products if not consumed in a curing reaction with epoxy. The use of the standard commercial particle size dicy in FBE formulations leads to an unusual type of coating failure. In this case, to remedy the problem, a separate step is performed on the standard commercial-sized powdered dicy used in FBE coatings to produce a "micronized" powdered dicy. If "micronized" dicy is not used, it cannot be fully incorporated into the un-cured FBE matrix during the short time in the extrusion process. This leads to very small regions of the crystalline dicy cross-linker remaining after cure. Because of its slight water solubility, tiny osmotic blisters are formed causing the coating failure. This same material, dicy, is used as a "blowing agent" in the formulation of intumesant paints. In this case the dicy particle size incorporated into the paint dictates the foam density produced on heating and decomposition. This impacts the thermal transfer value of the fire resistive paint.

Particle-size measurements associated with the paint and coatings industry has broadened in scope considerably over the past few decades. Not only must we evaluate the size, shape, and size distribution of the pigments, fillers, and emulsified resin particles used in the formulation of the coating system, but major efforts are now put forth to address environmental and applicator's health problems that are specific to particle size, nature, and morphology. Environmental and economic concerns have been a substantial driving force in the development of powder coating technology, which requires monitoring finished powder size and size distribution to ensure consistent application parameters.

We have learned that the size, shape, and nature of dust particles in the air we breathe during the manufacture, application, and abrasive removal of paints are of utmost concern to our health. Airborne dusts of silica and asbestos, as well as lead- and chromium-laden paint debris generated during abrasive blasting, are serious health threats. In an effort to protect the general public, government regulations now address the monitoring of small reparable dust particles of less than 10 μm ("R10" particles) during the abrasive removal of certain coatings.

In the production of electronic microcircuits, chips, and semiconductors, photo-resist coatings are applied to silicon wafers with line-to-line resolution of fractions of a micron. Dust particles, which are a fraction of this size, if allowed to contaminate the coated surface, will cause the production of defective chips. Dust has forced the development of more sophisticated clean-room technology in recent years. The reject rate of produced microchips caused by defects in the coating as a result of ultra-small particles of dust is a major problem.

As technology advances in the evaluation of smaller-size particle systems, materials used to standardize and calibrate the measuring/monitoring equipment must be developed. The necessity for standard traceable test materials, i.e., from the National Institute of Standards and Technology (NIST), formerly National Bureau of Standards (NBS), which are required to ensure the reliability of the measurements, has led to secondary industries that produce these standards from various materials.

Due to pressing global concerns with solvents emissions as well as the associated economic benefits, powder coatings as a class have grown at a very fast rate over the past 30 years. Many properties impacting the production, delivery, application, and film-forming characteristics are related to the average particle size of the manufactured powder coating. Often, of equal importance, is the amount of very small particles present. These "fines" impact fluidization and electrostatic application characteristics of the powder coating.

With the exception of physically sieving a powder sample using different sized screens, particle size analysis usually employs laboratory instruments. These lab instruments employ various physical principles. Current technology instrumentation has the ability to determine particle size as small as 0.003 μm utilizing "Quasi Elastic Light Scattering"

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to 1200 μm using "electrical resistance zone sensing." These technologies are addressed later.

Particle characterization methodologies currently employed include:

- Physically sieving using various screens having different size openings;
- Sedimentation (using centrifugal and gravity forces);
- Surface area determination (employing both gasses and liquids surface adsorption);
- Individual particle sensing (light blocking and electrical resistance);
- Direct microscope measurements (static and dynamic image microscopy, visual light microscopes and electron microscopes);
- Light attenuation and scattering;
- Liquid paint draw-down gage.

There are currently emerging techniques that employ the physical principle of ultrasonics. The specific instrumental techniques include Acoustic Attenuation Spectroscopy having a measurable size range of 0.05 to10 μm. With this technique concentrated colloids, emulsions, and suspensions can be analyzed. When the transmission of light through the sample is required to affect the particle size analysis, the sample must be diluted considerably. Unfortunately, some of these particle systems are not stable at these dilutions. The use of ultrasonic waves of a range of frequencies directed through the dispersed medium and accurately measuring the attenuation at each frequency allows collecting an attenuation spectrum that can be converted to a particle size distribution as well as a measure of the concentration of the dispersed phase. This has been made possible by the recent development of ultrasonic transducer and advancements in digital signal processing [1].

Another developing technique using ultrasonics is Electroacoustic Spectroscopy (Electrokinetic Sonic Amplitude) having a measurable size range of 0.1 to 10 μm. Single Frequency Colloid Vibration Current and Electrokinetic Sonic Amplitude have a measurable size range of 10 nm to more than 10 μm. A major benefit is the ability to accept samples as concentrated as slurries [2].

Although an understanding of the relationships of powder properties to product application characteristics and performance is important, quality assurance/quality control (QA/QC) requirements demand high-speed, on-line (real-time) monitoring. This demand for rapid, accurate analysis of particle characteristics has been a driving force in the development of current instrumentation. The availability of low-cost computers and pertinent software as well as highly reliable and stable energy power sources and detectors have allowed the development of fast, accurate, broad spectrum, and "in-process" instrumentation. The development of robust solid-state laser diodes has allowed the replacement of bulky gas lasers, which required optical table stability. Further, the development of fiber optics, as well as the technology associated with its ease of alignment, has assisted in downsizing the footprint of some current generation instrumentation.

A major objective of this chapter is to provide an understanding of many of the various methodologies available for evaluating particle size, shape, and distribution. The hiding power and light transmission characteristics of coatings are greatly affected by the particle size of included pigments and fillers. Tensile strength of the cured system, water and gas vapor transmission coefficients, chemical resistance, and interface anticorrosive activity are only a few areas impacted by the size, shape, nature, and size distribution of the pigments and fillers formulated into the coating.

This chapter will allow an educated choice of technologies based on the size-dependent measurement most related to the desired property of importance. An appreciation of the mathematics involved will aid in determining and understanding the limitations and potential errors inherent in the measurement.

History of Particle-Size Analysis

The earliest reported particle sizing was about 150 B.C. in Greek and Roman mining manuals using sieves made of leather, woven hair, and planks. The Germans introduced wire-woven screens in the 15th century. Microscopes were reportedly used in the 1700s for size analysis. Automated machinery was developed in the 1800s for weaving metal-wire sieve fabric. In the late 1800s to early 1900s, standards were developed defining sieve sizes. The first apparatus of record used for classification of pigment particles into different sizes was reported by Thompson [3] in 1910. Oden proposed the use of gravity sedimentation as early as 1916 [4,5].

Energy sources of various wavelengths, employing many different configurations, have been used to measure particle size. Visible light photometry was reported by Stutz and Pfund [6] in 1927. Gamble and Barnett [7] employed radiation in the near-infrared region. Atherton and Peters reported using light-scattering techniques in 1953 [8]. The electron microscope found use in the 1940s for characterizing very small particles as well as to define the corresponding surface topography. After the laser light source was invented, light scattering technologies were expanded. The development of better diode array detectors opened the way for developing the fast light-scattering and blocking instruments now widely used since the 1990s. The recent advancements in transducer technology and digital data collection are opening the way for the instruments using ultrasonics mentioned above.

The latest technology since 2010 includes laser diffraction spectrometry, ultrasonic extinction, and photon cross correlation spectrometry. There have been improvements in image analyses, both static and dynamic. These technologies allow a particle size measurement range of 1 nm to 10 mm [9].

Importance of Particle-Size Analysis

As the physical properties of paints, coatings, and polymers in general are impacted by the size, shape, and size distribution of the fillers included in the formulation, it is imperative that characterization of the pigment and filler system be correlated with the physical properties of the coating.

Because of the early importance of zinc oxide as a pigment in oil-based paints and its existence in multi forms and shapes, this material was studied in the 1920s and 1930s. Bunce [10] found that as the average diameter of zinc oxide in paint increased from 0.19 to 0.31 μm, the elongation of the film increased and the load at the breaking point decreased (Fig. 1). Eide [11] showed that coarse acicular zinc oxide imparted greater durability to a paint than did "round" zinc oxide. In related studies, Morris [12] and Nelson [13] found evidence that acicular asbestine of

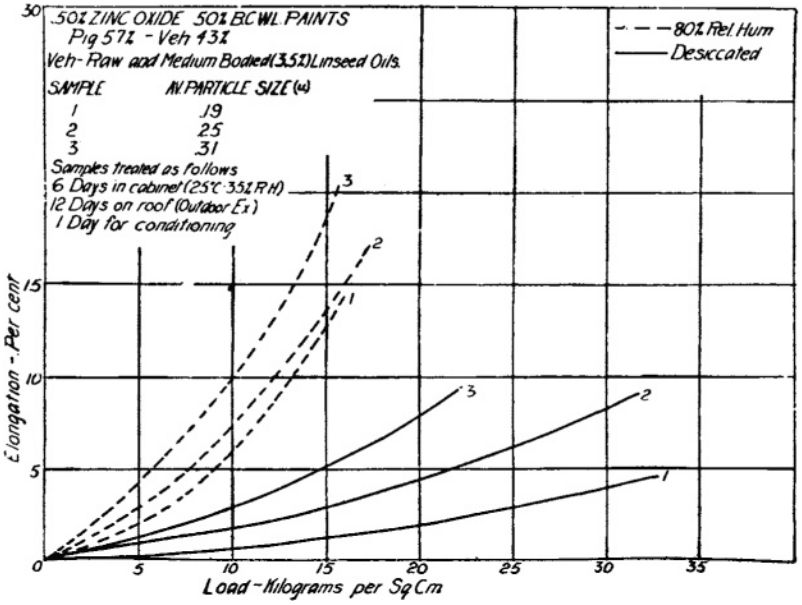


Fig. 1—Stress-strain curves of some paint films. These illustrate the effect of the particle size of zinc oxide on the strength of paint films.

a wide distribution of sizes favorably influenced the durability of paints, and a review by Jacobsen [14] cites many examples of the significance of particle size and shape of pigments and extenders on the optical and physio-chemical properties of coating systems.

Many surface properties are impacted by the pigment's and filler's particle size and nature of which gloss is one of the most prevalent. While the larger-size particles can "protrude" through the surface of the coating, causing a surface roughness related to the size of included particles, extremely fine particles can affect gloss by adsorbing binder to a point that the gloss is decreased due to a lack of available binder at the coating surface. The "oil adsorption" of the pigment is a function of its surface area and increases as the average particle size decreases. ASTM D1483 presents a standard test method for determining the oil absorption of a pigment [15]. The "critical pigment volume concentration" (CPVC) exists at a pigment loading such that there are just enough binder solids to completely wet out the included filler and pigment particles. Coatings formulated above the CPVC cannot be glossy. Abrasion resistance of the coating may be increased by the addition of hard fillers such as silica. The relationship between particle dimensions and film properties is depicted in Fig. 2. The National Paint, Varnish, and Lacquer Association has published a Pigment Index that gives information on the particle size of many of the pigments available on the American market [16].

Other coating properties impacted by variations in particle size and shape include the efficiency of contained ultraviolet (UV) blockers and absorbers such as carbon black pigments. The use of acicular (needle-like) pigments such as Wollastonite (asbestos free) is popular in many types of coatings. The tensile and compressive strength of coatings also can be modified by judicial choice of particle size and shape, and gas vapor and molecular water vapor transmission of a coating can be altered with the proper choice of pigment loading, shape, and size.

The coalescent and film-forming characteristics of emulsion binders are impacted by the particle size of the dispersed resin particles. Cold "touch-up," brush ability, and mechanical stability during pigment dispersion are a function of properties that are related, in part, to polymer particle size. Surfactant demand and effectiveness are a function of polymer particle size (as well as other binder variables). Because of the importance (dependence) of many coating properties on the small finite size of the pigment, fillers, catalysts, and polymers formulated into the coating, the demand for rapid, accurate analysis of particle characteristics has led to the refinement of many techniques.

CONSIDERATIONS IN SAMPLING TECHNIQUES

Normally, when a particle-size determination is made, one will not work with the total collection of particles comprising the bulk sample. A "representative" collection of particles is usually chosen. This sample is then reduced in size a few more times until only a few milligrams remain for the actual instrumental testing. The assumption is usually made that the fraction actually evaluated is, in fact, "identical" in particle size, size distribution, shape, and nature to the total of the bulk material. This, essentially, is never true. This sample test fraction, which usually does not exactly represent the bulk, can be a major source of error, introducing considerable bias and distortion to the results. The reliability of any measurement depends on the degree of "representativeness" of the test sample. Thus, the sampling technique is often more important than the actual particle-size measurement.

Theoretical Considerations of Variance in Sampling

To obtain a representative sample, the sampling process is usually divided into several steps during which a conscious effort is made to reduce bias. The bulk material is usually obtained in huge, ton lots. The first sample reduction

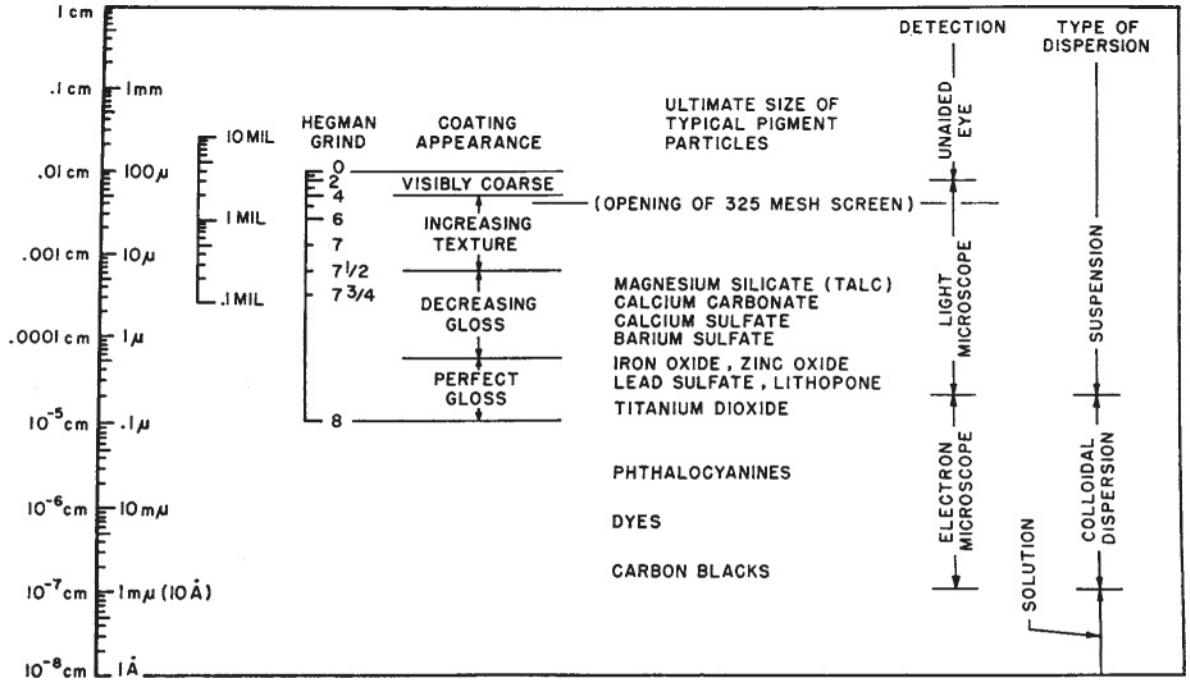


Fig. 2—Dimensions of granular pigments and their relation to surface properties (from Ref. [12]). (Courtesy of the *Journal of Paint Technology.*)

provides the "gross" sample, which is on the order of kilograms. This sample is then reduced to the "laboratory" sample, which is on the order of grams. The actual evaluation sample introduced to the instrument is on the order of milligrams. The reduction process, almost always, will introduce some bias, depending on the actual spread in the distribution. This bias will diminish as the consistency approaches unity, i.e., all particles approach being identical. The bias exists because the physical forces acting on the particles in a collection are not the same, but are, in fact, size dependent. The "fines" act differently in a pile than will the coarse particles. Their angle of repose is different, often resulting in particle stratification and some segregation.

There are some established rules that must be followed to minimize this bias. The "perfect" sample is one in which the differences seen between the evaluated characteristics and those that actually exist in the bulk can be ascribed to the expected number variations described by statistics. For a sand (A) and sugar (B) mix, the probability that the number fraction, *p,* of (A) in the bulk actually is represented by the number fraction (*pi*) in the sample is computed from the number of actual particles in the bulk *(N)* and the reduced sample *(n)* [17]. The equation is as follows:

$$\mathrm{Var}(p_i) = \frac{p(1-p)}{n}\left(1-\frac{n}{N}\right) \tag{1}$$

Theoretically, the expected deviation (i.e., standard deviation), σ_i, is the square root of the variation. Since the use of the weight fraction is often more convenient, the equation for variance is given by

$$\mathrm{Var}(P_i) = \frac{P(1-P)}{w}[Pw_B + (1-P)w_A]\left(1-\frac{w}{W}\right) \tag{2}$$

where the weight fraction in the sample and bulk are *P*; and *P,* respectively, *W* and *w* are the bulk weight and sample weight, respectively, and w_A and w_B are the weights of individual grains of A and B, respectively.

Even with the "perfect" sample, there is a finite probability that the measured sample will deviate from the actual bulk by some predictable value. To minimize this "guaranteed" deviation, a minimum sample size is required. One may calculate the minimum sample size required to yield values within preset statistical limits [18]. The equation relating the minimum sample weight of a gross sample is given by

$$M_s = \frac{1}{2}[\rho/\theta^2][1/w_\lambda - 2]d_\lambda^3 \times 10^3 \tag{3}$$

where:

M_s = the limiting weight in grams,
ρ = the powder density in g/cm³,
θ^2 = the variance of the tolerated sampling error,
w_λ = the fractional mass of the coarsest size class being sampled,
d^3_λ = the arithmetic mean of the cubes of the extreme diameter in the size class in cm³.

The collection methods used in obtaining the sample are important. Depending on the nature of the material being tested, samples should be gathered so as to minimize the introduction of bias. There are two "golden rules" of sampling that should be followed when possible [18]. These are:

- The sample should be collected while in motion.
- All of the stream should be collected for a short period of time rather than a portion of the stream for a longer period of time.

TABLE 1—Standard deviation in particle size determination of a sugar-sand mixture as a function of sampling techniques

	Standard Deviation (σ)[a]	
	Sugar-Sand	Sand-Sand
Cone and quarter (worst)	5.762	6.812
Scoop sampling	6.312	5.142
Table sampling	2.11 %	2.09 %
Chute riffler	1.10 %	1.01 %
Spinning riffler (best)	0.27 %	0.132 %
Random variation	0.09 %	0.08 %

[a] Binary mixtures of sand-sand and sand-sugar were used, and all particles of one component and none of the other would pass through a designated sieve. Density of sand and sugar, respectively, is 2.65 and 1.64 g/mL From Allen, T., and Khan, A.A., 1970, *Chemical Engineering,* Vol. 238, pp. 108–112.

This procedure will assist in minimizing the probability of error generated by stratification and segregation due to differing weights of the particles within the stream and of the way they act within the collective mass of the sample during transport. Special collection devices are available for affecting the sample collection.

Sampling Techniques and Equipment

Sampling techniques have been developed to minimize the systematic errors introduced both in collecting the gross sample and in reducing its size to the analytical sample. In the work done by Allen and Khan [19] using sand-sugar and sand-sand, mixtures were evaluated utilizing different collection techniques. These techniques included (1) cone and quartering; (2) scoop sampling; (3) table sampling; (4) chute riffling; and (5) spinning riffling. The data presented in Table 1 show the values obtained via each method as well as the expected standard deviation from the known sample.

Cone and quartering is a procedure in which the powders are piled into a cone. The cone heap is then carefully pushed down flat and divided into four equal sections. The assumption is that the cone will be symmetrical about its central axis and the flattened sections will all be representative of the bulk mixture. A problem exists as it is very difficult to produce perfect symmetry, which results in some size segregation from the center out. The technique is also operator dependent, and tests showed this technique to give the largest standard deviation of the five techniques evaluated (see Table 1).

Scoop sampling entails randomly dipping into and pulling a scoopful of powder from a pile of the material to be evaluated. Because the pile is usually not totally symmetrical and evenly distributed throughout, the technique is prone to errors. Since in this procedure the powder is not caught while moving, it will not be typical of the bulk lot of material.

Table sampling (Fig. 3) utilizes a tilted surface over which a powder sample is allowed to slide. A series of splitting wedges cut the sample into numerous sections where some portions fall through openings and are discarded. Ultimately, a decreased quantity of sample is collected, although it is necessary that the incoming powder be uniform and consistent.

Chute splitting utilizes a funneling or channeling device capable of alternately placing the powder sampling stream into one of two collection hoppers. The technique is subject to error and operator bias if segregation is allowed to occur in loading the bulk sampling trough. Such error is present when the two collected portions are not the same

Fig. 3—Table sampler: A 16 to 1 reducer with removable legs for portability. (Courtesy of Gilson, Inc.)

Spinning rifflers (Fig. 4) utilize a series of smaller collection tubes or holders mounted in a way to collect a flowing powder stream over a very short time period. This technique was found to be the most reliable method for sampling and, when tested with different operators, showed little operator bias. Such was not the case for the other techniques investigated.

PARTICLE CHARACTERIZATION METHODOLOGY

As indicated above, the size and size distribution characterization of powders utilize various physical principals and methodologies. These methodologies range from the simple as with physically sieving the powders using screens with different known size openings to very sophisticated instrumental ultrasonic attenuation.

Particle Size by Sieving

Sieving appears to be a simple means for separating pigments into fractions according to size. A significant addition to the physical laws governing the process has been made by Whitby [20], who investigated variables such as size distribution, mesh size, sieve loading, sieve motion, sieve material, and relative humidity. A comprehensive manual on sieving methods has been published by ASTM [21] and the W. S. Tyler Company [22].

For routine testing, sieves conforming to ASTM Specification for Wire-Cloth Sieves for Testing Purposes (E-11) are useful. These sieves are made of woven wire cloth, supported in frames of up to 12 in. (30 cm) in diameter. A skirt protrudes slightly below the sieve, allowing it to nest

Fig. 4—The spinning riffler. (Courtesy of Brinkman Instruments, Inc.)

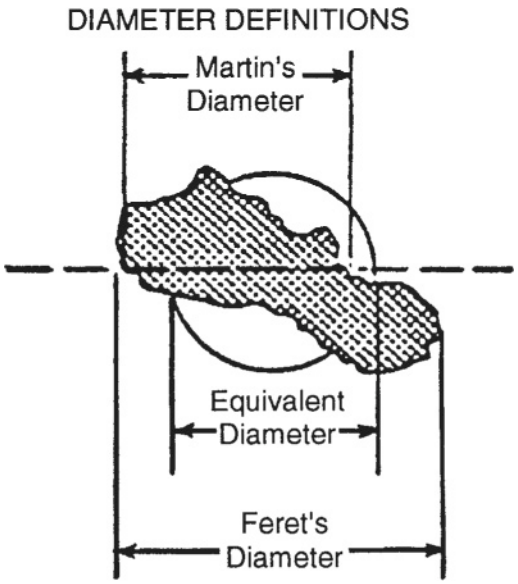


Fig. 5—The relationship of some stated diameters and the physical size of the particle.

into the frame of the next size sieve. The openings in successive sieves progress from a base of 1.00 mm in the ratio of the square root of 2 to 1 (i.e., 1.414:1). When selecting a range of sieves from the series, it is recommended that each sieve, each alternate sieve, or each fourth sieve be taken. In this way, the basic ratio between successive sieves remains constant.

The U.S. Series of sieves is patterned after the Tyler Series that was introduced in 1910. In fact, the two are now interchangeable, the only difference between them being the designations of the individual sieves. Those in the U.S. Series are identified preferably by the sizes of the openings in millimeters or micrometers, while an alternate means is by a number approximately equal to the mesh. Tyler sieves are identified by mesh. Equivalent sieves are available in both series. The sieves proposed as standard by the International Standards Organization (ISO) correspond to many of the sieves in the U.S. Series. Especially useful for sizes under 100 μm is a sieve made by a photoengraving and electroplating process [23]. Such sieves are intended to serve mainly as primary reference standards [see ASTM Specification for Precision Electroformed Sieves (Square-Opening Series) (E-161)].

HAND SIEVING

If the sieves are used singly, the following directions that appear in several ASTM test methods, among them D546, Sieve Analysis of Mineral Filler for Road and Paving Materials, may be used. After transferring the specimen to the sieve, "Hold the sieve, with pan and cover attached, in one hand in a slightly inclined position so that the specimen will be well distributed over the sieve, and at the same time gently strike the side about 150 times per minute against the palm of the hand on the upstroke. Turn the sieve every 25 strokes about one sixth of a revolution in the same direction each time. Continue the operation until not more than 0.05 g passes through the sieve in 1 minute of continuous sieving."

Sources of error in hand sieving are operator fatigue and casual attention to directions. While machine sieving eliminates these errors, some specifications still require hand sieving unless it can be shown that machine sieving gives the same results.

MACHINE SIEVING

Machine sieving has the advantages of uniformity of treatment and saving time since the operator is free to perform other tasks while the machine is working. Several types of machines are available. The conventional ones impart an oscillating or rotating motion (or both) to the sieve, with regular tapping. None appear to reproduce the motions of hand sieving.

Ro-Tap Sieve Shaker. This machine (Fig. 6) has been in use since the early 1900s and the company now has five models. The machine manipulates a series of sieves, graduated with respect to mesh size, so as to permit separation of a specimen into sizes. As the name implies, the sieves are given a special rotary motion accompanied at regular intervals by a tap. The nature of the specimen dictates the size of the sieve openings and the timing cycle. This type of machine is recommended in ASTM Test Method for Particle Size or Screen Analysis at No. 4 Sieve (4.75-mm) and Finer for Metal Bearing Ores and Related Materials (E-276). See www.wstyler.com/html/ro_tap.html for various models having one or two stacks of sieves.

Sonic Sifter. In the Allen-Bradley sonic sifter [24] (Fig. 7), the sieves are stationary, and agitation is imparted to the particles by an oscillating column of air. Sieve wear and particle attrition are said to be minimal. The sonic sifter consists of a sieving chamber, a diaphragm at the top vibrating at 60 Hz, and a motor with the necessary controls. The amplitude of vibration is adjustable to the nature of the specimen. A determination may require no more than 60-s operation of the machine.

Fig. 6—Ro-tap testing sieve shaker. (Courtesy of W. S. Tyler Co.) http://www.wstyler.com/html/ro_tap.html.

To make an analysis, the sieves, in descending order from top to bottom, are assembled in the holder, and the specimen (not more than 30 *g* or 10 ml) is transferred to the top sieve. The cone, coupling unit, and the diaphragm are added, and the stack is latched within the chamber. The complete assembly is positioned in the machine, the power level and the time interval are set, and the operation is started. After the sift interval, the stack is removed and opened, and the fractions are weighed and computed in the usual manner.

Air-Jet Sieve. A cross section of the air-jet sieve [25] is shown in Fig. 8. A specimen is seen being processed through the component parts. The complete operational unit includes a vacuum cleaner. The hose of the vacuum cleaner is fastened to the outlet at the lower left. The specimen is placed on the sieve, and the air, which comes from the rotating split nozzle on its way to the vacuum cleaner, agitates the specimen. The finer particles pass the sieve and are collected in a tared filter bag; the coarse particles are retained on the sieve. Sieves with different meshes are used for additional fractionations, and the procedure is repeated. New tared filter bags are used for each fractionation if retention of the fractions is desired. Air velocity must be regulated, and a manometer is used to indicate the vacuum in the housing.

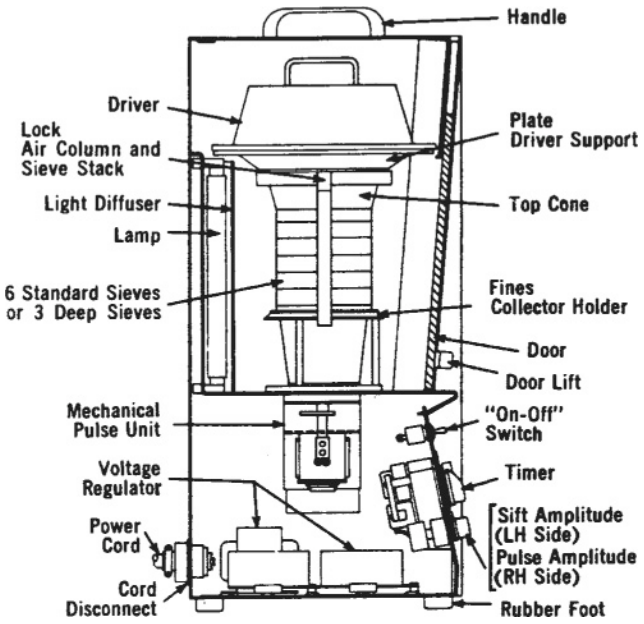


Fig. 7—Diagram of the Allen-Bradley sonic sifter. (Courtesy of Allen-Bradley Co.)

Particle Size by Sedimentation

The use of the principle that a particle will "fall" through a liquid medium at a rate dependent on its diameter (as well as other variables) is a popular sizing technique. By this method, the pigment particles are dispersed in a liquid and then allowed to settle under the influence of gravity or centrifugal force. The rate of particle movement through the liquid then gives the particle diameter. Among the methods for measuring the rate of particle movement in a fluid are: (1) collecting the particles on a balance pan suspended in the dispersion, (2) analyzing specimens withdrawn with a pipette from different levels, (3) determining density with hydrometers or "divers," and (4) measuring attenuated light transmission through the dispersion. With low-cost computers and extremely stable rotational control provided by advanced electronic feedback circuits, the sedimentation methods using centrifugal acceleration have become popular.

A prerequisite to analysis by the sedimentation process is that the particles must be at their primary size. Vigorous stirring, usually with a dispersant agent or surfactant, both with and without ultrasonics, is often necessary. Agents to prevent flocculation may be required, and adjustments in solution pH may be necessary to stabilize the system. These additives must be evaluated at different levels to determine impact on the derived values.

STOKES' LAW

For essentially spherical particles, one assumes that Stokes' law will be followed when particles are falling in a fluid under some accelerating potential such as gravity or centrifugal force. This assumption requires that the particles will fall freely under laminar flow conditions [26]. For a perfect sphere, the diameter can be calculated simply from the Stokes' equation

$$D = \left[\frac{18_{\mu\nu}}{g(\rho_p - \rho)}\right]^{1/2} \tag{4}$$

where:

D = diameter of sphere,
μ = medium viscosity,
v = velocity of fall under influence of gravity,
g = gravitational constant,
ρ_p = sphere density, and
ρ = medium density.

Most often, the particles are not exactly spherical. Because of this, it is difficult to relate a particle's dimensions directly to the observed settling rate. The usual procedure is to use Stokes' equation to determine the values for d from the sedimentation distance and its corresponding time. The value so determined is then the "Stokes' diameter" of the particle. The definition then becomes "the diameter of a sphere that has the same density and free falling velocity (in

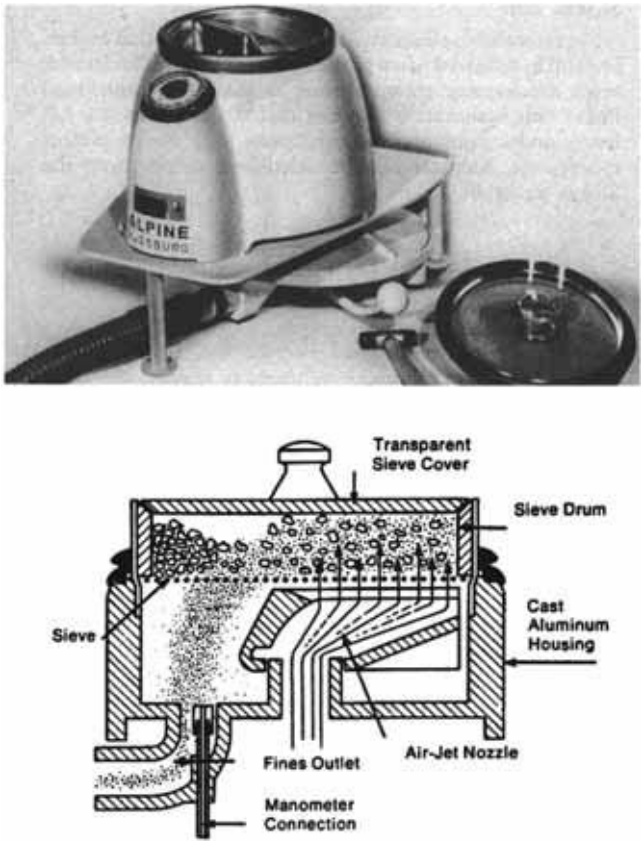


Fig. 8—Alpine air-jet sieve. (Courtesy of Gilson, Inc.)

a given fluid) as the particle being investigated (within the range of Stokes' law)".

This practice avoids the problem of variations in free fall velocities caused by shapes that differ from being a sphere. The assumption holds and permits useful comparisons of the size distributions when similar types of materials are evaluated. The size distribution of particles of different shapes may be compared provided that the phenomenon being studied is dependent on its behavior in the fluid.

While the concept of the Stokes' diameter is useful, it is necessary to appreciate its limitations. One should not equate the Stokes' diameter to a sphere of equal volume or other related quantity. Two types of errors may be introduced. In the first case, errors arise when the particle's movements depart from Stokes' law and, in the second case, errors are introduced by the experimental technique itself.

Departure from Stokes' law can occur when flow conditions are not met. Stokes' equation is valid under laminar flow only. Consequently, there is an upper limit to the size of a particle that can be evaluated in a given liquid. Large particles can experience too high a velocity in the liquid and create turbulent flow. Vortexes in the liquid in the vicinity of other particles also introduce errors. Laminar flow is determined by the Reynolds number experienced by the particle/ fluid system at the fall rate. The Reynolds number, *Re,* is defined as

$$Re = vd\rho/\eta \quad (5)$$

where v is the velocity in the fluid, d is the diameter in centimeters, ρ is density of the particle in grams per milliliter, and η is the viscosity in poise. According to British Standard (B.S.) 3406 [27], the value of *Re* cannot exceed 0.2 if the introduced error from Stokes' law deviation is to be less than 5 %. This would imply that the upper limit of particle size would depend on both the viscosity and density of the fluid. For water, this value would place an upper limit of about 60 μm. However, as might be anticipated from the Reynolds equation, this limit may be stretched somewhat when using either more dense or more viscous liquid media than water.

Another problem arises when the concentration of particles is too great. The Stokes' equation assumes single particles having no influence from the wall of the vessel or other particles in close proximity. Wall effects are minimized by employing properly sized vessels. While some investigators have recommended that the volume concentration should be kept less than 0.05 %, others recommend concentrations of up to about 0.5 to 1 % by volume. Certain investigators feel that this compromise introduces systematic errors and renders the method inappropriate as an absolute measure, although it is suitable as a routine control method. The flocculating nature of the powder in the test fluid will impact the maximum concentration that can be used. B.S. 3406 recommends a concentration of 1 % by volume, although it cautions that, under certain circumstances, a small interference may occur. Because of the potential introduction of systematic errors at higher concentrations, efforts to refine the technique so that reduced concentrations are used are underway. Precision with differentials no more than 4 % are usually expected.

Another problem that must be addressed is the temperature stability of the liquid. Not only is there a change in the liquid viscosity, but thermally produced convection currents grossly impact the sedimentation process. Because of the difficulty in maintaining thermostatic control over the long periods required for gravitational settling, there is usually a lower particle-size limit of about 2 μm when water is used as the suspending liquid.

GRAVITY SEDIMENTATION

The analysis of particles by sedimentation is possible because of Stokes" law, which states that the time of fall of a particle through a viscous medium is proportional to the particle's density (the difference between it and the medium) and its diameter. Of course, if the density of the medium were greater than the particle, the particle would float. Another requirement is that all of the particles must have a common density. This rules out mixtures of different minerals and pigments having different densities since they cannot be determined together.

Because of the time required for sedimentation to occur, the simple gravimetric method and the photometric method appear to be limited to pigments of sizes above 0.5 to 1.0 μm. Cadle [28] and Orr and Dallavalle [29] have reviewed the many variations of the method. Gravity settling was first proposed by Oden [30,31]. Calbeck and Harner [32] were among the first to use the technique for paint pigments; Jacobsen and Sullivan [33] brought the method to a higher degree of refinement by using an analytical balance with one of the pans replaced with a cup submerged in the suspension.

Hydrometer Method. The density of a dispersion is proportional to the concentration of the dispersed material, and methods for particle-size analysis based on the use of

the hydrometer have been developed. One such method is ASTM Method for Particle-Size Analysis of Soils (D422). Another, developed in large part by Bauer [34], is Technical Association of the Pulp and Paper Industry Method T649sm, Determination of Particle Size of Clay. Included in the method is a nomograph by Casagrande [35] to aid in the calculations. The same nomograph is found in Test Method for Particle Size Distribution by Hydrometer of the Common White Extender Pigments (D3360) [36].

Radioactivity Method. Connor and Hardwick [37] report on this method for determining the height of the sedimentation. The radioactivity is either induced in the specimen or is used as an external probe. The technique avoids disturbing the suspension by periodic sampling and can be used with both gravity and centrifugal sedimentation.

CENTRIFUGAL SEDIMENTATION

The centrifuge is used to provide an accelerating force for sedimentation analysis. Configurations exist using rotating disks with "see-through" ports as well as holders of small see-through cells.

Disk Centrifuge. The technique for the disk centrifuge was developed by Atherton et al. [38]. The apparatus might be considered to be a direct descendant of the single cell centrifuge of Donoghue [39] and the scratch start technique of Marshall [40]. The range is from 0.01 to 0.5 μm.

The apparatus consists of a centrifuge unit, a sampling unit, and an electronic control unit [41]. The rotor of the centrifuge is a cell (hollow disk) of plastic or glass that rotates on a horizontal axis (Fig. 9). The back wall is attached to the shaft of the rotor. The front wall has a hole in the middle that serves as an access port. The inside diameter of the standard cell is 10 cm, and the width is 1 cm. In operation, the cell takes liquid up to a minimum radius of 2.3 cm. The speed ranges from 500 to 8000 rpm.

The sampling unit (Fig. 10) consists of a probe connected to collection flask and a clock motor. The probe is an L-shape thin-wall steel tube arranged to rotate about the axis of one arm. The other arm terminates in a sharp bevel for scooping up the contents of the cell in a manner analogous to that of an inside cutter in a lathe. The center of rotation of the probe lies below the center of the rotor.

To make a test, an appropriate volume of "spin fluid," typically a 4 % sucrose solution, is transferred to the rotating cell. After swirling stops (20 to 30 s), the specimen—usually 0.5 ml of a 0.5 % dispersion—is expelled from a syringe against the back wall near the center of rotation. The specimen flows outward over the wall unit it reaches the free surface of the spin fluid, where it forms a band about 1 mm thick. The spin fluid and the dispersion do not mix because of the higher density of the former. Thus, zero time for the measurement is defined rather accurately.

After the desired time, spin fluid is withdrawn from the cell with the probe, which is driven by a clock motor at 1 rpm. With the pickup end of the probe in the 12 o'clock position, the motor is started automatically. All but 5 ml of the spin fluid is removed for measurement of the undersized fraction of the dispersed powder.

The development of detector systems must consider the action on a transmitted light beam. Light-scattering theory dictates that when light of intensity I_0 attempts to pass through a dilute suspension (i.e., no multiple scattering) of particles, it is lost or extinguished to an extent that I_t makes it through. Mathematically [42,43], the transmitted light is given by

$$I_t = I_0 \exp(-\alpha_{ext} L) \tag{6}$$

where L is the length through the suspension, and α_{ext} is the attenuation coefficient (turbidity). The value of α_{ext} is related to the number concentration of particles, N per unit volume, by

$$\alpha_{ext} = NC_{ext} \tag{7}$$

where C_{ext} is the extinction cross section of the particles. The extinction efficiency of a particle of cross-sectional Area A is conveniently expressed as

$$A = C_{ext}/Q_{ext} \tag{8}$$

This yields the relationship

$$\alpha_{ext} = N\pi d^2 Q_{ext}/4 \tag{9}$$

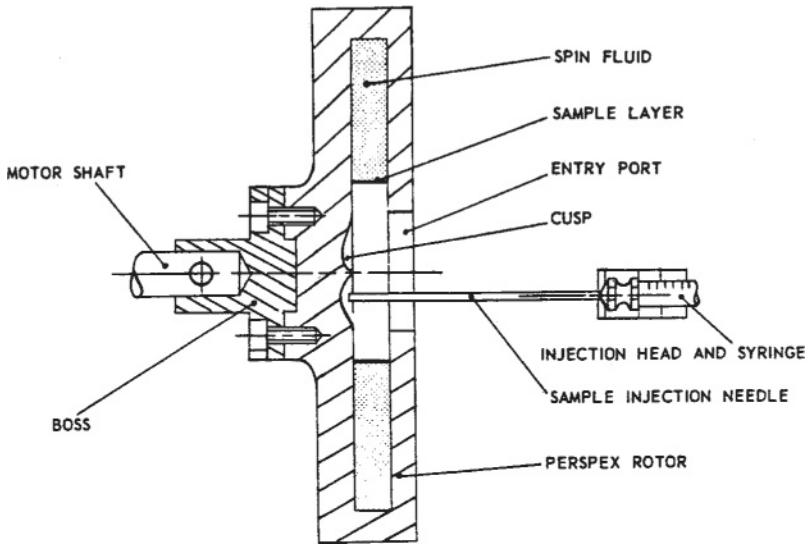


Fig. 9—Diagram illustrating the principle of the disk centrifuge. (Courtesy of Joyce, Loebl & Company, Ltd.)

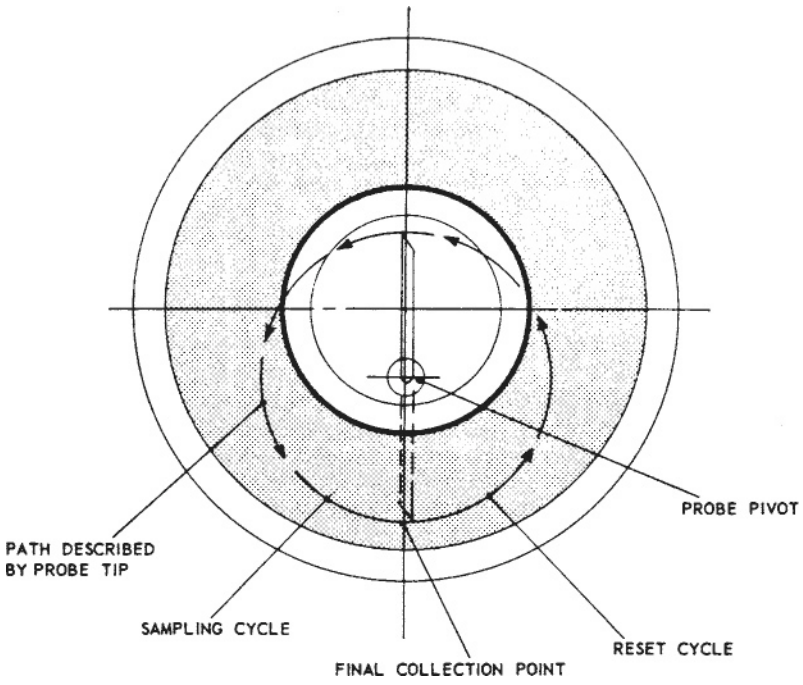


Fig. 10—Relationship of disk and probe of disk centrifuge sampling. (Courtesy of Joyce Loebl & Company, Ltd.)

Photo extinction detectors on modern turbidity instruments essentially determine α_{ext}. The internal calculation of Q_{ext} requires knowledge of the particle refractive index, size, shape, orientation, state of polarization, and wavelength of the scattered light as well as the refractive index of the suspending liquid. Using Mie theory [44,45], size may be deduced. Oppenheimer [45] has pointed out that a source of potential error is that the refractive index of the suspending liquid and particles must be known for each wavelength.

Rotating Cell Holder Centrifuge. Real time monitoring is provided on some instruments and is advantageous when irregular measurements force an abort. One such instrument can perform centrifugal as well as gravity analysis using the same on-board computers. With ten different rotor speeds switchable from 300 to 10,000 rpm, an accelerating potential of up to 9000 *g* is available. Particles as small as 0.01 μm are reported to be measurable.

The instrument uses two small, transparent rectangular cells (Fig. 11) mounted opposite each other on the balanced rotor. While they counterbalance each other, one serves as a reference for the suspension liquid, and the other holds the particle suspension system under analysis. Three photocells in the top monitor three opposite light-emitting diodes (LED) on the back side of the rotor. This allows real-time monitoring of the reference cell, the sample cell, and the rotor speed (Fig. 12). Data are displayed in real time on a built-in computer monitor as well as printed out on tape after the analysis for a permanent record. Graphs are presented indicating the absorbance versus time, frequency distribution, and cumulative distribution (either percent undersize or percent oversize).

Particle Size from Surface Area Employing Both Gasses and Liquids

It is often useful to use the approximation of size from surfaces to evaluate other parameters derivable from the volume function, such as specific surface area and density. The basic equations that describe a sphere's surface area and volume are given by

$$\text{Area of a sphere} = \pi D^2 \tag{10}$$

$$\text{Volume of a sphere} = \pi D^3/6 \tag{11}$$

These relationships allow determination of the mean particle diameter if the specific surface (area) is known. Particle-size characterizations that employ surface area techniques in the size determination yield average diameters. The surface area of a powder may be determined from gas adsorption experiments. By assuming uniform-size non-porous and spherical particles, the mean particle size may be determined from the surface area data. The "specific surface" obtained equals the determined surface area divided by the product of the particle volume and density. With appropriate units conversion

$$D = 6/[\rho A] \tag{12}$$

where:

D = particle diameter, μm,
ρ = particle density, g/cm^3, and
A = specific surface area, m^2/g.

Any shape other than a sphere, either regular or irregular, has a greater ratio of surface to volume, and consequently the particles will be smaller than calculated. Cracks, crevices, and pores are other factors leading to an increase in specific surface area and to a corresponding decrease in calculated particle size.

Perfectly spherical particles are seldom encountered in mineral pigments and fillers used in paint and coating applications since these particles result from shattering by crushers and high-speed pulverizers. Crystalline materials fracture along crystal planes, while some pigments are acicular (like needles). With the many shapes

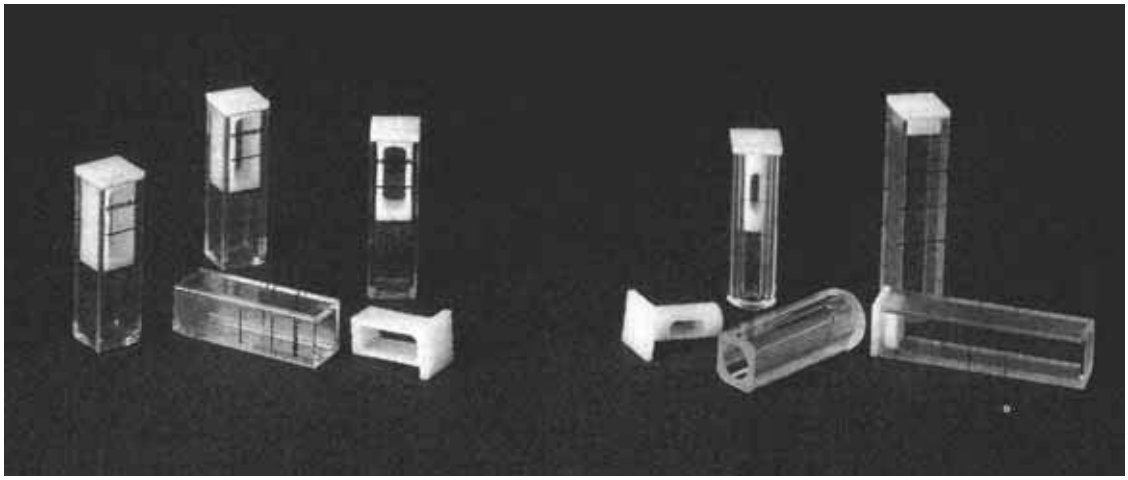
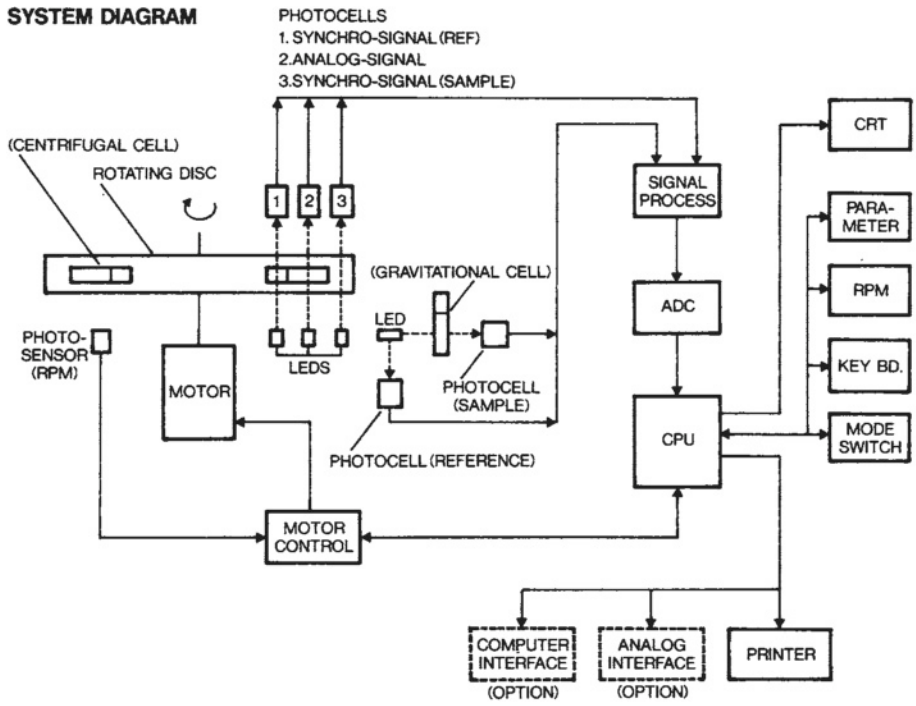


Fig. 11—Reference cells used in a centrifuge. (Courtesy of Horiba Instruments, Inc.). www.horiba.com/us/en/scientific/products/particle-characterization/particle-size-analysis/.

of particles to be evaluated and characterized, instruments that operate on different principles "see" different values of the size-dependent variable being monitored. As a result, a sample characterized by one machine may yield a somewhat different value when evaluated using a different technique. For this reason, the practitioner must be aware of the size-dependent variable to which his machine is sensitive.



The CAPA-700 system is comprised of an optical system, a centrifuge, computation circuitry and input/output functions. The rotating disc in the horizontally mounted centrifuge is connected directly to the motor to minimize gravitational effects, and electronic control keeps the rotational speed stable at the set value. The CPU monitors and controls automatic checking for fluctuations in rotational speed, computation formulae and deterioration of the light source and detector, assuring precision data at all times. In the optical system, a reference cell guarantees both optical and mechanical balance for each revolution, which, after CPU processing, gives even higher precision particle size distribution analysis.

Fig. 12—A modern instrument for determining particle size in real time.

Methods [46] for determining specific surface include adsorption of gases by the pigment, adsorption of solutes from solutions by the pigment, and permeability of pressed pigment particles to gases or liquids.

Adsorption of Gases

This method is based on determining the number of gas molecules that will adsorb as a monomolecular layer on the surface of the particles. Knowing the area occupied by one molecule and the number of molecules, the specific surface area of a specimen of pigment may be calculated from

$$\Sigma = nNA \tag{13}$$

where:

Σ = specific surface area in cm^2,
n = number of moles of gas per gram of pigment,
N = Avogadro's number, 6.02×10^{23}, and
A = area covered by each molecule.

Knowing the specific surface, the surface mean diameter may be calculated.

Brunauer-Emmett-Teller (BET) Method. The general procedure for this method [47,48] includes introducing the specimen into an enclosed space of known volume followed by degassing with heat and evacuation. A known amount of gas is admitted to the system, and its pressure is determined. The gas is then compressed to a new volume, and the corresponding pressure is determined. The procedure is repeated until enough data for the preparation are obtained. By means of the BET equations, the surface area is found, and from it the average particle size may be calculated.

Continuous Flow Method. This method makes use of the BET equation, but the adsorbed gas is determined by concentration measurements in a continuous flow system [49]. Nitrogen gas is adsorbed by the specimen at liquid nitrogen temperature from a stream of nitrogen and helium gas and is later eluted by warming the specimen. The amount of nitrogen liberated is estimated by thermal conductivity. For detecting changes in the amount of adsorbed nitrogen, Beresford et al. [50] used the Perkin-Elmer-Shell sorptometer with conductivity bridge and potentiometric recorder.

Gravimetric Method. In addition to the volumetric methods, a gravimetric method using balances patterned after that of McBain and Bahr [51] can be used. The procedure is much simpler but requires care as the apparatus is very fragile and the changes in weight are very small.

An essential part (Fig. 13) of the gravimetric method is a fused silica spring balance from which a small glass "bucket" for the specimen is hung. The balance assembly is located in a glass housing connected to a source of gas and to a manometer for determining the pressure. The bucket is hung on the balance, the housing is closed, and the specimen is degassed by evacuation. The zero point of the balance is recorded. Gas is admitted to the housing, and the change in weight of the specimen is determined by noting the change in the elongation of the balance with a traveling microscope. Details are set forth in Ref. 17.

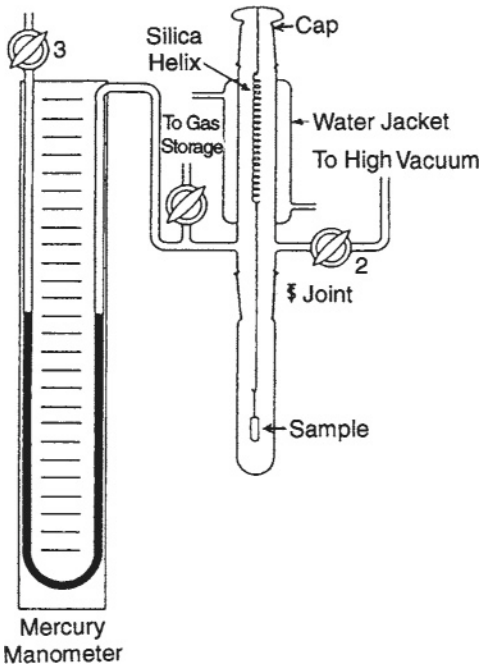


Fig. 13—The components of a basic gravimetric adsorption apparatus.

ADSORPTION OF NONGASEOUS MOLECULES

Adsorption of molecular species other than typical gaseous molecules is possible also. These include the adsorption of solvents and surfactants in special cases.

Adsorption of Solutes onto Pigments. This method depends on the adsorption of solute molecules onto a particle when it is wet out by a solution containing the dissolved surface active solute [52]. The process requires that the adsorbent be thermodynamically more active than the solvent and the kinetics be such that wet-out times be reasonable. Typical systems used are stearic acid in benzene, dyes in benzene, and wetting agents in water. The amount adsorbed will asymptotically approach a constant value with time. At this value it is assumed that the surface of the particles is covered with a mono-molecular layer of solute. The area occupied by a single molecule of solute may be obtained from tests made with solids of known areas. The amount adsorbed is obtained by analysis of the solution before and after adsorption.

A disadvantage of the method is uncertainty about the size and orientation of certain types of molecules. On the other hand, the method is rapid and easy to perform. For this reason it is suited to routine tests where its reliability has been established.

Soap Titration of Emulsion Particles. Maron et al. [53] determined surface area and particle size of a synthetic latex by titrating with a soap until the critical micelle concentration of the soap in the solution was attained. From the effective molecular surface area of the adsorbed soap and the amount adsorbed, surface area and particle size are calculated. The method is calibrated with electron micrographs. Brodnyan and Brown [54] also studied the technique.

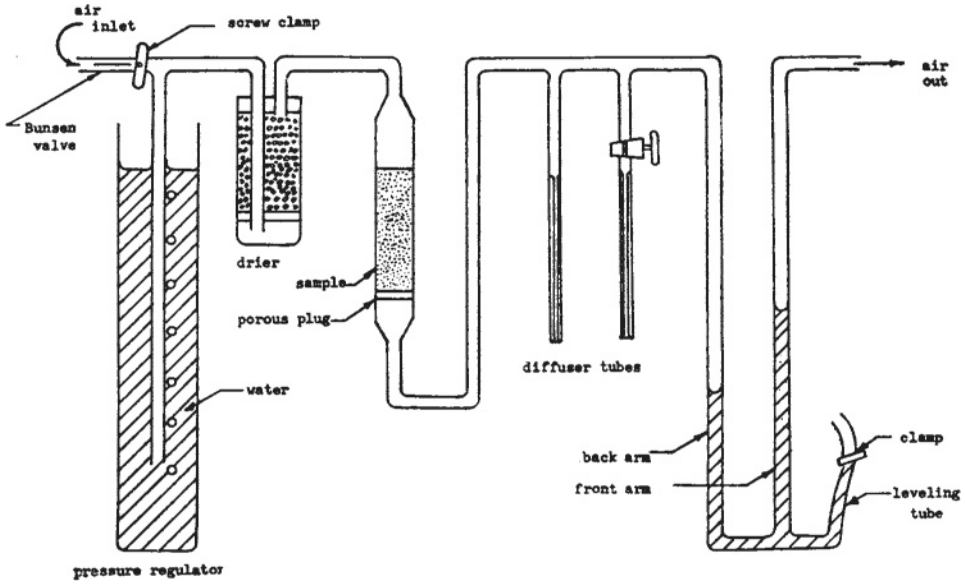


Fig. 14—Gooden-Smith apparatus for surface area. (Courtesy of *Official Digest.*)

Permeation Through Packed Powders

In this method, a gas, usually air, is forced through a compacted bed of the pigment. The rate of flow is a function of voids (pore space), pressure drop through the bed, specific surface of the pigment, and viscosity of the gas. Knowledge of all the other factors allows calculation of the specific surface area and, from it, the mean surface diameter. The method is fairly simple and is suitable for routine determinations of spherical or near-spherical particles.

Gooden-Smith Method. Using air as the gas, Gooden and Smith [55] designed a permeation method with two special features: (1) the weight of specimen used in grams is numerically equal to its density and (2) every specimen is packed to the same volume (Fig. 14). Together with a graphic calculator, these features greatly simplify the test and make it attractive for routine testing or research in the particle-size range 0.2 to 50 μm.

Hutto-Davis Method. The principal differences between this and the preceding method are: (1) the weight of the powder used to make the compacted pellet is calculated to give a definite porosity, and (2) the volume of air is kept constant for all plugs.

Hutto and Davis [56] modified the apparatus of Carman and Malherbe [57] by providing an improved manometer, better control of the volume of air, and an improved press for preparing the specimen. They also designed a nomograph for calculating specific surface and surface area. The apparatus consists of: (1) a U-tube with legs of unequal length and closed at each end with a sintered glass disk, (2) a manometer, (3) a capillary specimen tube, and (4) a leveling bulb containing mercury.

To provide the constant volume of air, the U-tube is inverted and filled through the stopcock at the bend. Then, with a capillary eyedropper, a weight of mercury equivalent to 1 ml is removed, leaving an equal volume of air after which the stopcock is closed and sealed. The mercury does not pass through the sintered glass disk at the pressure used in the test. To make a test, a plug of pigment is formed inside the specimen tube using the special press. The weight of the specimen is a function of its density and the desired porosity of the plug (usually about 0.5). With the leveling bulb in the lower position, the specimen tube is attached to the side arm of the apparatus, and a vacuum is applied by opening the stopcock at the upper right-hand corner. The vacuum is adjusted, and simultaneously the stopcock is closed, timing is started, and the leveling bulb is raised to its upper position, which forces the 1 ml of air into the system. The timing is stopped when the manometer returns to zero. The stopcock is then opened, and the bulb is returned to its lower position for another run.

Individual Particle Sensing by Light Blocking and Electrical Resistance

In this technology, individual particles are separated from each other by a diluted suspension in either air (by fluidization followed by entrainment in a flowing stream) or a constantly stirred conductive solution. The particles are then forced to pass through the sensing zone. In one air-fluidized instrument, the time of flight between two precisely placed laser light sources and detectors is used to calculate size. In another, the attenuated light as detected by a photodiode is used to calculate a size. In the liquid suspension instrument, a change in the established electrical resistivity through an electrolyte circuit is measured as a particle passes through a small orifice.

TIME OF FLIGHT FROM LIGHT BLOCKAGE

An instrument based on aerodynamic time-of-flight (TOF) technology was developed by Dahneke [58]. The measurement range is reported to be from 0.2 to 200 μm, with 150 channels per decade and a count rate of up to 100,000 particles per second. Output may be reported in either geometric or aerodynamic diameter. In this instrument, a gas (usually air for pigment particles) is used to break down agglomerate material and entrain them in a controlled flow; a specially designed "pulse-jet dispenser" is used where a

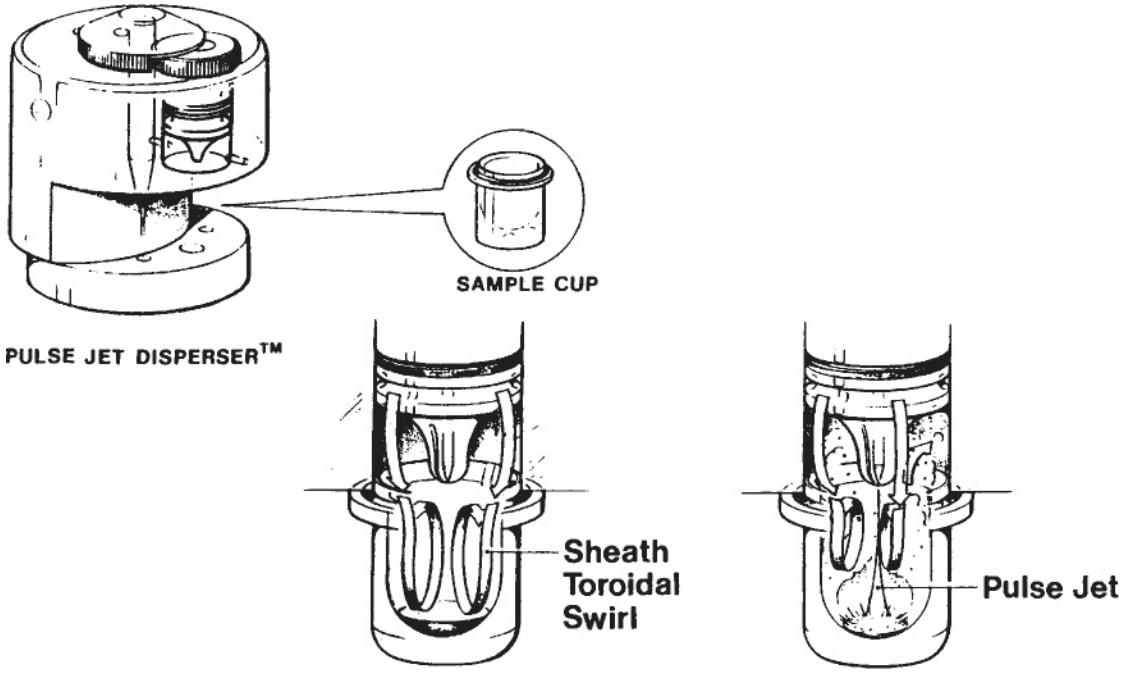


Fig. 15—A diagram of the operation of the dry-powder pulse jet disperser. (Courtesy of Amherst Process Instruments, Inc.)

controlled flow of air is directed down onto a sample placed into a small cup (Fig. 15). Depending on the nature of the sample, the operator sets the computer values for particle count rate, flow pressure, and pulse pressure. The disperser flow pressure controlling the carrier gas usually remains constant. The disperser pulse pressure determines the number of particles fed through the analyzer.

Measurements are made over 2 s intervals to ensure that the minimum count rate is met. Should the count rate fall below the predetermined count rate, the pressure is increased. Should the count rate exceed the maximum allowed, the pressure is dropped by a factor of 2, thus maintaining the number of counts between the allowed maximum and minimum.

The particles are deaggregated to primary size and fed into the injection tube of the sonic nozzle suspended as single particles in the air stream moving at about 6 L per minute. There is no operator involvement during the 1 to 5 min determination. Two laser beams set at a discrete distance apart and directed onto two photomultipliers make up the "sensing zone" (Fig. 16). As the particle passes through the set of laser beams, light that is attenuated and scattered is monitored by the detectors. Signal analysis using cross-correlation techniques give the particle's TOF with a resolution of 25 ns. The technique is reported to be able to discriminate between particles with only a 10 % size difference. Attachments to the instrument also allow the investigation of sprayed aerosol droplets as well.

ELECTRICAL RESISTANCE

According to the Coulter principle [59,60], when a particle suspended in an electrically conductive liquid enters a constricted path between electrodes, it changes the pathway electrical resistance between the electrodes. This change produces a fluctuation in the applied voltage that, under proper conditions, is inversely proportional to the volume of the particle. When the dispersion is made to pass through a hole small enough to pass the particles one by one, the resultant series of voltage fluctuations may be electronically amplified, scaled, and counted [61].

A functional diagram is shown in Fig. 17. The beaker and tube contain the suspension. When the stopcock is opened, a controlled vacuum starts flow of the suspension from the beaker into the tube and also unbalances the mercury in the manometer. The stopcock is then closed, and the mercury siphon continues the flow of the suspension. Electrical contacts in the manometer start and stop the counting of the particles. The volume of the manometer tube between the contacts determines the volume of the

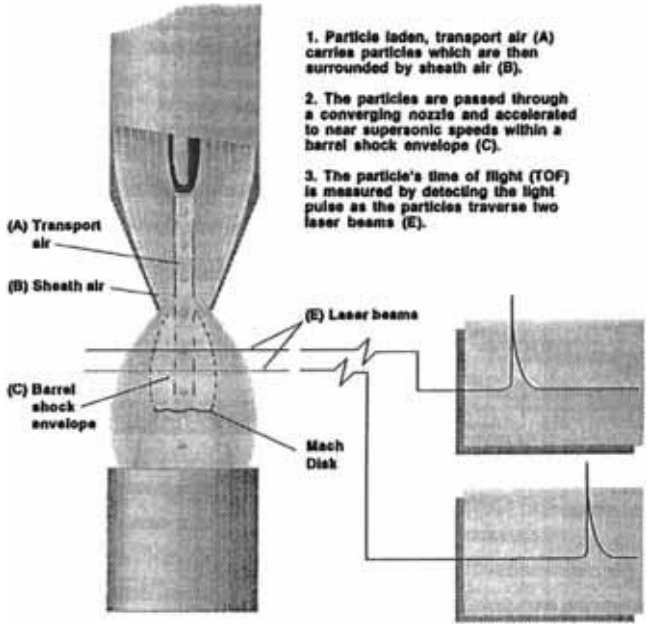


Fig. 16—Schematic of the aerosol beam generator and detection mechanism. (Courtesy of Amherst Process Instruments, Inc.)

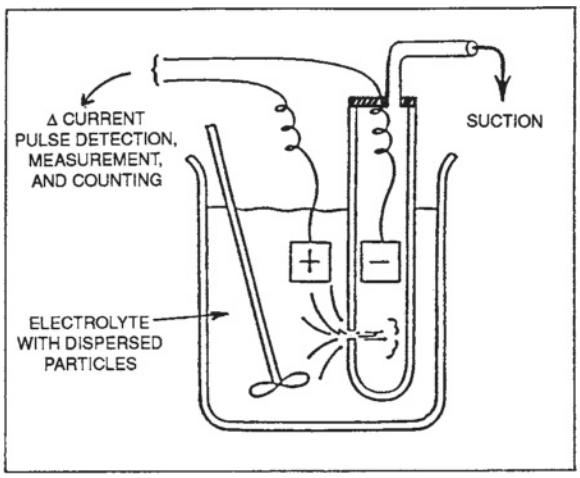


Fig. 17—The Coulter principle: A fluctuation in current flow occurs when a particle partially blocks the small opening between the electrodes. The size of the particle is related to the amount of change in current flow.

specimen. This ranges from 0.02 to 5 ml. A fresh volume is drawn for each count. A typical count requires from 3 to 30 s, depending on the size of the hole and the volume between the contacts in the manometer. The Coulter counter was found to be useful by Princen et al. [62] for particle-size determination of emulsified oil systems.

The principle utilized to determine individual particle size is the electrical resistance of the particle as it is forced to pass through a small hole in a glass envelope through which an electrical potential exists.

Direct Microscopic Measurement Using Visual Light Microscopes and Electron Microscopes

Microscopes, both optical and electron as well as automated image analyzers, are used to measure particle size directly. Optical techniques suffer somewhat from an inability to focus on the "edge" of a particle at very high magnifications due to a depth of field problem. The lower limit is set by its resolving power and the upper limit by its depth of focus. The microscope is especially useful for measurement of plate-like and needle-shape particles that do not obey Stokes' law, on which the sedimentation methods are based. Disadvantages of the method are that it is slow and laborious. Hence, it is used chiefly for the calibration of the more rapid relative methods. ASTM Practice for Particle-Size Analysis of Particulate Substances in the Range of 0.2 to 75 μm by Optical Microscopy (E20) and a paper by Loveland [63] are good references. Dark field illumination can use the detecting power of the microscope rather than the resolving power for sizes below the resolving power of the optical microscope.

Green [64] was the first investigator to systematize the use of the microscope for direct measurement. He dispersed the pigment in a medium on a microscope slide, photographed the dispersion at a known magnification, and projected the image on a screen to increase the magnification for measurement. Dunn [65] bypassed the photomicrograph by projecting the image of the particles directly from the slide on the screen.

Ideally, the pigment should be dispersed in the medium in which it is used, but this is rarely done. Green used turpentine, Allen [66] recommended a viscous vehicle, and Eide [67] used fused resins. Gehman and Morris [68] milled the pigment in rubber, dissolved the mix in a solvent, and applied the suspension to the slide.

Microscopes equipped with view-through linear scales, circles or ellipses in graduated sizes, may be used as a direct measurement method [69]. The comparison scale may be a micrometer eyepiece, an eyepiece reticule, or a scale engraved on the microscope side.

The use of the electron microscope for particle characterization is now a routine practice. The resolving power is many times that of the light microscope and may be used in scanning as well as transmission mode. With state-of-the-art surface analysis tools such as energy dispersive x-ray (EDX) built into the scanning electron microscope (SEM) equipment, elemental analysis of a single-pigment particle within the coating matrix can be done conveniently while the coating sample is in the instrument.

ARRAY METHOD USING OPTICAL MICROSCOPE

The array method of particle sizing lends itself to systems of monodispersed spheres, as in Fig. 18 (from Duke [69]). These are highly uniform with respect to diameter. When placed on a flat plate, the spheres tend to align themselves into hexagonal arrays. These are characterized by straight rows of the particles. Because of this, the rows can be measured, and the diameter of the particles may be derived by dividing by the number in the row.

TRANSMISSION ELECTRON MICROSCOPY

Transmission electron microscopy (TEM) is useful for the measurement of latex microspheres of 200 nm and larger [70,71]. The procedure usually utilizes the magnification factor of the microscope in the size determination from photomicrographs. Because this factor is not always dependable, photographs are sometimes made against a replica diffraction grating of known spacing. Fig. 19 shows 100-nm latex microspheres on a 2160-line/mm grating. Sources of error include uncertainty in the accuracy of the line spacing, the roughness of the lines, and the line thickness relative to the size of the particles. Duke [72] has used an internal standard of NIST traceable materials, as shown in Fig. 20, and reports accurate sizing to as small as 50 nm.

Chromatography: Angstrom Particle Sizing

The separation of angstrom-sized particles may be affected by the use of hydrodynamic chromatography. In this

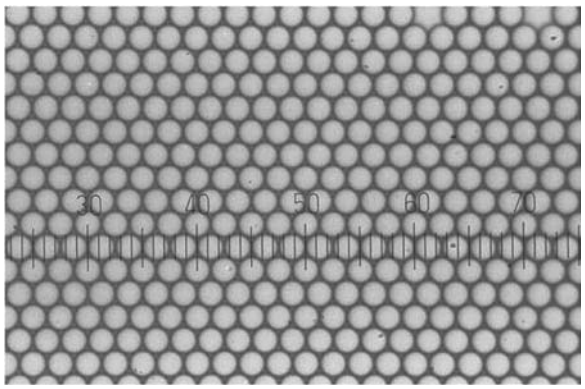


Fig. 18—Microphotograph of 10 micron particles in array. (Photo compliments of Thermo Fisher Scientific Inc.)

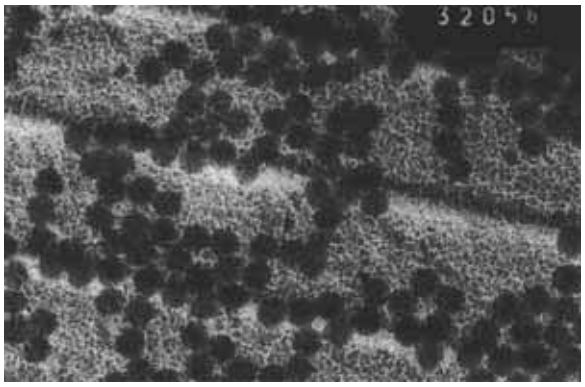


Fig. 19—Microphotograph of 100-nm latex spheres against a 2160-line/mm grating. (Photo compliments of Thermo Fisher Scientific Inc.)

technique, the mixture of very small particles is allowed to transgress a long capillary tube in which the liquid medium is flowing in laminar flow. It is well known that fluids, both gasses and liquids, will experience a pressure drop as a function of distance traveled and of the diameter of the tubing that occurs because the fluid in actual contact with the wall of the tube does not flow and is stationary. For noncompressible fluids (i.e., liquids), this variation in flow velocity from wall to center of tube may be used to separate particles of differing size.

For laminar flow, the velocity of flow through the cross section of the tube increases from the wall to the center, essentially in concentric "layers" [73]. This may be represented by the vectorial diagram in Fig. 21 of the flow velocity profile. The actual velocity of flow of one of the "concentric circular layers" will be a function of its distance from the wall of the tube. The flow velocity gradient is given by

$$V_r = \frac{(P_0 - P_L)R^2}{4\eta L}[1-(r/R)^2] \tag{14}$$

where:

V_r = liquid velocity at radius, r,
$(P_0 - P_L)$ = pressure drop for the distance, L,

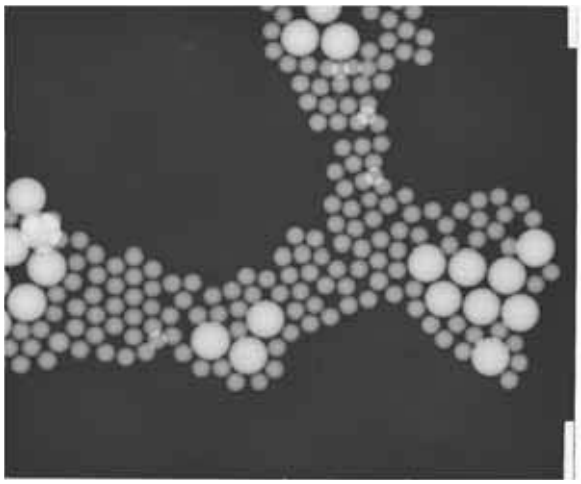


Fig. 20—TEM 450 nm particles with 100 nm microspheres on a smooth substrate with NBS SRM 1691 as an internal standard. (Courtesy of Thermo Fisher Scientific Inc.)

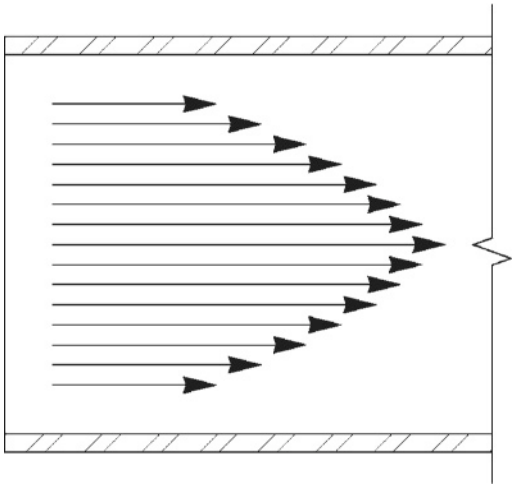


Fig. 21—Vectorial representation of the velocity of a fluid (gasses and liquids) in laminar flow. The velocity at the wall of a pipe is zero and a maximum at the center in the absence of turbulent flow. The rate of increase in velocity toward the center is a function of the fluid viscosity in the absence of turbulent flow. (Drawing compliments of George Mills, Jr. Building Design Solutions, LLC.)

R = inside radius of capillary,
R = effective radius of liquid at V_r,
η = viscosity of fluid in flow, and
L = length of capillary.

Because the larger particles tend to have statistically more volume in the fluid away from the wall, the larger particles are under a greater influence of the faster-moving fluid away from the wall more so than the smaller particles, which can physically fit in the slower-moving layer nearer the wall. Thus, the larger particles advance faster than the smaller ones affecting the separation.

Light Attenuation and Scattering Techniques

Spectrophotometric Techniques. Gamble and Barnett [74] developed a method for measuring particle-size distribution by the scattering of light in the near infrared. The pigment is dispersed in low concentration and placed in a transmission cell for spectrophotometric measurement. From the shape of the spectrophotometric curve, the relative size and size distribution characteristics of an unknown pigment are obtained in terms of calibrated samples (Fig. 22).

Bailey [75] also developed a spectral transmission method using infrared wavelengths from 0.4 to 2 μm. The spectrophotometric curve was related to size by graphic comparison with specimens of known sizes.

Atherton and Peters [76] measured light scattering by polydispersed system of spherical particles. The size distribution curves for the materials compared favorably with direct measurement with the electron microscope.

Leobel [77] used a spectrophotometer to obtain the effect of wavelength on turbidity in the determination of the size of latex particles. The sizes of particles used for calibration were determined from electron micrographs.

LIGHT-SCATTERING TECHNIQUES

When solid particles pass through a light beam, the light will interact with the particles in one or more ways. It can

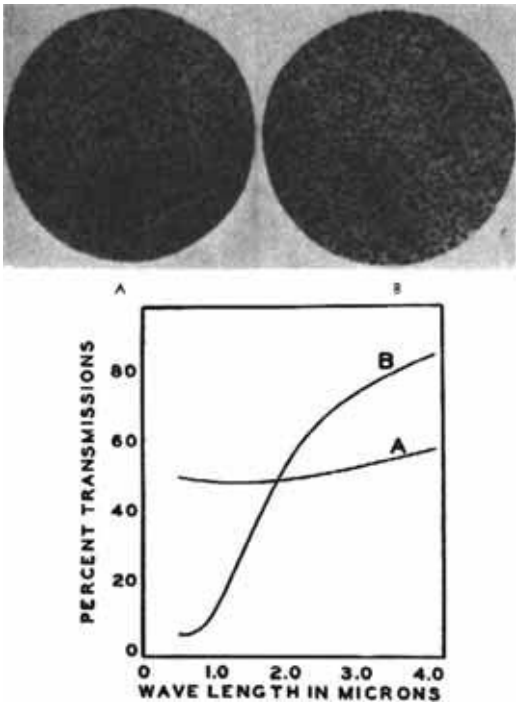


Fig. 22—Particle size may be determined from the scattering of radiation in the near infrared region of the spectrum.

either be reflected, refracted, diffracted, or adsorbed and reradiated. This is shown schematically in Fig. 23. The scattered radiation will present a pattern that is dependent on the shape and size distribution of the particles. By evaluating the scattered radiation detected at different locations relative to the beam direction and in different positions, much can be learned about the scattering media. Fig. 24 depicts some of the angular intensities of scattered light produced by particles of various sizes. With low-cost computers and stable detectors, instruments have been developed that can monitor this scattered radiation, giving fast and reliable data.

Angular-dependence techniques, which include detection and manipulation of signals from front (reflection) as well as side and rear (diffraction), have been integrated into a single instrument. Angular-dependence, light-scattering techniques have been widely studied for information concerning the sizes of both pigmentary and nonpigmentary particles. In the latter class, polymeric organic materials from molecular to latex sizes have been included. Debye and Bueche [78] described how to characterize the optical inhomogeneities related to size from information concerning the way a system scatters light.

Angular-dependence techniques include the work of Brice et al. [79], who designed a photoelectric photometer for measurement of molecular weight by applying the Debye theory.

Aughey and Baum [80] note that particles in the size range of large molecules produce variations in the intensity of light scattered at large angles to the illuminating beam. Progressively larger particles produce significant variation in the light scattered at small angles. The light source is a well-defined monochromatic beam. The cell containing the dispersion is stationary, and the photoelectric tube travels around the cell in an arc that covered a useful range from 0.05° to 140°. Scattered light reaches the tube

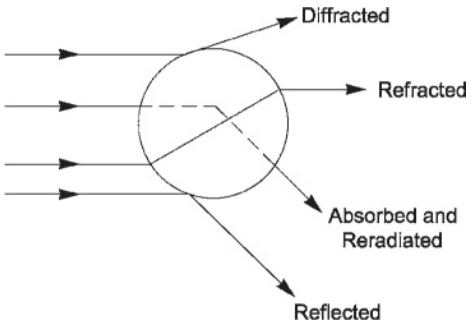


Fig. 23—Possible interactions when light strikes a particle. (Drawing compliments of George Mills, Jr. Building DesignSolutions, LLC.)

through a small aperture in the housing for the tube. The radii of the optical inhomogeneities range from 0.1 to 100 μm. Modern diode array detectors are now available to do similar tasks without the movement.

Diffraction of Laser Light. Instruments using diffraction of single-wave-length laser light have been made possible by the development of low-cost, highly stable lasers and diode array detector technology. By fluidizing the particles in a stream of air, they are directed through a cell being illuminated by a laser source. The He–Ne laser, emitting a coherent beam of 632.8 nm wavelength, is often used. To increase the cross-sectional area of the beam, expanders are often employed (Fig. 25).

The diffraction pattern that is seen by the detector is a pattern of rings varying in darkness depending on the size distribution of the passing particles. On-board computers use both the Fraunhofer diffraction and Mie scattering theories to calculate the particle-size distribution

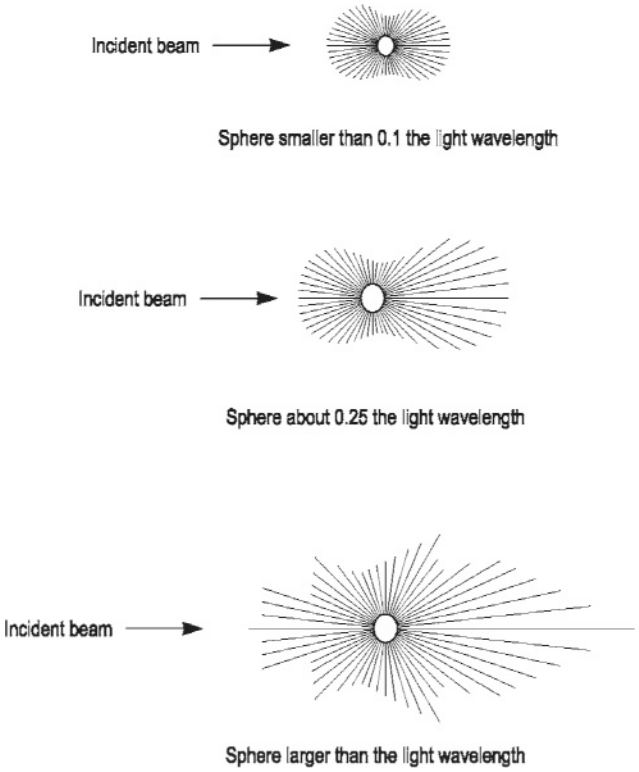
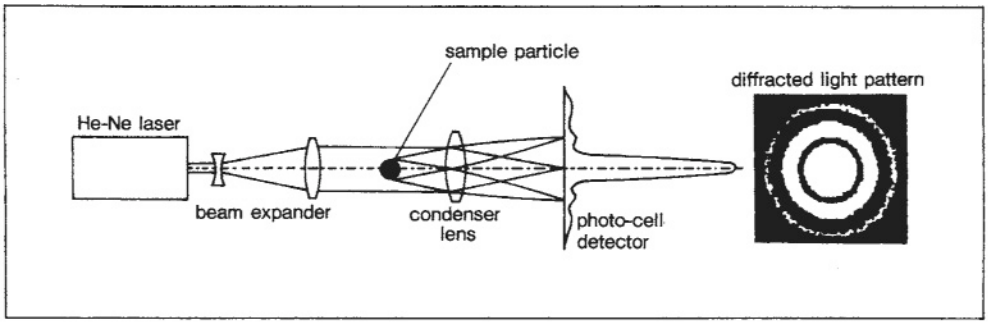


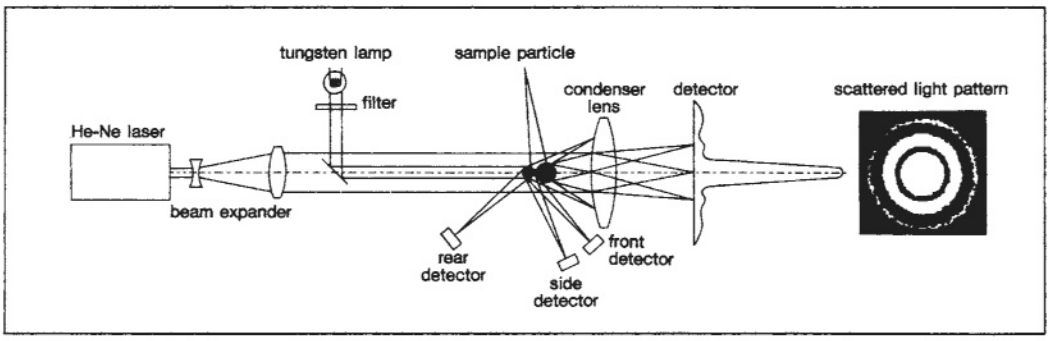
Fig. 24—Angular intensity of scattered light after striking a particle. (Drawing compliments of George Mills, Jr. Building Design Solutions, LLC.)



Principle of Operation

The He-Ne laser emits a beam of 632.8 nm whose flux is enlarged by a beam expander and radiated upon the particles suspended in the liquid. After it has been diffracted and dispersed by the particles, the laser beam passes through the condenser lens and its image is formed at the photo-cell detector located at the focal point of the lens.

The diffraction pattern that appears at the detector is a pattern of light and dark concentric rings that corresponds to the particle size distribution of the sample. Now, using both of the Fraunhofer diffraction and Mie scattering theories, the intensity values are used to calculate the particle size distribution of the sample.



Here is how the LA-900 works.

Light irradiating the particles is scattered at various angles. If the particles are comparatively large, this scattering tends to be concentrated in a forward direction. As the size of the particles decreases, the light is scattered in all directions. Therefore, to measure larger particles, data from a small angle of scatter is required; to measure smaller particles, a larger angle of scatter is required.

On the LA-900, to measure the distribution of low angle scattered light, a condenser lens is used with an array detector at the focal point of the lens. To measure large angle scattered light, detectors are used at the front and rear of the sample chamber. From angular measurement of the scattered light by all of these detectors, the particle distribution is calculated from Mie theory.

It is also true that as the wavelength of the light becomes shorter, so does the measurement size of the particles. Therefore the LA-900 uses a He-Ne laser beam and a red light beam and a blue light beam obtained by filtering a tungsten lamp to expand the measurable range.

Fig. 25—Schematic layout for the large-particle system. (Courtesy of Horbia Instruments, Inc.)

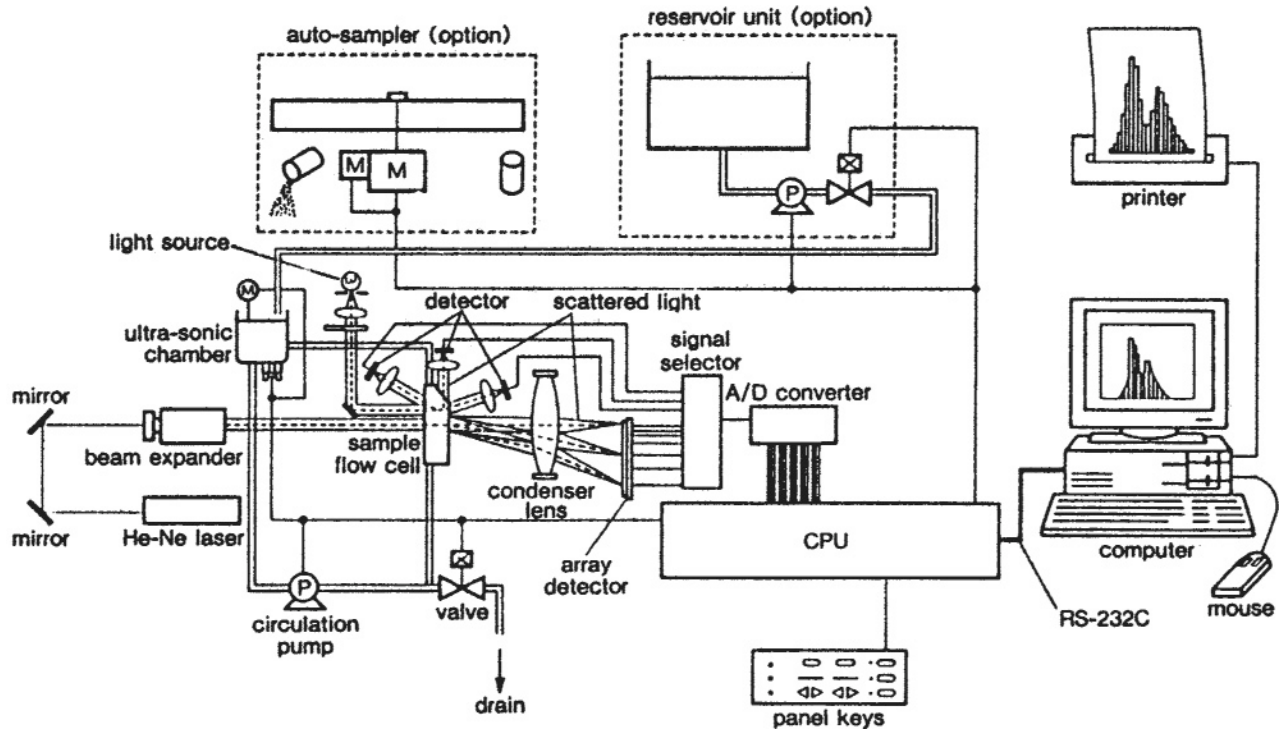


Fig. 26—Schematic layout for a system measuring both large and small particles. (Courtesy of Horiba Instruments, Inc.) www.horiba.com/us/en/scientific/products/particle-characterization/particle.

of the sample. These methods allow the determination of size distribution based on the intensity distribution of the diffracted laser beam. Since the intensity pattern is a function of the actual particle size, mixtures of particles having different densities may be measured together, unlike those relying on Stokes' law. The instrument is reported to address 0.1 to 200 μm particles.

Total Light Scattering. Instruments capable of monitoring light from all sides can effectively measure particles even smaller than the usual limit of 0.1 μm. This limit is imposed because of the physics relating the wavelength of the incident radiation and the interacting particles. By taking advantage of a set of detectors located strategically around the scattering cell, data relating to even very small particles less than 0.1 μm are determined. As the size of the particle decreases, the intensity of the scattered light obscures critical differences in the angular distribution. In practice, this difficulty in treatment of data leads to the so-called laser-diffraction measurement barrier.

Since there is an increase in both the side and rear scattering with very small particles, it is possible to take advantage of the phenomenon. Fig. 26 is an instrument diagram with an arrangement of detectors that allow a single instrument to measure a broad range of sizes. Light irradiating the particles is scattered at various angles. For relatively large particles, light is scattered in the forward direction, while, for smaller particles, the light tends to be scattered in all directions. By arranging a lens system and manipulating data from the detectors, the particle-size distribution is calculated from the Mie theory. Since the size of the particles measured is a function of the wavelength of the impinging radiation, the instrument uses a beam of filtered blue light to expand the range.

X-RAY SCATTERING

The Debye-Scherrer small angle x-ray scattering technique for observing interference effects related to particle size is well known [81]. Some generalizations on the use of the technique were addressed by Debye [82].

Yudowitch [83] and Danielson et al. [84] both employed the "diffraction peak" procedure for the determination of latex particle size. For control they used a latex whose size had been determined under the electron microscope.

Particles that are perfect spheres can be described by a single value representing the sphere's diameter. Calibrated microscopes are useful in reading such values directly from the reticule. They have some utility with spherical resin particles and with visual measurement of standardized test materials. Classification of most powders, on the other hand, must address particles of various shapes and sizes together as a collection.

A particle-size determination utilizes some size-dependent property that can be measured and then relates

TABLE 2—Definitions of particle size

Symbol	Name	Definition	Formula
d_v	Volume diameter	Diameter of a sphere having the same volume as the particle	$V = \frac{\pi}{6} d_v^3$
d_s	Surface diameter	Diameter of a sphere having the same surface as the particle	$S = \pi d_s^2$
d_sV	Surface volume diameter	Diameter of a sphere having the same external surface-to-volume ratio as a sphere	$d_{sv} = \frac{d_v^3}{d_s^2}$
d_d	Drag diameter	Diameter of a sphere having the same resistance to motion as the particle in a fluid of the same viscosity and at the same velocity (d_d approximates to d_s when Re is small)	$F_D = C_D A_{pf} \frac{V^2}{2}$ where $C_0A = f(d_d)$ $F_d = 3\pi d_d \eta v$ $Re < 0.2$
d_f	Free-falling diameter	Diameter of a sphere having the same density and the same free-falling speed as the the particle in a fluid of the same density and viscosity	
dst	Stokes' diameter	The free-falling diameter of a particle in the laminar flow region (Re <0.2)	$d_{st}^2 = \frac{d_v^3}{d_d}$
d_a	Projected area diameter	Diameter of a circle having the same area as the particle resting in a stable position	$A = \frac{\pi}{4} d_a^2$
d_P	Projected area diameter	Diameter of a circle having the same area as the projected area of the particle in random orientation	Mean value for all possible orientations $d_P = d_s$ for convex particles
d_c	Perimeter diameter	Diameter of a circle having the same perimeter as the projected outline of the particle	
d_A	Sieve diameter	The width of the minimum square aperture through which the particle will pass	
d_F	Ferer's diameter	The mean value of the distance between pairs of parallel tangents to the projected outline of the particle	
d_M	Martin's diameter	The mean chord length of the projected outline of the particle	
d_R	Unrolled diameter	The mean chord length through the center of gravity of the particle	$E(d_R) = \frac{1}{\pi} \int_0^{2\pi} d_R d\theta_R$

this property to a linear dimension. The measurement derives either from individual particles or as a property of the collection of particles that is often expressed as a diameter of sorts. Measurement of a single individual particle may have its size expressed in different "diameters" depending on the direction and method of view. Particle characterization may involve determining the rate of a particle's travel through a fluid (either under the influence of gravity or while being subjected to angular acceleration due to rotation), its actual surface area, its ability to pass through a screen of square or round holes of differing size, or its ability to scatter light of various wavelengths in various directions. For the new technology employing ultrasonics, the interference of sound transmission through a liquid is used to correlate a size distribution.

It is convenient to use the term "equivalent diameters" when comparing sizes. The value so determined for a given collection of irregular particles will vary somewhat depending on the technique used (i.e., the size-dependent variable being measured). The definition of some of these "diameters" is presented in Table 2 along with their mathematical representation. Table 3 lists some of the methods, the nominal particle-size range, and the size measured. The methods available for determining particle size take advantage of many different characteristics of the powder particle.

Definitions of Particle Size and Shape

Particle shapes are everything but spherical for pigments and fillers that are produced, essentially, by crushing and shattering. As the sizes get smaller, the actual particle shape plays an increasingly important role in its use in a coating as well as on the physical laws employed for its characterization. From the diagram in Fig. 5, the same particle may be defined in a number of ways [85]. Some of these include the following:

Martin's Diameter. The distance between opposite sides of a particle measured on a line bisecting the projected area. To ensure statistical significance, all measurements are made in the same direction regardless of particle orientation.

Feret's Diameter. The distance between parallel tangents on opposite sides of the particle profile. Again, to ensure statistical significance, all measurements are made in the same direction regardless of particle orientation. Note:

TABLE 3—Comparison of particle-sizing methods

	Nominal Range, μm	Size Determined
Gas Permeability	**0.1–40**	**Mean**
Gas Adsorption	**0.005–50**	**Mean**
Brownian Motion	**0.01–3**	**Mean**
Sieving		
Dry	>10	Passing through
Wet	2–74	minimum opening
Microscope		
Optical	0.5–500	Martin's, Feret's, or equivalent circle diameter
Electron	0.002–15	
Zone sensing		
Resistivity	0.05–500	Volume or area
Optical	1–500	
Elutriation		
Laminar flow	3–75	Equivalent spherical diameter (E.S.D.)
Cyclone	8–50	
Centrifugal classification	0.5–50	E.S.D.
Mercury intrusion	0.01–200	E.S.D.
Centrifugal sedimentation		E.S.D.
Mass accumulation	0.05–25	
Photo extinction	0.5–100	
X-ray	0.01–5	
Gravity sedimentation		E.S.D.
Pipettes and hydrometers	1–100	
Photo extinction	0.05–100	
X-ray	0.1–60	
Hydrodynamic chromatography		
Packed column	0.03–2	E.S.D.
Capillary column	0.1–60	
Cascade impactor	0.05–30	Aerodynamic diameter

Both Martin's and Feret's diameters are generally used for particle-size analysis by optical and electron microscopy.

Equivalent Circle Diameter. The diameter of the circle having an area equal to the projected area of the particle in random orientation. This diameter is usually determined subjectively and measured by ocular micrometers called graticules.

Equivalent Spherical Diameter (E.S.D.). This often affords a more useful measure, particularly where industrial processing is involved. This diameter is determined, in effect, by measuring the behavior of the irregular particle in a certain circumstance and relating that to the behavior of a sphere of otherwise identical properties.

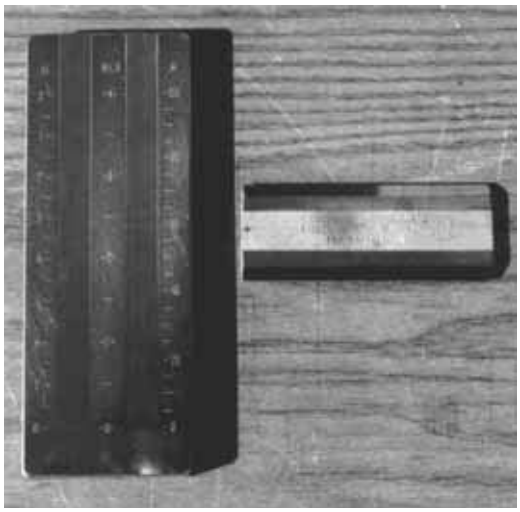


Fig. 27—Hegman fineness-of-dispersion gage. (Compliments of Lynn Shirey.)

Sedimentation (Stokes') E.S.D. The diameter of a sphere of the same density as the particle and having the identical free-fall velocity of the particle.

Volume E.S.D. The diameter of a sphere having the same volume as the particle.

Drawdown Techniques for Texture and Oversize

During the manufacturing of paints and coatings, there is a need for rapid, "on-the-floor" testing to determine whether a dispersion has reached its maximum grind. The "grind" gages were developed to provide quick, on-the-spot answers. Some of the tests could be done in the factory at the disperser during the grinding stage of production. Actually, during the production of paints and pigmented coatings, the pigments are not ground but are only wet out and dispersed to their "primary" size. This primary size is the smallest possible size supplied from the producer.

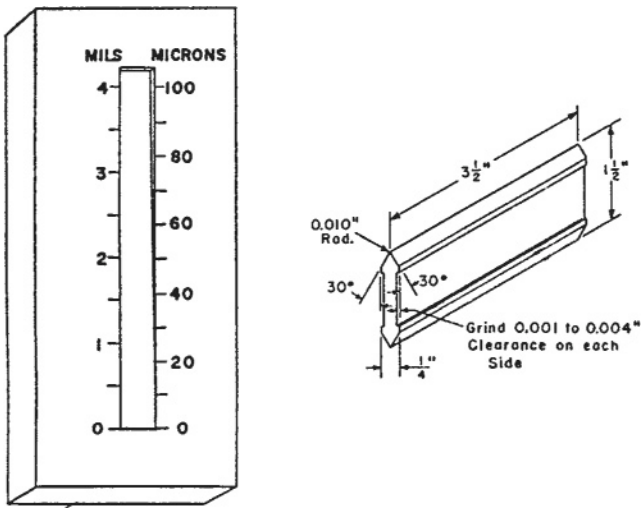


Fig. 28—ASTM dispersion gage and scraper.

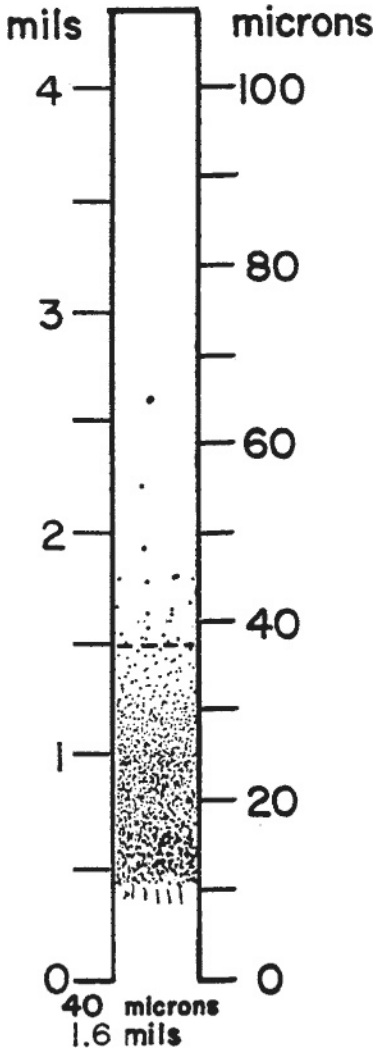


Fig. 29—Typical pattern produced by a dispersion gage.

THIN-FILM DRAWDOWN FOR OVERSIZE PARTICLES

This test [86] is suited particularly for detecting oversize particles that adversely affect the gloss of high-gloss industrial enamels. A 2-mL wet film of the enamel is spread on a glass plate with a Bird applicator blade. Inspection of the film is best made in a dimly lit room with the operator facing a light source such as a window or under a fluorescent light with a grid that can be reflected from the wet paint sample. With the eye focused on the silhouetted image of the window sash or the reflected pattern from the light or ceiling, extremely fine particles may be detected and compared with a visual standard. They appear as a roughness to the wet surface.

A variation of this approach is to illuminate the specimen at grazing incidence with a spotlight and view the film through a magnifier parallel to the specimen. Still another version is the use of wedge-shape or step-wise multithickness films.

FINENESS-OF-DISPERSION GAGES

Drawdown tests for the detection of oversize particles led to development of fineness-of-dispersion gages, or, as first called, fineness-of-grind gages. The gage is a steel block in which is cut a wedge-shape channel, tapering usually from 4 mils at the deep end to zero at the other end, though other depths and different widths and lengths of the channel are available. Some gages have twin channels. An excess of the sample is placed in the deep end of the channel, and the excess is drawn to the shallow end with a scraper. At some point along the channel, coarse particles or agglomerates become visible. The results are interpreted by reference to standard reference patterns. The addition of slow-evaporating solvents may be required to thin down the system to allow more time for reading the gage without experiencing volume loss by evaporation.

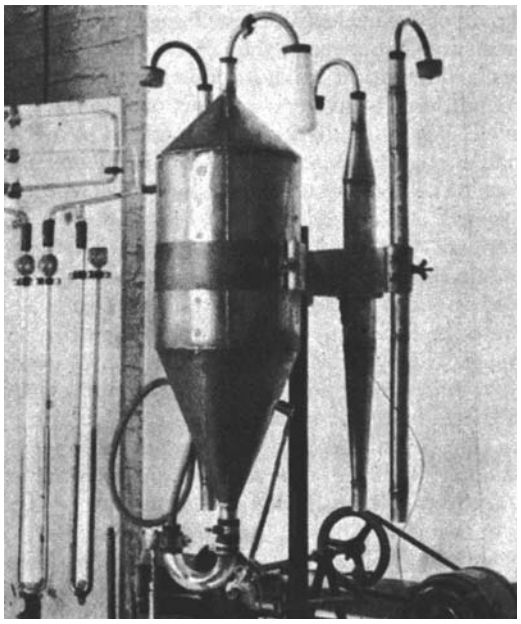


Fig. 30—The roller particle-size analyzer.

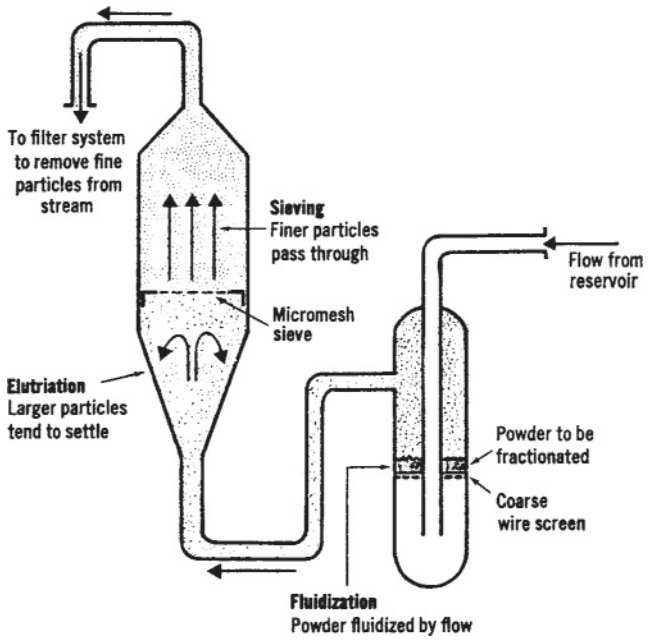


Fig. 31—Felvation. Fractionating powders into different sizes by a combination of fluidization, elutriation, and sieving. (Courtesy of *Chemical and Engineering News.*)

St. Louis Gage. This [87], the first of the dispersion gages, was designed to facilitate the use of the North Standards. The channel is 2 in. (51 cm) long and 0.005 in. (0.13 mm) deep at the deep end. The sample and the selected North Standard are placed side by side in the deep end, drawn by a scraper toward the shallow end, and compared.

Hegman Gage. The Hegman gage [88,89] (Fig. 27) made the North standards and the St. Louis gage obsolete. It is essentially a St. Louis gage with the addition of a scale to show the depth of the channel or the distance from the deep end. Instead of evaluating the dispersion in terms of the North standards, the distance from the deep end is reported. The finer the dispersion, the greater the distance. This is the reverse of the North standards, where the finer the dispersion, the lower is the number of the standard.

ASTM Gage. The gage specified in ASTM Test Method for Fineness of Dispersion of Pigment-Vehicle Systems (D1210) is almost identical to the Hegman. The steel block (Fig. 28) is about 180 mm long, 63.35 mm wide, and 12.7 mm thick. The channel is 100 μm deep at the heel. The gage is calibrated according to depth in steps of 10 μm along one edge and to the corresponding nearest 0.1 mil along the other. The dimensions of the scraper are shown in the diagram.

Experience has shown that the speed of drawdowns and the angle at which the scraper is held have no important effect on the results. However, the time lapse between the drawdown and reading, as well as operator technique, are important [87]. Readings should be made within 10 s after completion of the drawdown, especially for dispersions with a rating of seven or better due to the volume loss from solvent evaporation. Good practice suggests three drawdowns using fresh material each time. The first drawdown allows accommodation to the light source and a rough estimate of the dispersion pattern and the end point. Subsequent readings may then be made within 3 or 4 s. ASTM directs viewing the drawdown with the line of vision at a right angle to the long dimension of the channel and at an angle between 20° and 30° with the face of the gage in a light that renders the pattern readily visible. Diffuse subdued light is preferred.

Elimination of operator variance is aided by the use of six standard patterns. Fig. 29 illustrates reading of the end points, and the scales show the depth of the channel. This scale appears to have some advantage over both the North and the Hegman scales as it is related directly to the dimensions of the oversize particles. Other scales in use include the FSCT (Federation of Societies for Coatings Technology) scale, which divides the distance into ten parts.

Constant Depth Gage. The channels in this gage are of constant depth rather than tapered as in the gages previously described. The gage most often used has four channels, 1/2 in. (1.3 cm) wide and 6 in. (15 cm) long, having depths of 0.002 (0.005 cm), 0.0015 (0.0038 cm), 0.0010 (0.0025 cm), and 0.0005 in. (0.004 cm), equivalent to Hegman values of 4, 5, 6, and 7, respectively. Other depths can be supplied. The advantage of this type of gage is the long path available for inspection, a condition that should minimize the influence of bubbles and foreign matter on the ratings.

NPIRI Grindometer. Printing ink films are much thinner than those of paints or coatings. Relatively fine particles in the latter would be considered relatively coarse in the ink. Because of this, the printing ink range is addressed with a gage designed by the National Printing Ink Research Institute (NPIRI) called the Grindometer [90,91]. The channel of this gage is only 0.001 in. deep at the deep end, is 1 in. (2.54 cm) wide, and the scale is graduated in steps of 0.0001 in. (0.000 25 cm) [92].

X-RAY MICRORADIOGRAPHY TECHNIQUE

This technique detects undispersed clumps of pigment (inorganic types only) in paint. It uses low-energy x-rays [93] to resolve oversize material in the range of 1 μm or less, which is below the range detectable with fineness-of-dispersion gages.

A thin film of paint is spread over the surface of photographic-sensitized, fine-grain film. The specimen is exposed to x-rays and the film developed after removal of the paint. The film is enlarged optically to reveal silhouettes of the oversize materials on a photographic negative. Determination of size may be made following the methods used for light and electron microscopy.

Separation and Collection: Particle Size by Elutriation

This approach is primarily a means for separating or fractionating a quantity of pigment into portions according to particle size rather than providing a value of the sizes separated. Size determinations may then be made on the separated fractions. The technique has utility in evaluating the influence of pigment and filler particle size on the properties of the formulated product. After standardizing operating conditions for a material and measuring sizes by an independent method, approximate size distribution may be estimated for additional material.

Roller Particle-Size Analyzer. This device [94] uses elutriation by air to separate pigments into sizes. The glass U-tube at the bottom of Fig. 30 is charged with the specimen of pigment. Air under pressure is admitted through a nozzle that extends to the bottom of the tube. The other arm of the tube is connected to the metal settling tube. By proper selection of size of nozzle, size of settling tube, and velocity of the air, separation into desired fractions is obtained. The fractions are collected in paper extraction thimbles connected with a gooseneck to the settling tube. During the separating, the U-tube and the settling tube are vibrated vigorously. Using 25-g charges, the average time required for separations ranges from 62 min for particles up to 5 μm in diameter to 11 min for particles from 40 to 80 μm in diameter.

Felvation. This method [95] combines elutriating and sieving for fractionating fine powders. The basic apparatus (Fig. 31) consists of a column about 4 in. (10 cm) in diameter and 24 in. (61 cm) in height. The specimen is placed in the narrow tube at the right. Fluid is introduced and allowed to pass through at a relatively low rate. The powder soon becomes fluidized in the conical base of the column. The flow of the liquid is increased gradually. The smaller particles reach the sieve and pass through it. The throttling action of the sieve increases the flow through it. Hence, particles that have passed through do not fall back and clog the screen. Eventually, particles just larger than the sieve openings reach the sieve, but they do not block the screen as they reduce the flow around them and then tend to fall from the sieve.

The sieve functions only as a gage. It does not support the powder. Highly accurate electroformed sieves are used, but, because of their small size [1 in. (2.5 cm) in diameter], their cost is reasonable. Besides being economical, the method is rapid. Complete fractionations can be run in a period as short as 10 min.

THE ROLE OF PARTICLE-SIZE REFERENCE TEST MATERIAL

Carefully prepared particles of known size and composition have become an important part of testing for emulsions, powders, film, and processes. When properly used, reference particles are an important factor in demonstrating compliance with standards such as ISO-9000, U.S. Food and Drug Administration (FDA) Good Manufacturing Practices, and various military specifications [96]. In the past two decades, the need for instrument calibration has prompted the establishment of several businesses specializing in the production and supply of reference particles, which are available in assortment of materials of various sizes, densities, and grades.

A brief discussion of some typical applications will illustrate the usefulness of these test reference particles. They are used for instrument calibration, filter checking, flow tracing, and evaluation of processes such as blending, cleaning, and spraying, to name a few.

Instrument calibration and checking covers two broad classes: (1) particle-size analyzers and (2) particle contamination analyzers. Both types of instruments are calibrated or controlled by spherical particle-size standards, primarily polystyrene microspheres, which are normally measured and calibrated by methods traceable to the National Institute of Standards and Technology (NIST). The spherical calibration particles have fairly predictable instrument responses and are available as aqueous suspensions of highly uniform particles in discrete sizes (diameters) from 0.02 to 2000 μm. In addition to polystyrene spheres, which may be nonfluorescent or may contain various fluorescent dyes, calibration spheres are composed of silica and glass. Nonspherical materials such as alumina, quartz, and various milled powders are available as experimental materials or controls.

Particle-size spectrometers are used to measure the particle-size distribution of powders, suspensions, emulsions, and aerosols. Other than composition, particle-size distribution is probably the most important variable in product quality and performance. The major class of instruments, particle counters, is used to measure trace amounts of particle contamination in air, water, chemicals, beverages, and medicines. A recent variation of the particle counter can measure particle contamination on flat surfaces, such as silicon wafers, and a variety of optical and electronic parts. These instruments, as well as optical and electron microscopes, require calibration and reference particles to assure both the quality and traceability of measurements.

In addition to instrument evaluation and calibration, reference particles are used to verify retention ratings and pore-size distribution of air and liquid filter media. Using aerosol particle generators and precision particle counters up and down stream, high-efficiency particulate air (HEPA) filters can be certified for use in ultraclean manufacturing operations for rigorous contamination control. Polystyrene spheres with approximately a 0.25-μm diameter are frequently used for this purpose.

Another broad class of reference particle application is their use in validating processes, such as for cleaning, blending, dispersing, separation, and spraying. Fluorescent particles, which have bright and distinctive colors that can be contrasted with other background materials, are frequently used to follow the flow or direction of a process. Other materials such as pollens, ground walnut shells, refractory powders, or other materials of the desired particle size and specific gravity are available as model systems for evaluating processes.

In conclusion, reference particles are a key ingredient of modern testing methods, and their use should be considered at an early stage in any QA/QC program as quality management programs require the regular and timely evaluation and standardization of particle-sizing equipment.

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Rheology and Viscometry[1]

Richard R. Eley[2]

NOMENCLATURE

Φ = Fluidity integral
α = Rate of decay of roughness amplitude, s^{-1}
β = Time constant characteristic of a critical shear rate, s
γ = Dimensionless shear strain
γ = Shear strain rate, s^{-1}
γ_w = Wall shear rate in tube flow, s^{-1}
δ = Phase shift; thickness of adsorbed polymer layer
ε = Extensional (Hencky) strain, dimensionless
ε = Extensional (Hencky) strain rate, s^{-1}
η = Coefficient of viscosity
η_0 = Zero-shear viscosity
η_∞ = High-shear limiting Newtonian viscosity
η_d = Dispersion viscosity
η_e = Extensional viscosity
η_l = Liquid-phase viscosity
η_r = Relative viscosity η_d/η_l
η' = Dynamic viscosity
$[\eta]$ = Intrinsic viscosity (limiting viscosity number)
θ = Angle of inclination with respect to the vertical
λ = Wavelength of coating surface striations; elastic stress relaxation time constant
ν = Kinematic viscosity
π = Ratio of circumference of a circle to its diameter
ρ = Density
γ = Surface tension
σ = Shear stress; generalized stress
σ_0 = Stress imposed at zero time; Yield stress
σ_e = Tensile stress
σ_s = Tangential surface shear stress
σ_w = Wall shear stress
τ = Viscosity-kinetic time constant for drying, wicking, or thixotropy
ϕ = Volume fraction of internal (dispersed) phase of a dispersion
ϕ_e = Effective volume fraction for a dispersion
ϕ_m = Maximum packing fraction of a dispersion, where $\eta_r \rightarrow \infty$
ω = Angular frequency ($= 2\pi f$)(rad·s^{-1})
A = Area of shear face
De = Deborah number (λ/t)
F = Force
F_g = Force of gravity
G = Shear modulus
G_∞ = Plateau modulus
G^* = Complex shear modulus
G' = Storage modulus
G'' = Loss modulus
K = Consistency in power law model; constant in viscosity-molecular weight equation
L = Capillary tube length
M_w = Weight-average polymer molecular weight
M_c = Critical (entanglement) polymer molecular weight
P = Pressure
Q = Volumetric flow rate
R = Capillary tube radius; particle radius; air bubble radius
T = Absolute temperature
T_g = Glass transition temperature
a = Curvature parameter in Eq (15); amplitude of coating surface striations
a_0 = Time-zero amplitude of coating surface striations
e = Base of the natural logarithmic scale = 2.71828
f = Frequency, hertz
g = Gravitational acceleration
h = Film thickness
k = Boltzmann's constant; general rate constant
l = Length
m = Kinetic energy correction term for capillary tube flow, Eqs (74) and (75)
n = Power law exponent
t = Time
v = Velocity
x = Coordinate parallel to substrate
y = Coordinate normal to substrate

INTRODUCTION

THIS ARTICLE PRESENTS A BRIEF REVIEW OF principles and methods of rheological analysis for the coatings industry. However, the information and methodology discussed applies equally well to the characterization of coatings, adhesives, inks, and sealants. These products share a common task, in that they are applied to a sub-

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strate—and must function—as a thin film. The process of application and film formation obviously requires not only a large total deformation, but also a high degree of control of flow, in order to achieve success. Flow cannot be controlled unless it is properly measured. Typical industrial viscosity test methods have several faults: (1) the methods do not closely relate to actual industrial processes, (2) the test devices are unsuitable for non-Newtonian fluids, (3) the result is usually a single point, and (4) in general, such measurements do not correlate well to performance. The objective for the applied rheologist, therefore, is to develop methods of rheological characterization that

1. yield accurate data for complex fluids and
2. can be specifically related to the critical processes that paints must undergo. To meet the latter goal requires characterization methods that cover a wide range of stresses and time scales.

Though all other properties be acceptable, a coating will usually not meet with success if the rheology is not. Experienced formulators say that more than half the cost of new product development is consumed in "getting the rheology right." Furthermore, "minor" changes in a raw material or process can create significant and unexpected variability in product rheology, and such problems naturally require urgent solution. For these reasons and others, rheological analysis is a vital and cost-effective tool for the coatings industry.

The performance of coatings is governed by viscosity variations over a span of several orders of magnitude in shear rate or shear stress (at least four to as many as eight), if processes ranging from coating application, to leveling and sagging, to pigment settling are considered. To characterize fluid rheology over such a broad range of stress and deformation requires a "research-quality" rheometer. In order to take advantage of the capabilities built into the sophisticated rheological instrumentation now available, more than a passing knowledge of the subject of rheology is required. This chapter is therefore tutorial in style, aiming to provide the novice an entry point to the discipline. Certain concepts are discussed at some length because of their importance or complexity. One of these is viscoelasticity. It is worth the time because (a) a number of commercial instruments are capable of viscoelastic characterization of materials and (b) it is established that viscoelasticity exerts control over coating processes when present.

Finally, in the words of Professor Ken Walters, "rheology is a difficult subject." This is certainly true, as it combines several disciplines under one banner: mathematics, physics, physical chemistry, colloid and polymer science, fluid mechanics, etc. In addition, the experimental methods used are often complex and highly specialized. Furthermore, rheology requires mastery of concepts peculiar to the science, with which most persons have had limited opportunity to become familiar in the normal course of a technical education. Nevertheless, it is quite possible for the nonspecialist to acquire a useful working knowledge of the principles and practice of rheology, which may be used profitably to understand the link between formulation and performance of coatings.

DEFINITIONS OF BASIC TERMS

Rheology

The term "rheology" derives from the Greek *ρειν*, which means "to flow." Rheology is defined classically as "the study of the deformation and flow of matter," and may be defined operationally as "the study of the response of certain materials to stress." In order to quantify the deformation and flow behavior of materials, three basic terms must be defined. The first two of these relate to the measurement of the deformation (strain and strain rate) and the third to the measurement of the force required to deform a material (stress).

Deformation (Strain)

A *deformation* (or *strain)* is a change in shape and/or volume of a material in response to an applied stress. There are two principal types of deformation: *reversible* (elastic, rubber-band-like), and *irreversible* (inelastic or viscous). Irreversible deformation is the definition of flow. Rheologically interesting materials display a third type, in which either or both viscous and elastic response to stress can be seen, depending on the rate or the duration of stress applied.

During the lifetime of a coating the deformation history may be complex (see Table 1), the most important deformation types being simple shear and extension. For purposes of definition, we will limit our discussion to simple shear. Simple shear deformation is analogous to the spreading of a deck of playing cards, each card representing a thin volume element (or shear plane) displaced relative to its neighbor (Fig. 1). If a force F is applied to the uppermost volume element (thickness dy), the material will deform by the displacement of adjacent volume elements by a distance dx. The total thickness is Δy, and the total displacement is Δx. The shear strain γ is the ratio of the net displacement Δx to the distance of separation of the confining surfaces Δy,

$$\gamma = \frac{\Delta x}{\Delta y} \tag{1}$$

Strain Rate

Unlike solids (e.g., rubber band), liquids cannot support a constant deformation or strain. Thus, in order to measure the viscosity or resistance to flow of a fluid, we do not measure the deformation (strain), but, instead, the rate of deformation (strain rate). The strain rate is the change in strain per unit time, or the time derivative of the strain, symbolized $\dot{\gamma}$ (where the "dot" signifies "time derivative of"). Therefore, from Fig. 1,

$$\dot{\gamma} = \frac{\Delta x}{\Delta t} = \frac{\Delta(\Delta x/\Delta y)}{\Delta t} = \frac{\Delta(\Delta x/\Delta t)}{\Delta y} = \frac{\Delta v}{\Delta y} \tag{2}$$

For the case of simple shear deformation the strain rate is termed the shear rate. The dimensionality of γ is $LT^{-1}L^{-1}$ (e.g., cm · s^{-1} · cm^{-1}). Unit cancellation leaves reciprocal time (s^{-1}) as the unit of shear rate. It is conceptually helpful, however, to remember that, as shown by Eq (2), the shear rate is actually a velocity gradient ($\Delta v/\Delta y$, change in velocity per unit gap between shearing surfaces).

Stress

Force applied to a material creates a state of stress within the material. Stress can be expressed in units of force per unit area (e.g., dyn · cm^{-2}), or, equivalently, energy per unit volume (e.g., erg · cm^{-3}). In terms of Fig. 1, the shear stress σ is the force F necessary to maintain steady shearing

TABLE 1—Rheological components of coating processes

Process	Deformation Type or Attribute	Rheological Property
Roll coating	Squeezing flow	Biaxial extensional viscosity
	Stretching flow	Uniaxial extensional viscosity
	Shearing flow	Shear viscosity
	High strain rates	High-shear viscosity
	Large accelerations	Elasticity (G')
	Large decelerations	G' recovery
	Surface area transients	Dynamic surface tension
Spray	High shear rate	High-shear viscosity
	Large accelerations	Elasticity (G')
	High-strain-rate extensional deformation	Extensional viscosity/elasticity
	Surface area transients	Dynamic surface tension
Brushing/rolling	Medium shear rate	Shear viscosity
	Stretching flow	Extensional viscosity/elasticity
	Surface area transients	Dynamic surface tension
Leveling/sagging	Slow shear flow	Low shear stress viscosity
	Surface-stress driven	Dynamic surface tension
	Transient (nonequilibrium process)	Structure recovery kinetics
Curtain coating	Stretching flow	Extensional viscosity/elasticity
	Surface area transients	Dynamic surface tension
	Shear (pumping, extrusion)	Shear viscosity

motion against the resistance of the confined fluid, divided by the area of the shear face A,

$$\sigma = \frac{F}{A} \tag{3}$$

The stress is determined both by the magnitude of the applied force and by the area over which it is applied. Stress can therefore be thought of as a kind of "force intensity" or the "concentratedness" of the force. Consider the analogy of a bowling ball placed on a mattress. It sinks deep into the mattress because the area over which its weight is applied is relatively small. However, if a two-foot square board were placed under the ball first it would barely sink at all. The depth to which the ball sinks into the mattress depends on the area over which the force is applied. The smaller the area of contact of the weight with the mattress, the higher the stress, and the greater the resulting strain—the deeper the weight sinks.

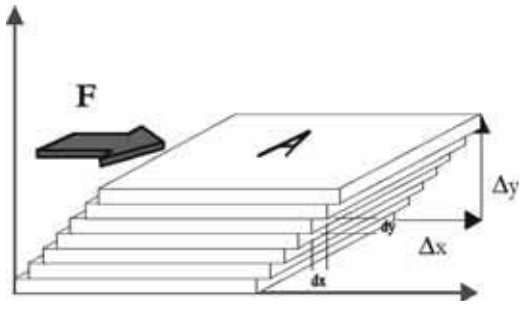

Fig. 1—Diagram for term definitions for simple shear.

Viscosity

The viscosity of a fluid characterizes its resistance to flow. The resistance to flow is, in turn, a measure of the friction between the flow units of the fluid (e.g., molecules), and may also be a measure of the forces of interaction between the flow units. Thus, a "viscous" fluid (one reluctant to flow) may be so because of high molecular weight (as in motor oil) or be of relatively low molecular weight, but having strong inter-molecular interactions (e.g., hydrogen bonds, as between sugar molecules in honey).

The interaction of molecules in flow dissipates energy, chiefly as frictional heat. Flow, therefore, is a process that costs energy, of which the viscosity is a measure. For the case of shear deformation, the viscosity η is calculated as the ratio of shear stress to shear rate. The viscosity, following from the discussion above, is therefore the energy per unit volume dissipated to attain a unit velocity gradient,

$$\eta = \frac{\sigma}{\dot{\gamma}} \tag{4}$$

Modulus

Materials comply with an applied stress by deforming or undergoing strain. For ideal Hookean materials, the strain will be proportional to the applied stress. The modulus is

TABLE 2—Units in various systems			
Variable	**cgs**	**MKS**	**SI**
Strain	Dimensionless	Dimensionless	Dimensionless
Strain rate	s^{-1}	s^{-1}	s^{-1}
Stress	dyne · cm^{-2}	Newton(N) · m^{-2}	Pascal (Pa) (=1 N·m^{-2})
Viscosity	Poise (P)	. . .	Pa·s (=10 P)
	Centipoise (cP) (= 0.01 P)		mPa·s (=10^{-3} Pa·s=1 cP)
Modulus	dyne · cm^{-2}	N·m^{-2}	Pa

the proportionality constant between the stress and strain, as in

$$G = \frac{\sigma}{\gamma} \tag{5}$$

where the shear modulus G is equal to the ratio of the shear stress to the shear strain. Most polymeric materials and coatings systems, in the solid state, are non-Hookean, i.e., the modulus is not a material constant, but will depend on both rate and extent of deformation.

Units

Various systems of units for rheological variables may be encountered in the literature. Until recently, the most common system of units for rheological terms was the cgs (centimeter-gram-second), or "small metric" system. However, international convention now specifies *Système Internationale* (SI) units as the standard. The SI system is based on the "large metric," or MKS (meter-kilogram-second) units, with some additional named units. The units associated with the above defined variables according to the various units systems are given in Table 2.

GENERAL CLASSIFICATION OF FLUID BEHAVIOR

Newtonian Fluids

Isaac Newton postulated that the force resisting motion of liquids is proportional to the rate at which one attempts to "separate the parts" of the liquid. In terms of our defined quantities, this would be expressed as a proportionality of stress to rate of strain:

$$\sigma \propto \dot{\gamma} \tag{6}$$

or

$$\sigma = \eta\dot{\gamma} \tag{7}$$

where η is the constant of proportionality, and is termed the coefficient of viscosity or simply the viscosity.

Equation (7) is the simplest example of a constitutive equation, an expression that allows one to predict the flow properties of a material in response to an applied stress. Fluids that obey Eq (7) over a range of shear rate are said to be Newtonian over that range. The viscosity of Newtonian fluids is a material constant (like the density or heat capacity) and depends only on the thermodynamic variables of temperature, pressure, and concentration. If the viscosity of a Newtonian fluid is measured at any arbitrary shear rate or shear stress, the viscosity under all deformation conditions is known.

Non-Newtonian Fluids

Fluids of commerce comprise a wide variety of materials, with a wide range of consistencies. In general, polymer solutions, emulsions, colloidal dispersions, and other suspensions of particulate solids will be *non-Newtonian*. For non-Newtonian materials, the viscosity is no longer a material constant, but is now a *material function*—in this case, a "function" of the shear rate (or shear stress). For non-Newtonian fluids, a viscosity measured at a single shear rate is not an adequate representation of the rheology of the system.

TYPES OF NON-NEWTONIAN BEHAVIOR

In the following sections, the various types of non-Newtonian behavior will be outlined. At the same time, some mathematical expressions that are commonly used to describe non-Newtonian flow will be introduced. Mathematical models are useful for summarizing flow behavior quantitatively. To be sure, materials can be evaluated merely by qualitative comparison of flow curves (e.g., by visual inspection), but the mathematical analysis of flow has value. For one thing, the model constants may have physical significance. For example, some models contain a yield stress term as a fitted parameter (see "Plastic (Yield) Behavior"). The magnitude of this parameter may be coupled to sag or leveling performance [1]. A later section of this chapter, "Leveling," gives examples of how leveling can be predicted for non-Newtonian fluids using constants from models discussed below. Furthermore, the values of model parameters may be related to formulation variables, allowing one, in principle, to optimize rheology by adjusting composition in a rational way.

It should be understood that the models about to be discussed are idealizations, and therefore are limited in their ability to represent the behavior of real materials. The models are able to describe real behavior at least over a limited range of stress or strain rate. Thus, a second use of mathematical models of flow is to make predictions of flow behavior, bearing in mind that it is risky to extrapolate the models beyond their range of validity.

As mentioned above, the simplest flow model is the Newtonian expression, which has only one constant, the coefficient of viscosity η. To describe more complicated behavior we will have to add additional coefficients and terms, the physical significance of which will be given when possible.

Shear-Dependent Viscosity

Materials for which the viscosity falls with increasing shear rate[3] are designated *shear thinning*. Simple shear thinning without either time dependence (see "Time-Dependent Fluids") or a yield stress (see "Plastic (Yield) Behavior") is termed *pseudoplastic* behavior. An increase of viscosity with increasing rate of shear is called *shear thickening*. The term *dilatancy* (see under "Shear Thickening Fluids") is often applied to shear thickening behavior, although this strictly refers to shear thickening accompanied by a volume

[3] Any definitions or descriptions of shear rate-dependent behavior may likewise be stated in terms of shear stress dependence.

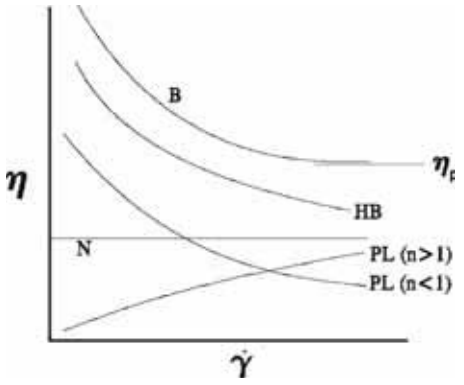

Fig. 2—Viscosity-shear rate curves for simple flow models. Symbols represent the following fluid models: N = Newtonian; B = Bingham (η_p = plastic viscosity); HB = Herschel-Bulkley; PL = power law (n = exponent).

increase, as the term implies. Fig. 2 shows curves illustrating viscosity-shear rate relationships for Newtonian and some non-Newtonian fluids.

Equation (4) describes Newtonian behavior, for which the viscosity η is a material constant and independent of shear rate (contour *N,* Fig. 2). More complicated viscosity-shear rate behavior requires a more complex expression to model it. The first level of complexity is to add a yield stress term σ_0 (see "Plastic (Yield) Behavior") to the Newtonian model, resulting in the Bingham equation [2]

$$\sigma = \sigma_0 = \eta_p \dot{\gamma} \tag{8}$$

Equation (8) says that above the yield stress the shear stress (minus the yield stress) is directly proportional to shear rate.[4] It is a common misconception that this corresponds to Newtonian behavior above the yield stress. Fig. 2, curve B shows that the Bingham model displays power-law-like behavior, but deviates from the power law (curve PL) at higher shear rate, approaching the so-called "plastic viscosity" η_p as a limit. Casson [3] obtained an equation similar to Bingham's except each term appears as the square root,

$$\sigma^{1/2} - \sigma_0^{1/2} = \eta_\infty^{1/2} \dot{\gamma}^{1/2} \tag{9}$$

The Casson model is not empirical, but was theoretically derived, specifically for systems whose primary flow units are rigid rods. Casson's equation is reputed to hold for a variety of paint systems, particularly as modified by Asbeck [4]

$$\eta^{1/2} - \eta_\infty^{1/2} = \sigma_0^{1/2} \dot{\gamma}^{-1/2} \tag{10}$$

which is somewhat surprising since few paints utilize rod-shaped particles as fillers or pigments. In fact, this author's experience is that the Casson model does not represent paint flow as well as certain other models (see below). Cohu and Magnin [5] showed that if the exponent 1/2 is replaced by 1/*n* the Casson form is able to describe paint rheology over several decades of shear rate. In Eqs (9) and (10), η_∞ (sometimes called the *Casson viscosity*) is not actually an "infinite-shear viscosity," but represents a limiting viscosity that is approached at high shear rate. The value obtained for the Casson viscosity will vary with the maximum experimental shear rate. As with all such models, the user must be aware that the constants resulting from a Casson analysis do not necessarily represent true physical properties because the analysis is merely a process of curve-fitting. For example, a finite yield value will usually be obtained by Casson analysis even when the material clearly does not exhibit yield behavior.

The next complication we will introduce is to let the exponent of the shear rate in the Newtonian law take values other than unity. In other words, the shear stress now will depend on some power of the shear rate

$$\sigma = K\dot{\gamma}^n \tag{11}$$

Eq (11) is known as the power law or Ostwald–deWaele model. Here, K is a constant sometimes called the "consistency,"[5], which has replaced the coefficient of viscosity η. This substitution of K for η is necessary because the exponent n can be other than unity, in which case K will not have proper viscosity units associated with it. The power law exponent n has been termed the "flow index." Its value characterizes the dependence of viscosity on shear rate, i.e., whether the viscosity rises or falls with increasing shear. A value of $n < 1$ corresponds to shear thinning behavior and $n > 1$ to shear thickening (Fig. 2 curves PL). Dividing Eq (11) through by $\dot{\gamma}$ yields a form of the power law that relates the viscosity to the shear rate

$$\eta = K\dot{\gamma}^{n-1} \tag{12}$$

If $n = 1$ in Eqs (11) and (12), the power law reduces to the Newtonian law.

The next complication consists in adding a yield stress term to the power law expression

$$\sigma - \sigma_0 = K\dot{\gamma}^n \tag{13}$$

giving an expression known as the Herschel–Bulkley equation. This model describes power law behavior above the yield point (curve HB, Fig. 2).

Fig. 3 shows a generalized equilibrium flow curve [6,7]. This figure represents the general features of the shear rate dependence of viscosity for non-Newtonian fluids (log-log axes). The term "equilibrium" means that time-dependence has been removed experimentally by measuring the equilibrium viscosity. Fig. 3 consists of four main segments: a low shear rate Newtonian regime, region I; a "power-law" shear thinning regime, region II; a high-shear Newtonian regime, region III; and a possible shear-thickening regime, region IV. The figure is explained in detail below (see *Shear Thinning Fluids).* The chief limitation of the power law models is that they are valid only over a limited range, namely, the linear portion of region II in Fig. 3. Power law models cannot account for the upper or lower Newtonian regions and, in fact, predict infinite viscosity at zero shear rate and zero viscosity at infinite shear rate, both unrealistic limiting behaviors. Nevertheless, the power law models are found to be useful within their limitations, particularly

[4] In the Bingham expression and in other models incorporating a yield stress term, it is important to note that the equations describe flow behavior only when $\sigma > \sigma_0$. When $\sigma \le \sigma_0$, $\gamma = 0$ (i.e., $\eta = \infty$), and there is no flow.

[5] Mathematically, K corresponds (in numerical magnitude but not dimensionally) to the viscosity at unit shear rate (1 reciprocal second).

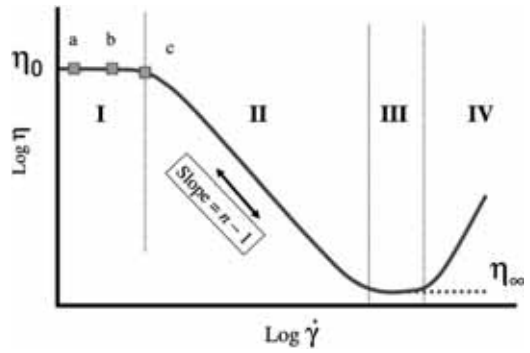

Fig. 3—Generalized equilibrium flow curve: η_0 = zero-shear viscosity (random structure, maximum disorder); η_∞ = high-shear limiting viscosity (maximum order). Region I is the first Newtonian plateau. Region II is the power law regime. Region III is the second Newtonian plateau. Region IV the shear-thickening regime (adapted from Ref. [6]).

for engineering-type calculations. The Herschel-Bulkley equation has been found to be superior to a number of other models in describing the flow behavior of a wide variety of coatings materials over a useful range of deformation conditions [8].

In order to account for the behavior outside region II in Fig. 3, more elaborate models are required. A simple extension of the power law model is to add an upper Newtonian limiting viscosity, η_∞

$$\eta = \eta_\infty + K'\dot{\gamma}^{n-1} \tag{14}$$

This expression is known as the Sisko model [9] and includes regions II and III of Fig. 3.

Of several proposed models encompassing regions I, II, and III inclusively, two in particular have found wide acceptance and utility in the literature. These are the Cross and Carreau models. Hieber et al. [10] wrote a general form of which the Cross and Carreau models are special cases (here modified to include Region III):

$$\eta = \eta_\infty + \frac{\eta_0 - \eta_\infty}{(1-[\beta\dot{\gamma}]^a)^{(1-n)/a}} \tag{15}$$

Here, η_0 is the first Newtonian plateau viscosity and a is a constant that determines the curvature of the transition region between the lower Newtonian regime and the power law regime. The value of a can be a measure of the molecular weight distribution of a polymer [10] or the particle-size distribution of a colloidal dispersion. Setting $a = 1 - n$ in the above expression yields the Cross equation, while setting $a = 2$ gives the Carreau-B model. The parameter n has the identical meaning as in the simple power law model [Eqs (11) and (12)], i.e., it is the slope of the power law regime in a log-log plot of shear stress versus shear rate. The constant β has the dimension of time and is actually a time constant representing a characteristic time of the system. This time constant may be related to, for example, the diffusional or rotational relaxation time of the flow units (be they colloidal particles or polymer chains) or to the time for rupture of particle flocs or aggregates under shear. The transition from the initial Newtonian plateau (region I) to the shear thinning regime (region II) in Fig. 3 is governed by the value of β, in an inverse sense: increasing β decreases the shear rate of the onset of shear thinning and vice versa. In other words, β defines a characteristic shear rate of transition, $\dot{\gamma}_{tr}$ [11–13]

$$\dot{\gamma}_{tr} = \frac{1}{\beta} \tag{16}$$

The constant β will be related to the time constant for Brownian diffusion of the primary flow units of a fluid. Stokes–Smoluchowski–Einstein theory gives the value of β for a dilute particulate dispersion as

$$\beta = \frac{6\pi\eta d^3}{k_B T} \tag{17}$$

where η is the viscosity of the continuous phase, d is the particle diameter, k_B the Boltzmann constant, and T absolute temperature. For a typical aqueous latex dispersion, d = 250 nm, η = 0.05 P, for which (at 25°C) β=0.36 s, corresponding to $\dot{\gamma}_{tr}$ =2.8 s^{-1}.

When the experimental shear rate equals $1/\beta$, the shear-ordering effect begins to dominate the randomizing effects of Brownian motion, and onset of shear thinning is seen [14] (see "Shear-Thinning Fluids"). This event corresponds approximately to point c in Fig. 3. Equations (16) and (17) tell how to control the transition from Newtonian to shear thinning behavior. Any change that increases the value of β (such as increasing the effective particle size or the continuous-phase viscosity, or lowering the temperature) will move the shear thinning transition to lower shear rates. Decreasing β extends Newtonian behavior to higher shear rates. While Eq (17) is strictly valid only for very dilute dispersions, it still provides qualitative guidelines for manipulating the rheology of dispersions. For concentrated dispersions, η should be taken as the viscosity of the dispersion [15–17].

It follows from the above discussion that the broader the size distribution of the flow units, the wider the

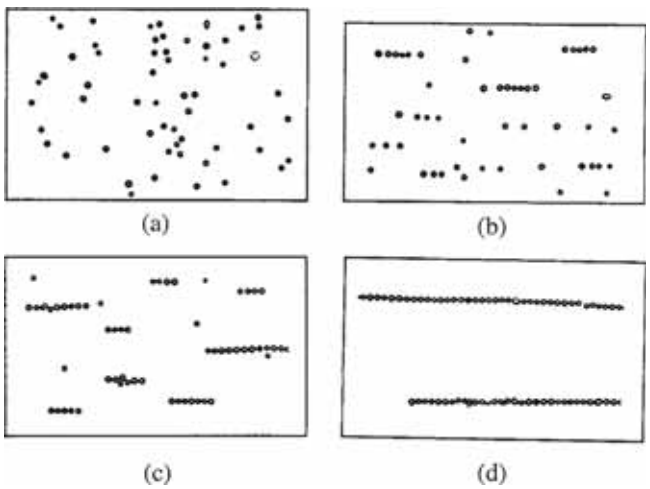

Fig. 4—Dilute suspension of glass microspheres in a polymer solution confined between glass plates with small plate separation: (a) just after loading, particles are randomly distributed; [(b)–(d)] after being sheared in a side-to-side direction at both increasing duration and shear rate. (By permission from J. Michel, R. Patzold, and R. Donis, *Rheologica Acta,* Vol. 16, 1977, p. 317. Cited in Ref. [20].)

spectrum of relaxation times and the more gradual the transition from region I to II (corresponding to a smaller value of *a)*. The shear rate of transition is fixed by β (a *mean* relaxation time), while *a* represents the *distribution* of relaxation times.

Shear-Thinning Fluids

The term *pseudoplastic* has been applied to fluids that decrease in viscosity with increasing shear rate (or shear stress) and implies shear-thinning behavior without yield stress. However, the term is passing out of use in favor of the more general description *shear thinning.* Particulate dispersions, polymer colloids, and polymer solutions can display this behavior above a certain concentration threshold.

Viscosity is a measure of the dissipation of energy or the "energy cost" to flow. Shear thinning behavior, therefore, implies that an increase of shear rate causes a structural change in the fluid that allows it to flow more efficiently and consequently with less energy dissipation. The mechanism[6] involves a shear-induced increase in order, or anisotropy, within the system. Thermal (Brownian) motion tends to keep systems disordered (of random order). Shear forces work against this, tending to impose orderliness. If shear rates are low, the randomizing forces win out and the micro-structure and hence the viscosity do not change for small increases of shear rate (point *a* to *b* in Fig. 3). Because of Brownian motion, the microstructure is no less random anywhere in region I than at zero shear rate, and therefore the viscosity is equal to η_0, the zero-shear value. As the shear rate approaches a critical magnitude (see "Shear-Dependent Viscosity"), the competition of thermal randomizing and shear ordering starts to favor ordering (point *c* in Fig. 3). In the case of polymers in solution, randomly coiled polymer chains tend to stretch in the direction of shear, partially uncoil, and align in more or less parallel fashion, at 45° to the shear gradient. In the case of a dispersion, the particles tend to line up like "strings of pearls" (Fig. 4) and eventually in ordered planes perpendicular to the shear gradient, according to Hoffman [18–20]. The result is a steadily decreasing viscosity with increasing shear rate as the degree of order increases. Ultimately, if the shear rate is high enough, the maximum amount of shear ordering possible is attained and the viscosity once again becomes independent of shear rate (Newtonian region III).

Fig. 3 shows the overall way in which viscosity varies with shear rate for systems such as those described above. Region I is the low-shear Newtonian regime (where Brownian motion controls structure). Region II is the shear-thinning segment of the flow curve (where shear forces control the structure). Here, the viscosity decreases exponentially with shear rate, hence, it is often referred to as the "power law" regime. Region III is the high-shear Newtonian regime. Here, the maximum degree of shear ordering has been attained—thus, the viscosity is once again independent of shear rate. The high-shear limiting Newtonian viscosity is usually given the symbol η_∞. Fig. 5 superposes the micrographs of Fig. 4 on the non-Newtonian flow curve

[6] The following discussion applies strictly to "stable" systems, i.e., those in which the net force between flow units is repulsive and which therefore do not flocculate. The shear-thinning mechanism for unstable systems (net interparticle force attractive) is discussed in the subsection entitled *Mechanism of Thixotropy*.

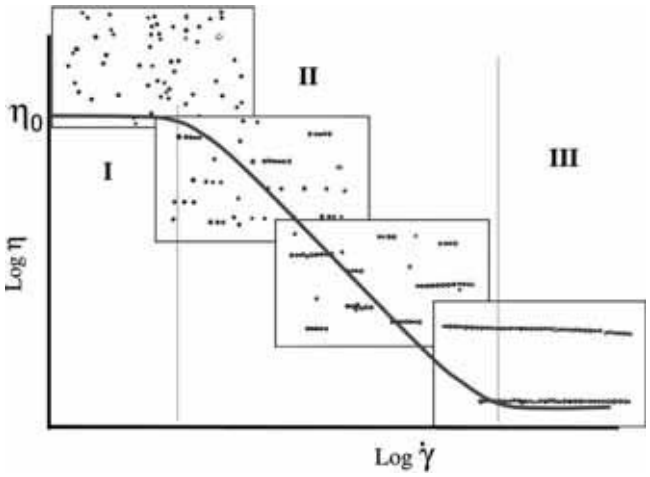

Fig. 5—Figs. 4(a)–4(d) superimposed on the equilibrium flow curve (Fig. 3) to illustrate the progression from random microstructure in region I through increasing degree of order in region II, to completely ordered microstructure in region III.

of Fig. 3, illustrating the microstructural state associated with each of the regions I, II, and III. Thus, in region I, the particles are isotropically (randomly) distributed due to Brownian motion. In region II there is a progressively increasing degree of order, culminating in a completely ordered micro-structure in region III.

Region IV is a shear-thickening region that is occasionally seen, especially with concentrated dispersions. In actuality, shear thickening in dispersions may occur at virtually any shear rate, depending on dispersion concentration [21], so that one or more of the other regimes are obliterated. That is, the equilibrium flow curve may consist of regions I to IV; I, II, and IV only; I and IV only; or IV only.

Note, once again, that structural order and viscous dissipation are inversely related. An increase in order means decreasing viscosity (Region II), while a decrease in order results in an increase in viscosity (Region IV) [22]. It follows that, for Newtonian behavior, no change must occur in structural ordering with shear. If the disperse system is unstable, i.e., tending to flocculate, the dotted curve may be followed (Fig. 6) instead of displaying a low-shear Newtonian regime [7]. Some systems may possess an apparent yield stress (see "Plastic (Yield) Behavior"). (See

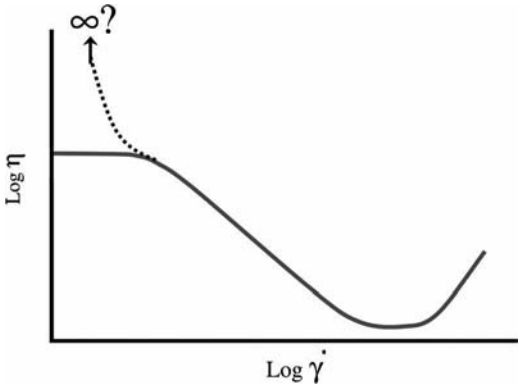

Fig. 6—Flow curve seen for unstable (flocculating) dispersions is indicated by the ascending curve going toward infinite viscosity at low shear rate.

"Dispersion Rheology" for additional discussion of particulate system rheology.)

As a general statement, the range of accurate measurement of most laboratory viscometers (for typical coatings fluids) is in the power law region. It may require extraordinary methods or special instrumentation to characterize fluid behavior in regions I or III.

SHEAR-THICKENING FLUIDS

We have seen above that shear thinning involves a shear-induced increase in order of a system. This allows the elements of a fluid to move or flow with minimum expenditure of energy. Conversely, shear thickening implies that shear has caused a decrease in order of a system. The resulting disordered system dissipates more energy during flow and hence is more viscous. An example of this is provided by the catastrophic increase in viscosity observed by Hoffman [19], which he attributed to the "buckling" or "log-jamming" of ordered, layered arrays of particles. Hoffman has recently reviewed the differing viewpoints on the mechanism of shear thickening [23].

A frequently encountered type of shear thickening behavior is dilatancy. Properly, dilatant behavior is shear thickening accompanied by an increase in volume of the fluid. It is most commonly observed in relatively concentrated disperse systems. In a dilatant system, the disperse phase particles are minimally lubricated by the liquid continuous phase. Furthermore, at rest, the particles of the disperse phase are in a random close-packed structure for which the interstitial volume is relatively minimal as well (Fig. 7). If the dispersion moves only slowly, adequate time exists for the meager liquid phase to flow sufficiently to maintain the dispersed phase in a "wetted" or lubricated state, and the system is able to maintain its close-packed structure. Faster or more forceful motion causes a liquid-starved condition because the interstitial volume increases as the system is deformed or made to flow (Fig. 7). Consequently, there is no longer enough liquid to lubricate the system. The particles are, therefore, incompletely wetted and forced flow would ultimately create microscopic voids, leading to fracture of the material. The surface of a dilatant material may appear dry when stressed due to the withdrawal of surface liquid into the increased interstitial volume. This can be seen when walking on wet sand on the beach. The resistance to deformation of the material can increase tremendously with increased deformation rate due to these effects.

During the course of a pigment grind operation, a fairly sudden maximum in viscosity is often seen and is an indication that a good grind (i.e., to primary particles) has been achieved. In fact, the surge in viscosity and power draw result from the grind having become dilatant. Dilatancy is desirable here because it facilitates energy transfer throughout the grind. Thus, dilatancy is frequently an indicator of the achievement of a stable dispersion of primary particles. In general, dilatant systems are not also thixotropic, and therefore will flow under even very low stresses. For this reason, coating systems in a dilatant state may suffer from rapid settling and be difficult to redisperse. For most coating operations, dilatancy is undesirable. Pumping of dilatant dispersions may result in high back-pressure in lines, excessive wear of system components, high power consumption, and loss of metering. In industrial rollcoating, dilatancy shortens coating lifetime on the roll, causing "dry edges" and loss of film thickness control.

Dilatancy is very sensitive to dilution and can be dramatically reduced or eliminated by a small reduction in solids. Also, addition of polymeric flocculants or electrolyte, or of a particulate phase of different particle size, or warming can alleviate undesirable dilatancy. Flow curve measurement is an excellent way to quantify the degree of reduction of dilatancy achieved by these measures.

Time-Dependent Fluids

Time-dependent fluids are those whose viscosity is a function of time, as well as shear rate (or shear stress). The most common such behavior encountered in coatings is time-dependent shear thinning or *thixotropy* [24]. Barnes has written a comprehensive review of the subject of thixotropy [25]. At constant shear rate and temperature, the viscosity of thixotropic fluids will fall, eventually reaching a constant value representing equilibrium between structure breakdown and restructuring processes. If the shear rate is changed, the viscosity will approach a new equilibrium value at a characteristic rate. This behavior is illustrated in Fig. 8, showing the way viscosity changes for a time-dependent system when the imposed shear rate (or shear stress) is changed in steps. Initially, the shear

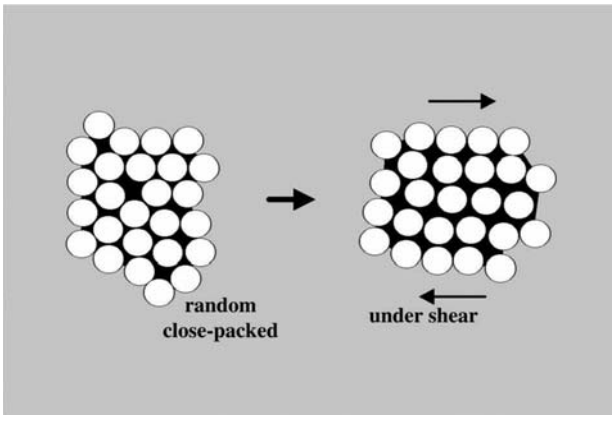

Fig. 7—Dilatant behavior is volume expansion under shear. Random close-packed structure gives way to less-efficient packing with necessary volume dilation.

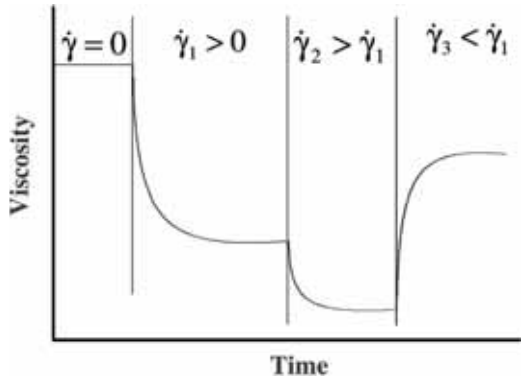

Fig. 8—Time-dependent fluid behavior. At $\dot{\gamma}$ = 0, viscosity is high (or infinite). Imposing $\dot{\gamma} > 0$ causes viscosity to fall exponentially, reaching new equilibrium value. Subsequent changes in $\dot{\gamma}$ result in re-equilibration of structure, hence viscosity.

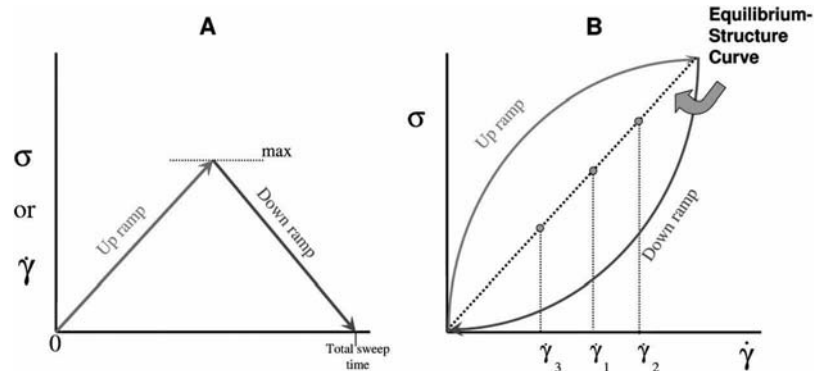

Fig. 9—(A) Shear rate or shear stress ramp experiment. Shear rate or stress increases linearly (or logarithmically) to pre-selected maximum over a selected sweep time period, resulting in a given acceleration gradient ($\dot{\gamma}$) or stress rate ($\dot{\sigma}$); (B) Thixotropic loop. Equilibrium structure curve (approximately bisecting loop) corresponds to data from experiment as in Fig. 8.

rate is zero, and the viscosity is very high or infinite for a thixotropic system. If a shear rate greater than zero is imposed ($\dot{\gamma}_1$), the viscosity drops exponentially, ultimately reaching a constant value. Increasing the shear rate to $\dot{\gamma}_2$ decreases the viscosity further to a new equilibrium value. A decrease of the shear rate to $\dot{\gamma}_3$ results in an exponential rise of viscosity to a higher equilibrium value. If, instead of a multiple steady-shear experiment, just described, we were to carry out a shear rate (or shear stress) ramp experiment [Fig. 9A], the time dependence would result in a loop [Fig. 9B]. The explanation of the loop is given below, but has to do with the fact that in a ramp experiment the equilibrium structure is never attained. The circuit in Fig. 9(*b*) is called a *thixotropic loop*. Roughly bisecting the loop is the equilibrium-structure curve generated from the equilibrium viscosity data of Fig. 8. The analogous time-dependent behavior for shear thickening materials has been called *rheopexy* (a rather rare phenomenon). The preferred term now for the latter is *antithixotropy*.

"Thixotropic Index" Test

We emphasize that the most important characteristic of thixotropic behavior is not shear thinning alone, but time dependence. The relatively slow change of viscosity provides a means of control of flow behavior and is the reason thixotropy is formulated into coatings. Hence, it is important to correctly characterize the time-dependent aspect of the behavior. For this reason, the so-called "thixotropic index" test is of limited benefit for characterization of such systems.

We will digress for a moment to discuss the thixotropic index test since it is very widespread in practice. This misnamed test determines the ratio of viscosities measured at arbitrary high- and low-shear conditions. ASTM Test Method D2196 specifies taking the ratio of viscosities measured on the Brookfield Synchro-Lectric viscometer at two speeds, representing a tenfold speed ratio. Since only equilibrium viscosities are measured, the test yields no information about time dependence and should be called the "shear-thinning index" instead (it is so termed in ASTM D2196). Its value, like many quality-control tests, is in its simplicity and "quick-and-easy" character, requiring no interpretation. As long as a given coating formulation changes little, so that the hidden kinetic factor would be expected to change little, the "thix index" can reveal when something has gone awry (i.e., can be useful as a gross indicator whether a formulation error has occurred). However, it is always possible that the recovery kinetics of the system might change, and this would go completely unnoticed if the thix index were the only test used to evaluate the rheology. Below, we will present test methods which can be almost as simple as the thix index, but which give more useful, relevant, and complete information about thixotropic systems.

Mechanism of Thixotropy

Thixotropy is formally defined as an isothermal, reversible sol-gel (fluid-solid) transformation [26]. As stated, it is experienced as a viscosity which is both time- and shear-dependent. Its origin is the breakdown under shear of internal fluid structure to smaller flow units, or the reassembly of structure from smaller units when shear is relaxed.

The mechanism of shear thinning in thixotropic (time-dependent) systems is different from that in pseudoplastic (time-independent) systems. In pseudoplastic systems, shear thinning is the consequence of order externally imposed by shear [14]. In thixotropic systems, an internally imposed, viscosifying structure exists at rest, and the viscosity falls because of the collapse of that structure under shear. (Flocculated systems possess extra mechanisms of energy dissipation [27]; therefore, their viscosity will be higher than that of a deflocculated dispersion of the same composition.) A further important difference between the two is in the amount of time the structure requires to respond to changes in shear rate. In the case of time-independent systems, rapid structural equilibration quickly accommodates to changes in shear rate. The accommodation process essentially is particle diffusion, which is rapid for submicron particles (see "Shear-Dependent Viscosity"). The viscosity (a measure of structure) thus always "keeps up" with changes in shear rate for such systems. For thixotropic systems, the rate of structural reorganization is slower than the experimental rate of change of shear rate ($\dot{\gamma}$) or slow with respect to the time of observation at constant shear rate. In a "shear rate ramp" experiment (see below), the structural breakdown always lags behind the ever-increasing shear rate, so that the viscosity on the "up" ramp will be higher than the equilibrium viscosity at a given shear rate. On the "down" side of the ramp, the rebuilding of structure lags behind the rate of reduction of

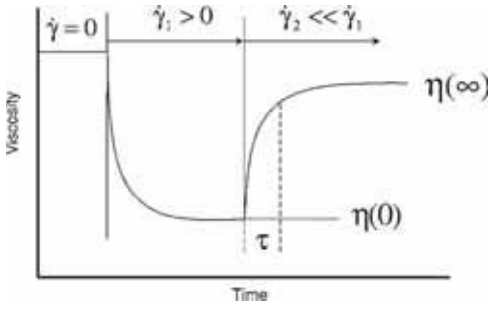

Fig. 10—Step-shear method for thixotropic recovery. High shear rate $\dot{\gamma}_1$ simulates application process, followed by low shear rate $\dot{\gamma}_2$, emulating film after application. Viscosity recovers from zero-time value $\eta(0)$ with a characteristic time constant τ, eventually reaching final level $\eta(\infty)$.

shear rate, so that the measured viscosity is always lower than the equilibrium value. Thus, a thixotropic loop is seen, the size of which should be proportional to the structural time constant for a given ramp time. Holding the shear rate constant, as in the description above, allows the structure breakdown process to "catch up." The viscosity then continues to change until equilibrium between structural breakdown and recovery rates is achieved.

Thixotropy Test Methods

Two common test methods for experimental characterization of thixotropy are the thixotropy index test, and the thixotropic loop test, described above. In the latter, a programmed increase and decrease of shear rate (or shear stress) is applied to a material [Fig. 9A], resulting in the generation of a loop [Fig. 9B]. The size of the loop can be obtained by numerical integration and is taken as an indicator of the rate of structural breakdown and recovery for a given ramp time (the larger the loop, the slower the breakdown-recovery rates). This method is a difficult one to do correctly, however, and is more complex than first appears. The result (loop size) depends on the shear history of the sample—the time interval since its last shear experience—and the magnitude of the shear undergone. It also depends on the shear rate (or shear stress) maximum in the loop experiment and the ramp rate ($\ddot{\gamma}$ or $\dot{\sigma}$).

A better method is one which puts the thixotropic material into a known state, i.e., having had a controlled shear experience, followed by the test itself. Such a method is the step-shear test (Fig. 10). In it, a high shear rate (order of 10^4 s^{-1} desirable) is applied to the material, allowing time for the viscosity (hence, structure) to reach equilibrium; then the shear rate is suddenly reduced to a very low value (e.g., order of 1 s^{-1}). The equilibrium amount of structure, which can exist at the lower shear rate, is greater than at the previous high shear rate, so reassembly of fluid structure occurs, accompanied by an approximately exponential rise of viscosity. Meaningful physical constants can be extracted from the data by fitting the following equation to the recovery curve

$$\eta(t) = \eta(0) + [\eta(\infty) - \eta(0)][1 - e^{-t/\tau}] \quad (18)$$

where $\eta(t)$ is the viscosity as a function of time, t, $\eta(0)$ the sheared-out viscosity (at time zero), $\eta(\infty)$ the infinite-time recovered viscosity level, and τ the time constant describing the recovery rate. The ratio $\eta(\infty)/\tau$, which may be termed the *Recovery Parameter,* has been found in our laboratories to correlate well to thixotropy-related properties such as sag resistance and air entrainment [28]. Table 3 shows data for two gel coat formulas, one sagging and one nonsagging. The conventional thix index results do not predict the sag behavior and, in fact, are opposite what would be expected from the observed behavior. The step-shear experimental parameters τ and $\eta(\infty)$ are given, along with their ratio. The nonsagging formula ("with additive") has both a shorter recovery time and a higher final recovered viscosity, and the recovery parameter takes both of these into account to predict significantly better sag resistance than for the "without additive" material.

The step-shear test puts useful thixotropy characterization within reach of any formulation laboratory, for it can be performed on an inexpensive viscometer (such as the Brookfield Synchro-Lectric or Wells–Brookfield Cone/Plate Viscometer) as well as on more sophisticated instrumentation. The latter offer advantages, of course, particularly with viscoelastic characterization capability. The ideal way to characterize thixotropic recovery is to break down the structure under high, steady shear (as in the step-shear method), then step down to a small-amplitude (small strain) oscillatory-shear test, as described by Dodge [29] (Fig. 11). The rebuilding of structure can then be followed by means of the viscoelastic parameters, which are sensitive probes of the fluid structure responsible for thixotropy. This method more faithfully mimics processes occurring in the relatively quiescent film after application. Fig. 12 shows the recovery curves of the viscoelastic moduli G' and G'' (see *The Viscoelastic Parameters and Their Measurement)* obtained from such a step-shear experiment. Note

TABLE 3—Gel coat thixotropy test data comparison: τ is the recovery time constant and $\eta(\infty)$ the recovered viscosity level from a step-shear experiment; $\eta(\infty)/\tau$ is the recovery parameter.

Composition	τ, s	$\eta(\infty)$, P	$\eta(\infty)/\tau$, P/s	Thix Index	Sag?
With additive	8.9	116	13	4.04	No
Without additive	18.2	97.3	5.4	4.24	Yes

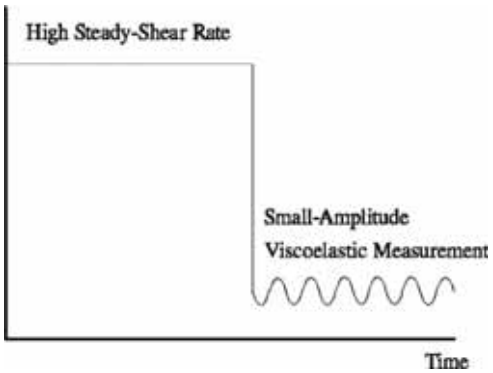

Fig. 11—Viscoelastic characterization of structural recovery by step-shear method using small-amplitude oscillatory strain for recovery phase.

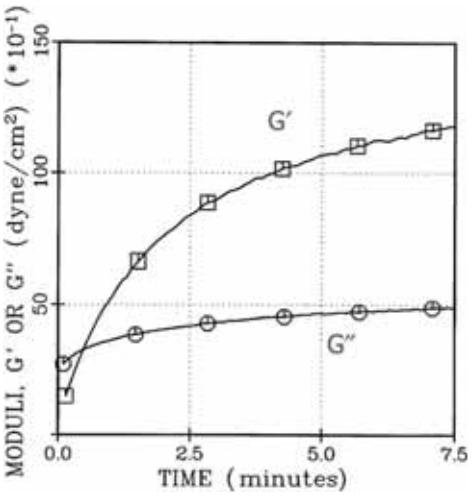

Fig. 12—Experimental curves of G' (elastic modulus, □) and G'' (viscous modulus, O) versus time for a viscoelastic step-shear experiment.

the transition from fluid to solid as the elastic modulus G' crosses over and exceeds the viscous modulus G''.

Plastic (Yield) Behavior

An ideal plastic material behaves as an elastic solid until a critical stress is applied, whereupon it will "yield" and become fluid. This critical stress is the yield stress, the minimum stress necessary to initiate flow. Ideally, the properties of a material exhibiting yield behavior would be those of an elastic, or "Hookean," solid, below the yield stress. For such materials, the steady-shear viscosity would be infinite (or undefined), the deformation linear with stress, and the yield value a material constant. For most real materials, however, deformation below the yield point is a combination of elastic strain and viscous flow. This is because interparticle forces ("secondary bonds") are comprised of a range of types, having a corresponding range of relaxation times [30]. As a consequence, the measured yield value will depend on the rate at which the stress is increased up to the point where flow occurs (the faster the rate of stress increase, the higher the measured yield value).[7]

Barnes and Walters [31] have suggested that many if not most materials with an apparent yield stress will be found, in reality, to have a high but finite viscosity if measured at sufficiently low stresses. In practical terms, yield stress behavior can have important consequences for the processing, stability, and application of coatings. There is quite clearly some sort of flow discontinuity that occurs at low stresses, the magnitude of which is apparently related to the number and strength of interparticle attractive forces [30,32]. The yield stress is therefore an "engineering reality" [33] that must be taken into account when formulating paints or dispersions. A yield stress may be desirable or undesirable depending on the process in question. Materials with a yield stress will often exhibit thixotropy and viscoelasticity as well [34].

[7] For this reason, yield stress values cited in the literature are meaningless unless the exact experimental methodology is provided.

Static Versus Dynamic Yield

There are two types of yield stress that may be measured. The first is the static yield stress, measured by the startup of flow from nonflowing conditions. The second is the dynamic yield stress, which is the shear stress at which a presently fluid material suddenly turns solid (or exhibits a sharp flow discontinuity). Experimental methods exist for measuring both types of yield values [35], and one should measure the type that is relevant to the process in question. For example, for long-term suspension of solids or for start-up flow in pumps, the static yield stress is important. Postapplication leveling and sag behavior on the other hand would be governed by the dynamic yield stress, but the kinetics of structural recovery (rate of approach to the yield point) must also be taken into account (see thixotropy in "Time-Dependent Fluids"). Some have used curve-fitting techniques to obtain a value for the yield stress by fitting flow curve data to a rheological model. The Bingham, Herschel-Bulkley, and Casson models contain a yield stress term and have been commonly used to obtain a yield stress from measured flow behavior. Such methods are questionable, however, since one is attempting to infer a property of the solid state from behavior of a fluid [27,36].

Yield Stress Test Methods

Startup-of-flow methods include the use of penetrometer-type instruments such as a thermomechanical analyzer, where increasing force is applied to a standard probe. The yield stress is determined as the break point of a force-penetration curve [37].

An instrument known as a "controlled-stress" rheometer is well-suited to measurement of yield stress and other properties of structured materials. For this type of instrument, the shear stress is the independent (or controlled) variable, while the dependent (or measured) variable is the shear rate. This allows the applied stress to be gradually increased from a low value as the instrument registers zero shear rate (i.e., infinite viscosity) until the applied stress reaches the yield value, whereupon the viscosity becomes finite. This value is recorded as the measured yield stress.

Another fairly novel method employs a special vaned rotor to remedy problems of wall slip with filled materials [38–40]. The vaned rotor consists of rectangular blades or vanes fixed to a rotating shaft. Advantages of this geometry are as follows: (1) There is little disturbance of the sample when this type of probe is inserted, and (2) when the rotor turns, the material moves as if a "solid cylinder." Thus, the yield surface is within the material itself, avoiding problems of wall slip.

With the vaned rotor attached to a "controlled-strain-rate" type rheometer, the yield stress is measured by monitoring the torque as the geometry is rotated at a constant low rate. The torque will go through a maximum, corresponding to concerted yielding along the "virtual" cylindrical surface defined by the vane radii. The yield stress is related to the maximum torque T_m according to [39]

$$\sigma_0 = \frac{T_m}{K} \tag{19}$$

where K is the vane geometric constant given by

$$K = \frac{\pi D^3}{2}\left(\frac{H}{D} + \frac{1}{3}\right) \tag{20}$$

where D is the rotor diameter and H the vane height.

Using a controlled-stress rheometer, measurement of the yield stress using the vaned rotor is straightforward. The torque is ramped slowly and the stress at which a finite displacement is detected is reported as the yield stress.

Practical Aspects of Yield Behavior

Some of the practical consequences of yield behavior occur in the processing of pigment dispersions, for example. Dispersions with high yield stresses may be difficult to dispense accurately or reproducibly via automatic metering systems. Pumps may actually refuse to move or such materials may cavitate while being pumped; solenoid valves may "freeze." Coatings with significant yield stresses may exhibit poor leveling [1] since, as the shear stress decreases during the course of the leveling process, the material effectively becomes immobile when the dynamic yield stress is reached.

On the other hand, a small yield stress can be of great value in inhibiting settling of particulate suspensions. The shear stress exerted on the surrounding medium by a spherical particle falling under the influence of gravity may be calculated using the following relationships:

$$\sigma = \frac{F_g}{A} = \frac{\text{Force of gravity on particle}}{\text{Surface area of particle}}$$

$$F_g = \frac{4}{3}\pi R^3(\rho_p - \rho_l)g; \quad A = 4\pi R^2$$

$$\sigma_g = \frac{R}{3}(\rho_p - \rho_l)g$$

where R is the particle radius, ρ_p is the particle density, ρ_l is the liquid density, and g is gravitational acceleration. For a titanium dioxide particle of radius 0.2 mm and density 4 g·cm^{-3}, the shear stress acting on the particle due to gravity is about 0.2 dyne/cm^2. To prevent settling of such a particle, the surrounding medium need only resist with an opposing stress of greater than 0.2 dyne/cm^2. Even this, alas, is impossible for a Newtonian liquid, be it water or honey since it will flow under all stresses no matter how small (it is only a question of how slowly). A pigment particle will inevitably settle out of such a fluid, especially for viscosities of practical magnitudes. However, if the suspending medium possesses a yield stress equal to or greater than the particle shear stress, the particle "thinks" it is suspended in a solid and will remain suspended indefinitely. This argument assumes more or less ideal yield behavior, which, as described above, may rarely be encountered. A medium with a measured yield stress of apparently sufficient magnitude may or may not permit the particle to settle over long periods of time due to the possibility of viscous flow below the apparent yield point. In addition, ambient vibration can break the structure locally around a particle, leading to settling even where the measured yield stress appears adequate. Therefore, to ensure practical stability, one should build in a higher yield value than that calculated from the above.

Elastic Liquids (Viscoelasticity)

In ideal viscous flow, all input energy is converted either to heat or energy of motion. None is stored (i.e., none is converted into potential energy). Therefore, viscous flow results in irreversible deformation. Newtonian liquids show essentially ideal viscous (also called "inelastic") behavior over a wide range of deformation rate. For ideal elastic ("Hookean") substances, all the energy of deformation is stored, similar to a stretched rubber band. Consequently, elastic deformation is not permanent, but is in fact completely reversible. Real materials can display a mixture of elastic and viscous character, in varying degrees. Hence, the term *viscoelastic* is applied to such materials. Not all non-Newtonian fluids have significant elastic properties, but many do. Significant elasticity in fluids generally indicates the presence of some association network or microstructure. That is, elementary flow units are linked together in some fashion such that the structural relaxation time (see below) is measurably long. This structure, and particularly the destruction and rebuilding process that occurs during and after coating application, can have great consequences for application and film formation processes. An example of this is the influence of elasticity on leveling of an applied coating [41] (see also Massouda [42], Glass [43], and Cohu and Magnin [44]).

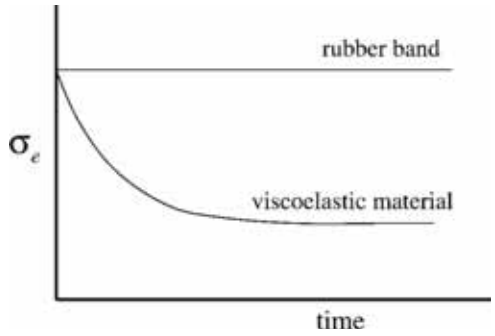

Fig. 13—Viscoelastic stress-memory loss: stretch-force experiment. Rubber band is cross-linked polymer, does not relax stress (σ_E) when stretched. Viscoelastic material can accommodate to strain by molecular motion (viscous flow), allowing elastic stress to decay.

As the term implies, viscoelasticity refers to a material response, which is a combination of viscous and elastic behavior. Viscous flow superimposed on elastic strain results in the "relaxation," or gradual disappearance, of stress within the strained object. This is manifested as an imperfect, or fading, stress memory. Fig. 13 illustrates the material response to an applied elongational stress for a material with permanent stress memory (e.g., rubber band) and one with fading stress memory (e.g., "bouncing putty").

The Viscoelastic Parameters and Their Measurement

A convenient way of experimental characterization of viscoelastic materials is by alternating the direction of strain (or stress). Most often, a sinusoidal deformation is employed (Fig. 14). The strain amplitude must be kept small so that the material response remains in the linear viscoelastic regime, where stress and strain are linearly related.[8] For perfectly elastic behavior (Hookean spring), the stress and strain are "in phase" with each other. That is, upon

[8] This is a requirement because the equations used are valid only for linear viscoelasticity.

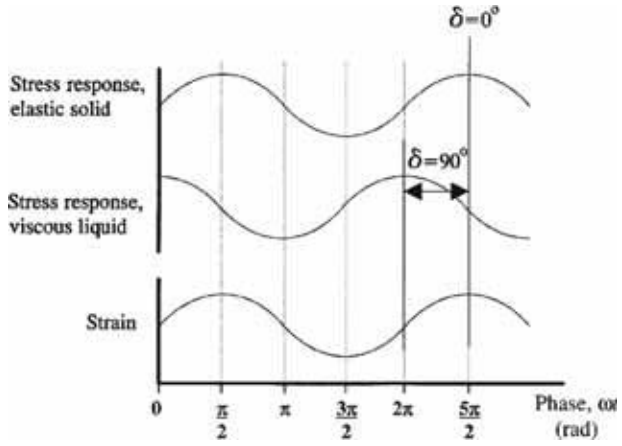

Fig. 14—Stress response to oscillatory strain for ideal viscous and elastic bodies. Stress is in phase with the strain for an elastic solid; the stress leads the strain by phase shift δ =90° for an ideal viscous liquid.

deformation, the maximum stress and maximum strain occur at the same instant in time. However, if there is any viscous (energy-loss) component in the material response, the stress and strain maxima will not be coincident but will be "out of phase." This happens because viscous flow continually relieves the stress within the material, causing the stress to reach a maximum and die away before the strain maximum. That is, as the rate of strain decreases near the maximum (or minimum) of the strain sine wave, stress relaxation "catches up" and overtakes the stress-building effect of the strain. Thus, the maximum in the stress must occur before the maximum in strain, and will do so earlier in the deformation cycle the more rapid is the viscous relaxation. The separation of the stress and strain maxima is called the *phase shift* (or *phase angle,* the angular part of a complete cycle in degrees or radians represented by the phase shift). The phase shift is often given the symbol δ. The faster the viscous stress-relaxation process, the earlier in the cycle the stress maximum will occur, i.e., the larger the phase shift will be. The limiting value of the phase angle for purely viscous liquids is 90° (see Fig. 14). This is because for sinusoidal deformation the maximum strain rate (maximum slope of the strain sine wave) occurs 90° ahead of the maximum strain, and for Newtonian liquids the stress is proportional to strain rate. Therefore, the maximum stress must occur at the maximum strain rate, which corresponds to a phase shift of 90°.

The derivation of viscoelastic parameters from a sinusoidal shear experiment begins with the calculation of the complex shear modulus G^*. This is simply the ratio of the maximum stress, σ_0, to the maximum strain, γ_0 ($G^* = \sigma_0/\gamma_0$). From G^* may be separated G' the modulus of elasticity (storage modulus) and G'', the viscous modulus (loss modulus). Fig. 15 demonstrates the geometric relationship of G^* to its in-phase and out-of-phase components G' and G'', governed by the phase angle δ. It is obvious from geometry that when δ is zero, $G^* = G'$, and when δ =90°, $G^* = G''$. The physical meaning is that when δ = 0, the measured modulus is comprised solely of an elastic response, and when δ = 90°, the modulus is due entirely to a viscous response. This follows from the discussion of the phase shift, above. By trigonometry, $G' = G^*\cos\delta$ and $G'' = G^*\sin\delta$. Alternately

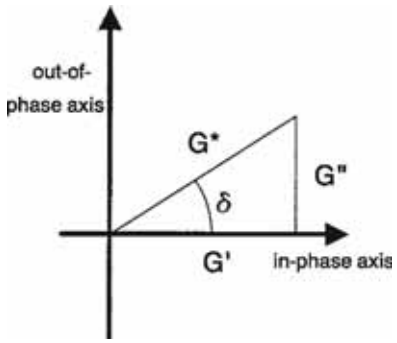

Fig. 15—Viscoelastic relationships in the complex plane.

stated, G' is the component of the complex shear modulus, which is in phase with the strain. G' therefore represents the elastic part of viscoelastic behavior. The viscous component (G''), on the other hand, is derived from the part of the modulus which is out of phase with the strain but in phase with the strain rate.

Consider a dynamic test in which a sinusoidally varying strain is applied to a viscoelastic material. The angular frequency of the deformation is given by $\omega = 2\pi f$, where f is the frequency of oscillation (s^{-1}) and ω is in rad/s. Now, the amplitude of the strain with time is given by

$$\gamma = \gamma_0 \cos \omega t \tag{21}$$

which describes a cosine wave of maximum amplitude γ_0 and period $1/\omega$. The strain rate experienced by the material is then

$$\dot{\gamma} = -\omega\gamma_0 \sin \omega t \tag{22}$$

The oscillating strain produces a stress response

$$\sigma = \sigma_0 \cos(\omega t + \delta) \tag{23}$$

where δ is the phase shift, advancing the phase of the stress relative to the strain. Eq (23) may be equivalently written [45]

$$\sigma^* = \sigma_0 \cos\delta \cos\omega t - \sigma_0 \sin\delta \sin\omega t \tag{24}$$

which describes a complex stress where, by complex plane relationships analogous to Fig. 15, $\sigma_0 \cos\delta$ is the stress component in-phase with strain and $\sigma_0 \sin\delta$ the stress component that is out-of-phase with the strain (but in-phase with the strain rate). We therefore can define a dynamic viscosity η' as the quotient of the stress in-phase with the strain rate, divided by the strain rate

$$\eta' = \frac{\sigma_0 \sin\delta}{\dot{\gamma}_0} = \frac{\sigma_0 \sin\delta}{\gamma_0\omega} = \frac{G^* \sin\delta}{\omega} = \frac{G''}{\omega} \tag{25}$$

The above expression is obtained using the relationships γ_0 (strain-rate amplitude) = $\gamma_0\omega$ and $G^* = \sigma_0/\gamma_0$.

The magnitudes of G'' and G' reveal the relative importance of viscous and elastic behavior in the mechanical response of a material. In Fig. 15, again by trigonometry, the tangent of the phase angle equals the ratio G''/G'. Thus, tan δ quantifies the balance of energy storage and loss measured under particular conditions of temperature, pressure, and frequency or rate of deformation. For solids, tan δ *as*

a function of frequency can be useful to predict the likelihood of brittle or ductile failure of a polymer or the sound absorption or vibration damping properties. For liquids, tan δ can monitor the progress of fluid restructuring in thixotropic recovery. The latter may be useful in computing sag resistance, for when tan S becomes less than unity the system has essentially become immobilized (i.e., reached a "dynamic yield point"). When tan $\delta > 1$, viscous flow (i.e., a steady-state viscosity) is possible. When tan $\delta < 1$, however, the material is more elastic than viscous (i.e., a percolating network extends throughout the bulk, and it is essentially an elastic solid).

Viscoelastic Models

It turns out that viscoelasticity can be rather realistically modeled by simple mechanical analogues. These are useful not only as an aid to conceptualization of viscoelastic behavior, but also in helping to understand the elementary mathematics of viscoelasticity. As we have said, viscoelasticity is a combination of two idealized behaviors: Hookean elasticity and Newtonian viscosity. The mechanical analogue of Hookean behavior is a spring of force constant G, and that of Newtonian flow is a "dashpot" (a piston-in-cylinder filled with a fluid of viscosity η). These elements are combined in various ways to model viscoelastic mechanical response.

To build our first model we will connect a spring and dashpot in series (Fig. 16), an arrangement known as the Maxwell model. To imagine what response the model has, let us apply a constant stress σ_0 to one end, the other being fixed. By the way, our dashpot is considered to be infinitely long so that the piston never runs out of travel. This being the case, one can see that an equilibrium strain would never be reached but rather the dashpot would continually move as long as the stress is applied. Since the model can "flow" without limit, this is obviously a model for viscoelastic liquids (sometimes called "elasticoviscous"). We have just described what is known as a creep experiment, in which a sudden stress σ_0 is applied, and the evolution of the strain, or deformation, is followed with time. The creep of a Maxwell liquid is not very interesting, however. The strain-time curve consists merely of a straight line with intercept equal to σ_0/G and slope of σ_0/η [Eq (28)].

We will use the Maxwell model to illustrate how equations describing viscoelastic behavior may be derived. Just as the stress is the same in every part of a stretched string, so is the stress the same on both elements for the Maxwell model, and also, therefore, the rate of change of stress is identical as well

$$\sigma_{\text{total}} = \sigma_{\text{clastic}} = \sigma_{\text{viscous}} (= \sigma_0) \tag{26}$$

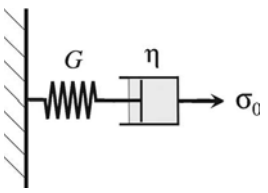

Fig. 16—Maxwell model for viscoelastic liquid behavior. G is force constant (modulus) of spring, η is the viscosity of the dashpot fluid, and σ_0 is the applied stress.

and

$$\dot{\sigma}_T = \dot{\sigma}_E = \dot{\sigma}_V \tag{27}$$

Furthermore, the total strain is clearly the sum of the strains undergone by the two elements

$$\gamma_T = \gamma_E = \gamma_V = \frac{\sigma_E}{G} + \frac{\sigma_V t}{\eta} \tag{28}$$

The expression on the right follows from the definition of the modulus ($G = \sigma/\eta$), Eq (4), and the fact that $\gamma = \dot{\gamma}_t$. It is also true that

$$\dot{\gamma}_T = \dot{\gamma}_E = \dot{\gamma}_V = \frac{\dot{\sigma}_E}{G} + \frac{\sigma_V}{\eta} \tag{29}$$

An alternative to the creep method that is particularly useful for viscoelastic solids is to apply a sudden deformation and follow the decay of stress with time. This is similar to the experiment depicted in Fig. 13 and is known as *stress relaxation*. Sudden imposition of a strain γ_0 results in instantaneous lengthening of the spring. The dashpot experiences, in turn, an initial stress σ_0 from the extended spring, causing a gradual movement of the dashpot's piston, resulting in relaxation of the stress. By manipulation of the above equations, we can arrive at a quantitative way of describing this relaxation process.

Since the strain γ_0 in a stress-relaxation experiment is constant, the total strain rate $\dot{\gamma}_T = 0$. Therefore, from Eq (29)

$$\frac{\sigma_V}{\eta} = -\frac{\dot{\sigma}_E}{G} = -\frac{d\sigma/dt}{G} \tag{30}$$

rearranging

$$\frac{d\sigma}{\sigma_V} = -\frac{G}{\eta} dt \tag{31}$$

Integrating Eq (31) from time 0 to time t results in the Maxwell stress relaxation expression

$$\sigma = \sigma_0 e^{-Gt/\eta} \tag{32}$$

Fig. 17 illustrates the decay of stress in a constant strain or stress relaxation experiment for the Maxwell model, described by Eq (32). Note that the quantity η/G has the

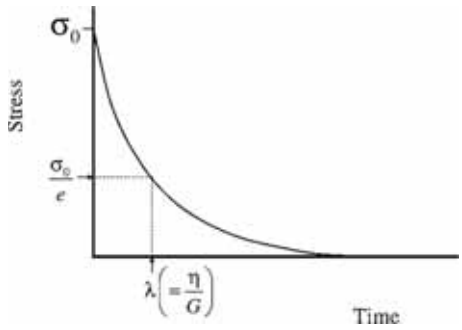

Fig. 17—Stress relaxation experiment. A fixed strain is imposed, creating an initial elastic stress σ_0, which relaxes viscously with time constant λ (=η/G). λ is the time at which the stress has decayed to σ_0/e.

dimension of time. We will assign to this quantity the symbol λ and refer to λ as the stress-relaxation time constant. It can be seen from Eq (32) that when $t = \eta/G$, $\sigma = \sigma_0/e$. Therefore, λ represents the time required for the stress to fall to 1 /*e* of its initial value (Fig. 17) and gives a convenient way of quantifying the rate of decay of stress in viscoelastic materials.

The time constant, λ, could also be called the stress memory time constant since it is related to the time it takes for a viscoelastic material to "forget" its initial elastic stress level when subjected to a constant strain. As such, λ determines the role that viscoelasticity plays in an industrial process. That is, elastic materials generate an "elastic extra stress" when deformed, which can result, among other things, in the stabilization of fluid structures that would ordinarily collapse too quickly to be of consequence. These include, for example, liquid fibers and webs, which result in roller spatter [46], and the formation of ribs on rollcoating [47]. The latter effects are particularly sensitive to extensional viscoelasticity [48] (see "Extensional Rheology.") The magnitude of the undesirable effect will depend on the rate at which the elastic extra stress decays or "relaxes," as we will see below.

In modern rheometers, sinusoidal oscillation is a common method of viscoelastic characterization. (Creep is also available as a viscoelastic test mode for controlled-stress instruments and stress relaxation for controlled-rate instruments—see below.) Equations derived for the Maxwell model [49,50] show how the viscoelastic time constant λ may be obtained from the oscillatory data

$$\eta'\omega = G'' = \frac{G_\infty \omega\lambda}{1+\omega^2\lambda^2} \tag{33}$$

and

$$G' = \frac{G_\infty \omega^2\lambda^2}{1+\omega^2\lambda^2} \tag{34}$$

from which

$$\tan\delta = \frac{G''}{G'} = \frac{1}{\omega\lambda} \tag{35}$$

where G_∞ is the plateau modulus (limiting value of G' reached at high frequency = Maxwell spring constant). Eq (35) says that when G' and G'' cross over (tan δ=1), $\lambda = 1/\omega_c$ (ω_c is the crossover frequency). The plateau modulus can be obtained from Eq (34), as well, since at the crossover point $G_\infty = 2G'c$. Similarly, at crossover, the zero-frequency plateau viscosity, $\eta_0 = 2\eta'_c$ [from Eq (33)].

If the mechanical elements are connected in parallel rather than in series, they each experience identical strain, but the stresses are now additive. This arrangement is called the Kelvin–Voigt model (Fig. 18). Because the elements are now in parallel, the Kelvin–Voigt model can only undergo finite strain, limited by the extensibility of the spring. Therefore, this is a model for a viscoelastic solid below its yield point. Equations for creep, stress relaxation, and tan δ for the Kelvin–Voigt model are:

Kelvin–Voigt creep

$$\gamma = \frac{\sigma_0}{G}(1-e^{-t/\lambda}) \tag{36}$$

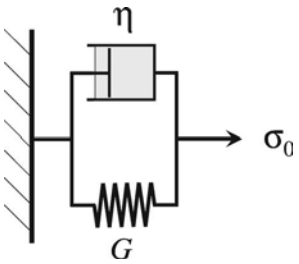

Fig. 18—Kelvin-Voigt model. Symbol definitions same as Fig. 16.

Kelvin–Voigt stress relaxation

$$\sigma = \gamma_0 G \tag{37}$$

and

$$\tan\delta = \omega\lambda \tag{38}$$

These equations describe an exponentially increasing strain at constant stress [see Fig. 19 and Eq (36)] and a nonrelaxing stress at constant strain [Eq (37)], respectively.

The Maxwell and Voigt models, by themselves, are too simple to accurately describe most real viscoelastic materials. However, a Maxwell element connected in series with a Kelvin–Voigt element turns out to model the linear viscoelasticity of many real systems rather well. Fig. 20 shows such an arrangement, known as the Burgers model. For completeness (and also because an error in the Burgers stress-relaxation expression has crept into the literature), equations describing creep and stress relaxation behavior for the Burgers model are given:

Burgers creep

$$\gamma = \frac{\sigma_0}{G_2} + \frac{\sigma_0 t}{\eta_2} + \frac{\sigma_0}{G_1}(1-e^{-t/\lambda_1}) \tag{39}$$

Burgers stress relaxation

$$\sigma = \gamma_0 G_2 e^{-t/\lambda_2} + \gamma_0 G_1 \tag{40}$$

where $\lambda_1 = \eta_1/G_1$ and $\lambda_2 = \eta_2/G_2$. The creep and stress relaxation behavior for the Burgers model are shown in Figs. 21 and 22. Modern rheometers of the type known as "controlled stress" (see "Rotational Instruments") are capable of performing creep measurements. Viscoelastic constants

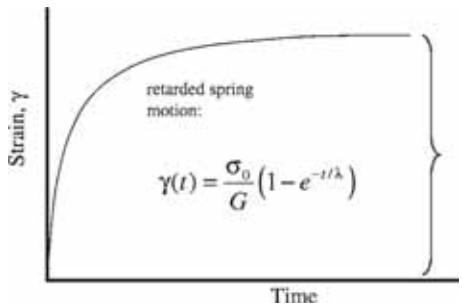

Fig. 19—Kelvin-Voigt creep experiment. At constant applied stress σ_0 the strain γ increases exponentially with time constant λ ($=\eta/G$).

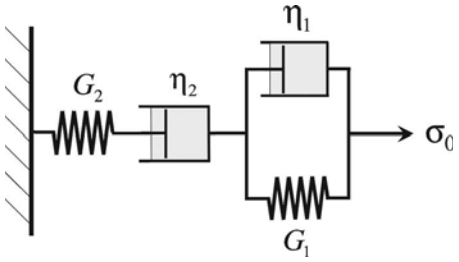

Fig. 20—Burgers model. Symbol definitions same as Fig. 16. Subscript 1 refers to the Voigt element; subscript 2 to the Maxwell element.

can then be extracted from the data by analysis according to one or more of the above models.

Viscoelasticity and Industrial Processes

The role of viscoelasticity in an industrial process depends on the rate (or frequency) of deformation. Put another way, the response of a viscoelastic material depends on how long a stress is applied ($1/\omega$), relative to the time required for any elastic "extra" stress to decay. This suggests taking a ratio of the stress relaxation time λ to the time (duration) of the process stress, t

$$De = \frac{\lambda}{t} \tag{41}$$

This ratio is a defined rheological term known as the Deborah number, *De*. It is named for the Biblical prophetess Deborah, who prophesied that the "mountains flow before the Lord" [51]. This is a perfectly accurate statement (long before being verified by the science of geology) of the fact that, on God's time scale, rock formations can be observed to undergo permanent deformation, or flow. In other words, if the stress time scale, t, greatly exceeds the relaxation time, λ ($De \ll 1$), the material will respond as a viscous fluid (because elastic stress has time to decay). Conversely, if $De \gg 1$, the stress duration is too brief to provide an opportunity for viscous relaxation, and the material behaves as if an elastic solid. Thus, the Deborah number quantifies the proportion of elastic to viscous control of a process. This is one reason why a determination of the viscoelastic properties of paints and coatings is important. Keunings and Bousfield [41] give the following expression for the effect on leveling rate a of elastic extra stress, through the relaxation time constant λ

$$\alpha = \frac{\alpha_{Newt}}{1 = \lambda\alpha_{Newt}} \tag{42}$$

where α_{Newt} is the leveling rate in the absence of viscoelastic relaxation. Since the Newtonian leveling rate is always positive, elasticity ($\lambda > 0$) always retards leveling, in the above expression. Eq (42) can be adapted to the situation of a typical paint, and the influence of elastic-stress relaxation is seen in Table 4.

To be sure, real materials may not exhibit simple exponential stress decay (i.e., a single relaxation time), but rather may possess a spectrum of relaxation times. However, the mechanical response will be dominated by a "mean" relaxation time (or sometimes the longest relaxation time [41]), obtained from experiments such as described in foregoing sections. Simple viscoelastic dispersions can show Maxwellian behavior with a single relaxation time [52,53].

One of the reasons that associative thickeners (ATs) have been so successful in being able to thicken paints without at the same time adversely affecting flow and leveling is no doubt due in part to their low elasticity. Even though ATs generate a three-dimensional network structure within the fluid,[9] they often have negligible G' values, in contrast to typical cellulosic thickeners, for example. This is believed to be due to the extreme lability of the micellar junctions of the associative network, resulting in very short network relaxation times [52,54]. Thus, the decay of elastic stress in ATs is so rapid that such stresses are virtually unobserved ($De \ll 1$).

As stated before, the process consequences of viscoelasticity are due in part to the stabilization of otherwise unstable liquid structures by the elastic "extra stress." Thus, liquid fibers and "webs," which would ordinarily collapse by surface tension, are stabilized, producing, for example, excessive rollcoat spatter (or "misting") and ribbing, and inhibiting atomization of sprayed materials. The importance of viscoelasticity for a particular process

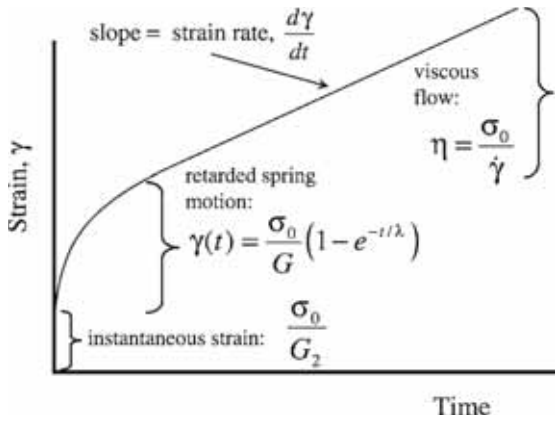

Fig. 21—Burgers creep experiment. Under constant applied stress σ_0, the Burgers model undergoes instantaneous deformation of magnitude σ_0/G_2. The next segment of the curve is retarded spring motion where strain increases exponentially with time. Finally, the spring is fully extended and viscous flow occurs with a constant strain rate $d\gamma/dt$.

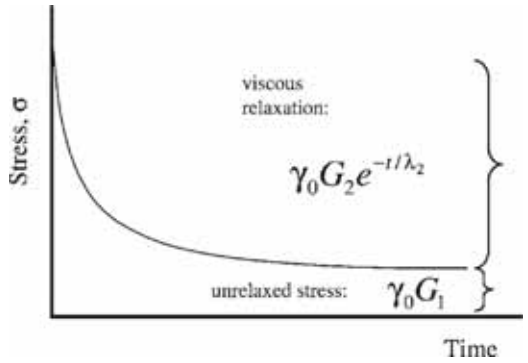

Fig. 22—Burgers model stress relaxation. Imposition of constant strain γ_0 causes stress which decays exponentially, governed by the relaxation time λ_2 ($=\eta_2/G_2$). Voigt element contributes unrelaxed stress $\sigma_\infty = \gamma_0 G_1$.

[9] See Chapter 33—Thickeners and Rheology Modifiers.

TABLE 4—Leveling rate dependence on Maxwell relaxation time, λ. α = *da*/*dt*, where a = roughness amplitude, and $t_{1/2}$ = time for a→0.5a_0 (initial amplitude).

λ, s	0.0	0.1	1	10	50	100
α, s^{-1}	34.5	7.75	0.972	0.0997	0.02	0.01
$t_{1/2}$	0.02	0.09	0.67	6.95	34.7	69.3

is gauged using the Deborah number, by the ratio of the stress-relaxation time constant to the time duration of the process stress. Of course, both the magnitude and lifetime of the elastic stress will be important, for together they will govern the degree of stabilization.

The analysis of the industrial problem of viscoelastic effects is complicated by the fact that many processes, particularly of coatings application, involve strain magnitudes beyond the range of linear viscoelasticity. Approaches to nonlinear viscoelasticity exist, but are beyond the scope of this chapter. Quantitative prediction of viscoelastic effects would require the use of a model for the fluid behavior, or viscoelastic constitutive equation, also outside the scope of this presentation. However, it is often possible to build experimental correlations between coating elasticity and performance problems, so that guidance may be provided for formulation efforts to solve them.

For most modern coatings, in particular, the origin of elasticity is likely to be an associated structure built up from a dispersed phase rather than polymeric entanglement. Such particulate flocs are generally shear-sensitive and are reduced or destroyed by high-shear application processes. The elastic modulus G' will be seen to decrease with increasing strain and strain rate outside the linear regime. Thus, in most cases, G' is a measure of structure that has its greatest effect at low strain and strain rate (unless the elastic character is due to polymeric entanglement). Therefore, under most conditions of application, structure (and elasticity) is destroyed and must rebuild in the applied film. Herein, it is seen that thixotropy and viscoelasticity are kindred phenomena for disperse systems.

EXTENSIONAL RHEOLOGY

In addition to simple shear, the other important mode of deformation that is important for coatings is extensional (or elongational) deformation. Extensional or "stretching" deformation causes an increase in length and decrease in cross section of an object. In a simple shear field, particles or polymer coils (i.e., the flow units) rotate with a velocity $\dot{\gamma}/2$. The rotational motion lessens the friction between the solvent and solute particles. In an extensional flow, this rotational accommodation to the flow field is not possible because there is no velocity gradient normal to the flow direction. The separation of flow units is thus more costly in terms of energy dissipation due to friction. Thus, the viscosity of a Newtonian fluid in extension turns out to be three times greater than its viscosity measured in shear (Trouton rule).

The extensional viscosity (η_e) is calculated as the ratio of tensile stress to extensional deformation rate

$$\eta_e = \frac{\alpha_e}{\dot{\varepsilon}} \tag{43}$$

The strain in extension is usually defined as a Hencky strain, $\varepsilon = \Delta l/l_0$, where l_0 is the original length and Δl the increase in length under tensile stress σ_e. The Hencky strain rate is then the time derivative of the strain or

$$\dot{\varepsilon} = \frac{1}{l}\frac{dl}{dt} = \frac{d(\mathrm{In}\, l)}{dt} \tag{44}$$

Extensional Viscosity in Coatings Processes

Many coatings processes involve stretching (elongational) flows (Table 1) and when coatings can support large extensional stresses (i.e., possess high extensional viscosity) performance can be dominated by such flows. As mentioned, the viscosity of a Newtonian liquid in extension is three times that measured in shear. For non-Newtonian fluids, the Trouton ratio $[\eta(\dot{\varepsilon})/\eta(\dot{\gamma})]$ can be as much as 10^4. Furthermore, whereas the shear viscosity is usually a decreasing function of shear rate, extensional viscosity frequently displays strong extensional strain rate thickening. For example, Lu [55] observed that polyacrylamide thickeners in latex paint systems showed extensional thickening behavior, whereas hydroxyethyl cellulose-type thickeners did not. Coatings application processes are generally high strain rate, so it is clear that η_e can possibly dominate the mechanical response, generally leading to detrimental consequences. Extensional stresses can stabilize liquid "webs" and fibers, such as form in direct rollcoating, allowing them to grow large instead of dissipating. This can result in heavy ribbing and "misting" (roll spatter) [56]. On the other hand, the breakup of a liquid jet to form atomized droplets in spray application is suppressed by a high extensional viscosity because the liquid fibers formed intermediary to droplet formation are inhibited from disintegration. J. E. Glass has been the chief proponent of the study of extensional viscosity in relation to paint performance, correlating it to roller spatter [46] and the performance of sprayed coatings [57]. Massouda did a clever and, unfortunately, largely overlooked study of the relationship of extensional stress measurements to viscoelastic relaxation kinetics and thence to spattering of paints [42].

Extensional Viscosity Measurement

There have been, unfortunately, few commercial instruments suitable for extensional measurement on coatings. The Spin-Line Rheometer (SLR) formerly offered by TA Instruments, utilizing the fiber-spinning geometry, and the Rheometrics (now part of TA Instruments) RFX rheometer, using opposed-nozzle flow to measure extensional forces, are no longer commercially available. However, the recent introduction by Thermo Electron Corporation of the CaBER Rheometer (Capillary Breakup Extensional Rheometer) provides a promising method of extensional rheometry that is appropriate for paints, adhesives, inks, gels, and polymer solutions. With the necessary electromechanical design and fabrication resources, one might attempt to build a simple extensional rheometer, perhaps patterned after that of Gupta [58]. The relatively simple technique of convergent flow analysis was used by Lu for measuring extensional properties of latex paints [55]. An overview of extensional rheometry has been published by James and Walters [59].

POLYMER MELT AND SOLUTION RHEOLOGY

High-polymer solution rheology is a subject of relatively little interest with respect to coatings due to the shift from solvent-borne to environmentally compliant technologies, such as waterborne, higher solids, and powder coatings. The polymers used for high solids and powder coatings are little more than oligomers in order to achieve necessary flow for satisfactory processing and film formation. Even the polymers used in solvent-borne varnishes and paints are below the entanglement molecular weight M_c, hence both their neat and solution rheology are Newtonian. Similarly, powder coating melts are Newtonian until near gelation [60]. The viscosity of polymer solutions below M_c is proportional to the weight-average molecular weight, M_w

$$\eta_0 = KM_w (M_w < M_c) \tag{45}$$

where K is a constant dependent on chain flexibility (T_g), polymer-solvent interaction, temperature, etc. If $M_w > M_c$, the motion of entangling polymers becomes much more complex, and the viscosity now depends on M_w raised to the power of approximately 3.4 [61]

$$\eta_0 = KM_w^{3.4} (M_w > M_c) \tag{46}$$

The viscosity of polymermelts follows a similar relationship. It should be noted that polymers having highly polar or hydrogen-bonding functionalities (such as commonly used in high-solids formulations) can show nonlinear dependence of viscosity on molecular weight even below M_c due to transient intermolecular associations [62].

The sole use of high-polymer binders in coatings today is where they exist as a separate phase dispersed in a liquid carrier medium[10]. Such materials are known as polymer latexes, or latex dispersions Because the latex polymer is segregated from, and therefore non-interacting with, the solvent, the rheology of latexes is much simpler than for the same high polymer in the solution state. The rheology of polymer dispersions will be discussed below.

DISPERSION RHEOLOGY

Dispersions of solids in liquids, for example, titanium dioxide particles dispersed in a liquid medium, play a central role in the manufacture and performance of coatings. Fully dispersed, stable dispersions favor the attainment of optimum intrinsic properties, improved process ability and workability, improved storage stability (shelf-life), and can provide higher solids at application viscosity. Rheology is particularly useful for dispersion characterization because of its sensitivity to the microstructure. Both stability and quality of dispersions can be evaluated. Dispersion rheology has two broad aspects: (1) The dependence of viscosity on the concentration of the dispersed phase, and (2) the dependence of viscosity on shear stress and shear rate (discussed in "Classes Of Non-Newtonian Behavior"). A third important aspect is the viscoelastic properties of dispersions, that will not be discussed here. Factors that determine the foregoing properties include particle shape, rigidity, particle size and size distribution, and interparticle forces, both attractive and repulsive. All these elements combine to determine the microstructure of the dispersion, its response to stresses, and hence its rheology.

A dispersion (or suspension) consists of a suspended or dispersed discontinuous phase contained within a continuous phase. As an example, this might be a system in which a fine particle size solid is wetted by and thoroughly mixed in a liquid. However, the dispersed phase may be a liquid (an emulsion), a solid (suspension), or gaseous (a foam) as well. The dividing line of terminology between "dispersions" and "suspensions" is essentially one of particle size. Dispersions are generally of colloidal dimension, about 10 nm to 1 μm. Due to their small size and mass, colloidal particles are very slow settling or nonsettling because Brownian motion effectively keeps them randomly suspended. Suspensions above 1 μm generally exhibit rapid settling because Brownian forces are ineffective with such massive particles, and also because Van der Waals attractive forces increase in proportion to particle size.

Addition of a particulate phase to a liquid increases its viscosity in proportion to the *volume fraction* ϕ of the dispersed phase. ϕ is the fraction of the total volume of the dispersion occupied by the dispersed material (a dimensionless number),

$$\phi = \frac{\text{volume of particles}}{\text{volume of dispersion}} \tag{47}$$

A convenient way of expressing the effect of a dispersed phase on the viscosity of a liquid is by normalizing the dispersion viscosity to the pure-liquid viscosity. This ratio is termed the *relative viscosity* η_r and is also dimensionless

$$\eta_r = \frac{\eta_d}{\eta_l} \tag{48}$$

The contribution of a single particle to the viscosity of a dispersion is characterized by its *intrinsic viscosity* (or *limiting viscosity number)* $[\eta]$, a function of particle shape and deformability. $[\eta]$ is obtained as the slope of a plot of $\eta_r - 1$ (formerly known as the *specific viscosity*) versus ϕ

$$[\eta] = \lim_{\phi \to 0} \frac{\eta_r - 1}{\phi} \tag{49}$$

It is reasonable that the viscosity of a liquid will be augmented by a factor equal to the product of the particle intrinsic viscosity and the concentration of particles

$$\eta_r = 1 + [\eta]\phi \tag{50}$$

Einstein [56] was the first to calculate the intrinsic viscosity for noninteracting rigid spheres in a Newtonian liquid, obtaining the number 2.5

$$\eta_r = 1 + 2.5\phi \tag{51}$$

The intrinsic viscosities of other particle shapes (e.g., prolate and oblate spheroids—discs and rods) have been calculated [63] and are always greater than 2.5. This means that any deviation from spherical particle shape will increase the viscosity of a dispersion. Equation (51) is valid only in the very dilute regime ($\phi < 0.05$), where the flow around a

[10] Some high-molecular-weight, water-soluble polymers are used as thickeners. However, they are used at low levels, and their effects on rheology are mainly colloidal/osmotic rather than as solution polymers.

single particle is not affected by the presence of other particles. At higher concentrations, the motion of particles is perturbed by interactions with other particles. These interactions are accounted for by higher-order terms in ϕ, as, for example, by Batchelor [64], who extended the rigorous treatment to somewhat higher volume fractions by using a second-order expression in ϕ

$$\eta_r = 1 + 2.5\phi + k\phi^2 \tag{52}$$

The value of k is of the order of 5. Fig. 23 illustrates the typical dependence of η_r on ϕ for actual dispersions (using data of Eilers [65]) and shows curves corresponding to the predictions of Einstein's and Batchelor's equations. It can be seen that Batchelor's equation predicts a finite viscosity at $\phi = 1$, which is not realistic. Also in Fig. 23, it is seen that η_r rises toward infinity at a volume fraction considerably less than unity. The volume fraction ϕ_m corresponding to $\eta_r \rightarrow \infty$ is called the maximum volume fraction, or maximum packing fraction. At $\phi = \phi_m$, the density of particle packing is such that the dispersion can no longer flow. The value of ϕ_m will be system-dependent (also shear dependent) and will be determined by particle shape, particle-size distribution, the ionic strength of the medium, the degree of particle flocculation, and the manner in which the particles arrange themselves (pack) in three-dimensional space.

Numerous models have been proposed containing ϕ_m [15,66,67]. Probably the most successful in fitting a variety of data is the Krieger–Dougherty equation [68]

$$\eta_r = \left(1 - \frac{\phi}{\phi_m}\right)^{-[\eta]\phi_m} \tag{53}$$

Fig. 23 shows the fit of the Krieger–Dougherty model to data of Eilers [65] using a value of $[\eta]$ close to the Einstein value. The maximum packing fraction will have different, unique values at low and high shear rates because the strength of the shear field determines how efficiently

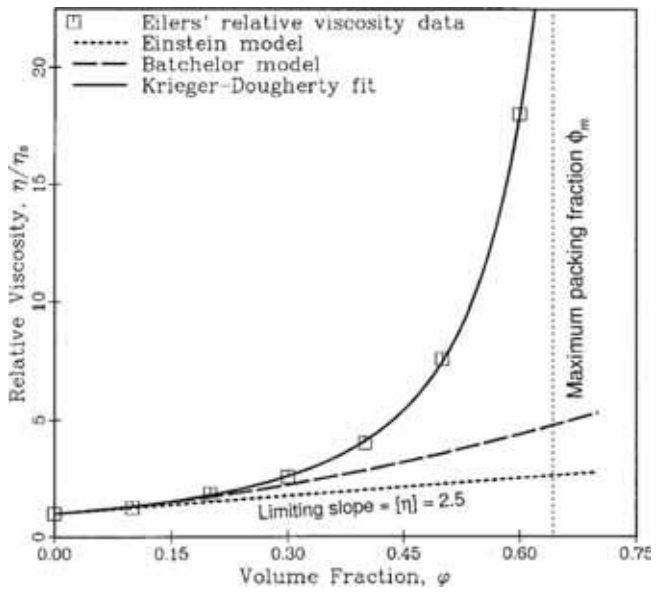

Fig. 23—Dispersion relative viscosity data of Eilers, together with best-fit curves for the Einstein model, Batchelor model, and the Krieger-Dougherty model.

particles are able to pack together. Reviews of the rheology of polymer colloids are recommended for further reading [6,14,69].

It should be noted here that although the dispersion rheology is controlled by the disperse-phase volume fraction ϕ, the effect of the particle phase on the rheology may be greater than expected solely on the basis of the volume of material added to make up the dispersion. This is because the disperse-phase volume may be augmented by various effects tending to increase the effective particle radius. It is the "hydrodynamically effective" particle volume that determines the rheology. Thus, the rheological behavior will be found to scale with the effective volume fraction ϕ_{eff}, rather than with the formulated volume fraction ϕ.

There are two mechanisms that can cause ϕ_{eff} to be greater than ϕ. In the first, the effective particle radius increases as a consequence of various methods of dispersion stabilization. For example, adsorption of a polymeric stabilizer onto the surface of a particle adds the thickness of the stabilizer layer to the particle radius. By steric-osmotic interactions between stabilizer layers, the close approach and flocculation of particles is prevented, resulting in *steric stabilization*. If the thickness of the steric stabilizing layer on the particle is δ, the effective volume fraction is [69]

$$\phi_{\text{eff}} = \phi\left[1 + \left(\frac{\delta}{R}\right)^3\right] \tag{54}$$

where R is the original particle radius. Quantitative viscometric methods have been developed for inferring the adsorbed-layer thickness [69,70].

The effective particle radius and hence the effective volume fraction ϕ_{eff} can also be increased by the effects of particle electrical charge. Aqueous dispersions are often stabilized by association of repulsive electrical charge with the particle, known as electrostatic stabilization. The charge may be due to adsorption of ions, anionic or cationic surfactants or polyelectrolytes, or, in the case of polymer colloids, to the presence of ionizable groups which are part of the polymer molecules. (In the case of functionalized polymer latexes, such groups tend to migrate to the particle surface.) The surface ionic charge surrounds the particle with an electrical field, which propagates into the aqueous phase a distance inversely proportional to the ionic strength of the medium. In the presence of dissolved counterions, an ionic atmosphere envelops the charged particle. These phenomena are the origin of the so-called electroviscous effects, which have to do with the way the electrical field surrounding the particle affects the effective volume fraction or collision cross section, and also the nature of the hydrodynamic interaction between particle and surrounding liquid [63,71]. The rheology of a dispersion can be greatly altered as a consequence of these effects, as the solution ionic strength or pH are varied. In a study by Krieger and Eguiluz, in a dispersion of uniform polystyrene latex spheres (ϕ = 0.4) the η_r decreased from 10^6 to 10 as the result of increasing the concentration of electrolyte by two orders of magnitude [72]. In that study, the low-electrolyte latexes exhibited apparent yield stress behavior, a consequence of the increase of the effective volume fraction of the latex particles due to the expansion of the repulsive electrostatic field. The effect is so great that the particles

become "locked" into crystalline arrays that can diffract light, producing striking iridescent colors. As the electrolyte concentration is increased, the counterion "cloud" both shrinks the electrostatic field and shields particle fields from each other. Consequently, the viscosity drops dramatically (remember that the volume change depends on the cube of the radius change).

A second mechanism by which ϕ_{eff} can exceed ϕ is flocculation. When particles form flocs, the liquid phase contained within the interstices of the floc is not free-draining, but effectively becomes part of the floc. Thus the volume of a flocculated phase is augmented by the volume of trapped interstitial liquid. Consequently, the disperse-phase volume fraction is higher than for the deflocculated system.

Dispersions can exhibit the full range of rheological behavior mentioned previously, including Newtonian, shear-dependent, time-dependent, plastic, and elastic behavior. A dispersion of noninteracting spherical particles will be Newtonian up to about ϕ = 0.2 [15]. Above this concentration, onset of non-Newtonian character begins due to particle interactions and hydrodynamic factors. Mechanisms for these effects are discussed in the section "Shear-Thinning Fluids."

RHEOLOGY AND FILM FORMATION

In the next two sections two coating flows, *sagging* and *leveling,* are discussed. These two flows occur early in the "film formation" phase in an applied coating layer. In sagging flow, gravity acts on the wet coating layer on a vertical substrate, causing drainage downward, which can lead to unsightly dripmarks. In leveling flow, surface tension attempts to level out any nonuniformities in surface height. Oftentimes good leveling and acceptable sagging are in opposition. Acceptable appearance of a paint layer will be dependent on proper rheological control of these flows.

In discussing how coating rheology influences these flows, there is an important point to be made: Both sagging and leveling are driven by specific shear stresses, which can be calculated from the forces acting (gravity and surface tension, respectively) and the geometry of the film. However, the shear rates over which these processes occur can vary widely depending on the coating's viscosity at the acting shear stress. The shear rate is a *dependent* variable, for real processes. The appropriate *independent* variable to best differentiate the performance of paints according to their rheology is the shear stress. For this reason (and others), it is preferable to plot flow curves as viscosity versus *shear stress*, as opposed to viscosity versus *shear rate,* which is the more common practice. To do otherwise is wrong in principle and will result in incorrect relative ranking of paints by their rheology with respect to their rates of sagging, leveling, pigment settling, or to their ease of application. This issue is key to using rheological data correctly in the interpretation of flow curves.

Viscosity versus shear rate plots are in fact an incorrect representation of the flow properties of paints with respect to specific coating processes, which are governed not by shear rate but by shear stress. Plotting with shear stress as the independent variable, as in Fig. 24, permits a direct comparison of paints *at the shear stress specific to a particular process*. Viscosity is a nonlinear function of

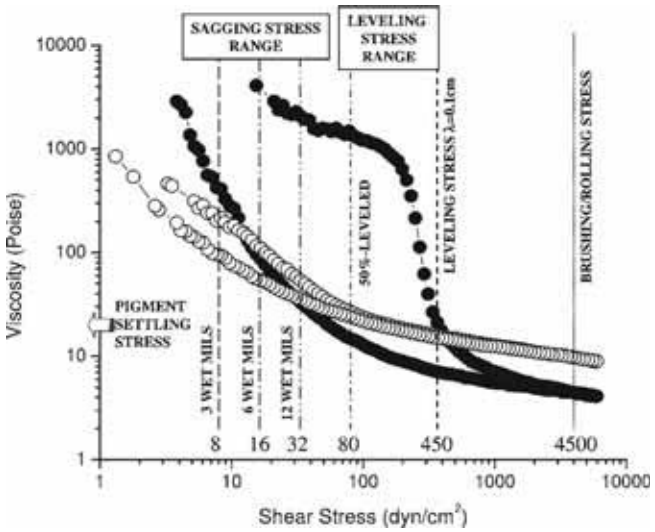

Fig. 24—Log-log plot of viscosity versus shear stress for two paints: ○ = Paint 05; ● = Paint 07. "Stress-Map" plot showing shear stresses calculated for specific coating processes, indicated as dashed vertical lines, with calculated stresses, in dyne- cm^{-2}, attached. Process stresses indicated are for brush/roller application; initial leveling of sinusoidal striations of wavelength 0.1 cm and same when 50 % leveled; sagging stresses at 3, 6, and 12 wet-mils film thickness. (From Eley, R. R., *Rheology Reviews 2005,* 173-240, K. Walters and D. M. Binding, Eds., British Society of Rheology (2005). Used by permission of British Society of Rheology.)

the shear stress, and each part of the sometimes complex curve has a role to play in various coating processes. Furthermore, because of geometrical and process variables, the shear stress for a given process may not be constant for the duration of the process. The process stresses illustrated by dashed lines in Fig. 24 are for (a) application by brush or roller, (b) surface tension-driven leveling of surface roughness, and (c) gravity-driven sagging of 3-, 6-, and 12-mil wet films. Gravitational settling of pigment particles occurs at even lower stresses. The point is that, for a given process, the shear stress acting on a coating layer is independent of the rheology (for a given geometry, density, surface tension). The shear rate for the process, however, is dependent on the rheology, and will vary with the viscosity of a particular coating at the process shear stress. Fig. 25 shows the same two paints as in Fig. 24, but this time with the viscosity plotted as a function of shear rate. Note that the constant-shear-stress dashed lines now slant to the left, and shear rates for the processes identified in Fig. 24 are shifted to the left for the higher viscosities. The constant-shear-stress lines cut the flow curves at the shear rate of the process for that paint. It can be seen for the two paints that shear rates for some process stresses are shifted nearly two decades (100-fold). Clearly, the assumption that processes such as leveling and sagging occur at a constant shear rate (say, 1 s^{-1}) can be wrong by orders of magnitude.

Fig. 25 also shows that if one were to predict comparative paint performance from viscosities at constant shear rate, the viscosity ratios would be several times smaller than the correct ratios measured at the true process shear stress. Table 5 shows viscosities at selected shear stresses and at approximately corresponding shear rate values from

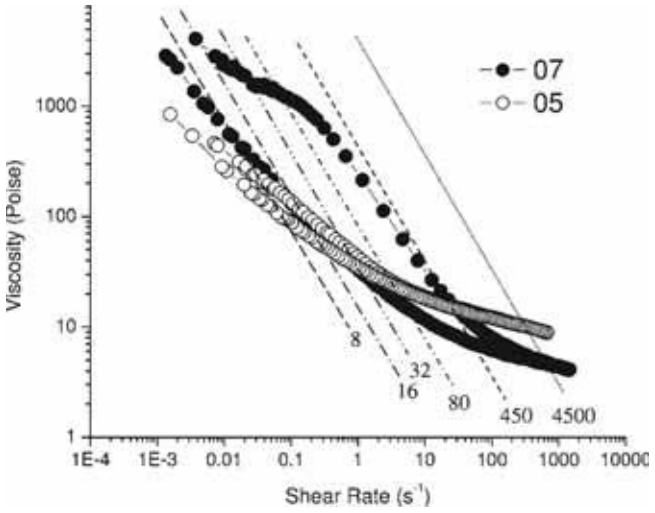

Fig. 25—Log-log plot of viscosity versus shear rate for two paints: ○ =Paint 05; ● = Paint 07. Shown also are the same dashed lines representing constant process shear stresses as in Fig. 24, now leaning leftward. As consequence of the leftward slant, ratios of the viscosities of the two paints at an arbitrary shear rate are much smaller than those at roughly similar shear stress in Fig. 24. See Table 4. (From Eley, R. R., *Rheology Reviews 2005,* 173–240, K. Walters and D. M. Binding, Eds., British Society of Rheology (2005). Used by permission of British Society of Rheology.)

Fig. 25. "Crossover" rheological behavior, as in Figs. 24 and 25, is very common among paints and can often lead to a failure of "lab-bench" measures of rheology to correlate to paint performance.

SAGGING

A coating layer on a nonhorizontal surface will experience a tangential shear stress due to gravity, given by

$$\sigma_g = \rho g h \cos\theta \tag{55}$$

where ρ is the liquid density, g is the gravitational acceleration, and h is the uniform layer depth. θ is the angle of inclination of the substrate to the vertical. For a vertical substrate, $\sigma_g = \rho g h$ (Fig. 26).

TABLE 5—Viscosity ratios at constant shear stress versus constant shear rate for Paints 05 and 07. (From Eley, R. R., *Rheology Reviews DCMP48 2005*, 173–240, K. Walters and D. M. Binding, Eds., British Society of Rheology (2005). Used by permission of British Society of Rheology.)

	Viscosity, Poise			
	Shear stress =8 dyn·cm^{-2}	Shear rate =0.01 s^{-1}	Shear stress =80 dyn·cm^{-2}	Shear rate =1.0 s^{-1}
Paint 05	210	410	26.7	42.6
Paint 07	8000	2526	1445	259
Viscosity ratio	38	6.2	54	6.1

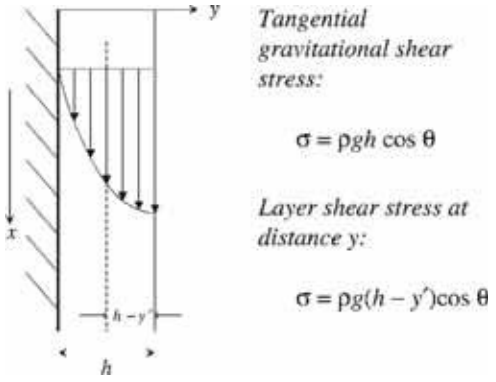

Fig. 26—Sagging driven by gravitational shear stress. Gravity acts in the *x*-direction, film thickness coordinate is *y*, wet film thickness is *h*. Shear stress is maximum at the substrate surface, due to the "weight" of outer layers of coating.

The shear stress on any layer within a coating will be equal to the load from the outer layers. For a vertical surface

$$\sigma_g = \rho g(h - y') \tag{56}$$

is the shear stress acting on a layer a distance y' from the substrate, due to the weight of the outer layer of thickness $h - y'$ (Fig. 26).

Coating layers having a yield stress σ_0 (see "Plastic (Yield) Behavior") will not sag unless the gravitational shear stress exceeds the yield value. The shear plane where yield occurs will therefore be at y' (for ideal yield behavior) when the following expression is satisfied

$$\sigma_0 \le \rho g(h - y') \tag{57}$$

Since only layers deeper than y' experience sufficient stress to flow, it follows that the layer $h - y'$ (from y' to the free surface) is solid and slides as a solid sheet over the fluid inner layers. For a coating with a large yield stress, the load necessary to cause yield and flow is correspondingly greater. Therefore, the yield plane moves deeper into the coating layer, leading to a phenomenon known as slumping. Slumping, therefore, is diagnostic of the presence of a significant yield stress. Fig. 27 illustrates the effect of a yield stress on sagging, leading to plug flow (slumping). Croll [73] showed direct evidence of plug flow in a sagging coating possessing a yield stress.

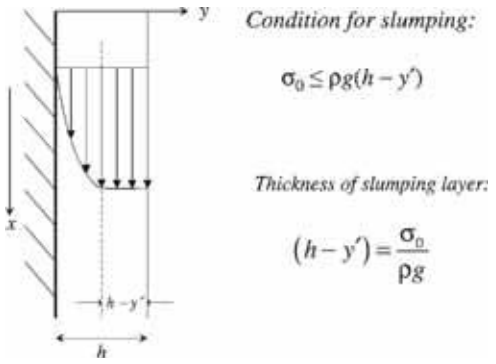

Fig. 27—Slumping (plug flow), caused by the presence of a yield stress, σ_0. Coating layer of thickness h-y' will "slump" or slide downward as a solid sheet over liquid sublayer if $\sigma_0 \le \rho g(h\text{-}y')$.

Wu [74] gives sagging velocity expressions for various types of non-Newtonian behavior. The surface velocity of a sagging Newtonian liquid is

$$v = \frac{\rho g h^2}{2\eta} \tag{58}$$

Sagging transmits substrate imperfections to the coating surface and amplifies them [75]. This is because any surface irregularity necessarily results in fluctuations in the local coating thickness normal to gravity and therefore in the local sagging shear stress. Furthermore, any local variations in film thickness due to application or to substrate features (e.g., a hole or a corner) can produce local accelerations of sagging in which thicker elements overtake thinner elements. This is a self-accelerating process, leading to drips, "tears," "runs," or "curtaining" [76]. Such undesired flows can be minimized by proper characterization and control of rheology [77].

The sagging of a coating is similar to the problem of drainage of a liquid layer from an inclined surface. The difference between the two is that, in sagging, the coating layer is assumed infinite in extent; hence, sagging causes no change in the local coating thickness, on a flat substrate. If this assumption is not correct, then gravitational flow will result in thinning of the coating layer at the top and thickening at the bottom of a finite substrate. The distinction between the two processes may be useful for those desiring to calculate, for example, the degree of "wedging" on a dip-coated part as against simply calculating a sag length or sagging velocity. Again, in the case of sagging, h is assumed constant and a sagging distance x may be calculated, whereas for drainage the thickness h varies with distance x down the substrate. The equations describing the flow are otherwise identical and interchangeable. By a derivation similar to that of Wu [74,78] for sagging, the expressions below, describing drainage, can be obtained.

For a Newtonian liquid, the thickness at time t at a distance x down from the upper edge of the liquid layer is given by

$$h = \sqrt{\frac{\eta x}{pt\cos\theta}} \tag{59}$$

The angle θ is as defined above. Most coatings are non-Newtonian, however, which will have great impact on the drainage behavior. For example, shear-thinning fluids will drain to a much more uniform film thickness than Newtonian fluids. The gravity drainage of a power law fluid (see "Shear-Dependent Viscosity") is given by

$$h = \left[\left(\frac{n+1}{n}\right)\left(\frac{x}{t}\right)\right]^{n/(n+1)}\left(\frac{K}{\rho g\cos\theta}\right)^{1/(n+1)} \tag{60}$$

In the above, K is the "consistency" term and n the exponent in the power law expression (see "Shear-Dependent Viscosity"). Here we see a practical application of mathematical flow models. The parameters obtained from fitting the power law to an experimental flow curve can be inserted into the above equation and the sagging behavior of a coating formula can be calculated and graphed. For shear-thinning fluids with yield stress, the drainage equation is

$$h = \left[\left(\frac{n+1}{n}\right)\left(\frac{x}{t}\right)\right]^{n/(n+1)}\left(\frac{K}{\rho g\cos\theta}\right)^{1/(n+1)} + \frac{\sigma_0}{\rho g} \tag{61}$$

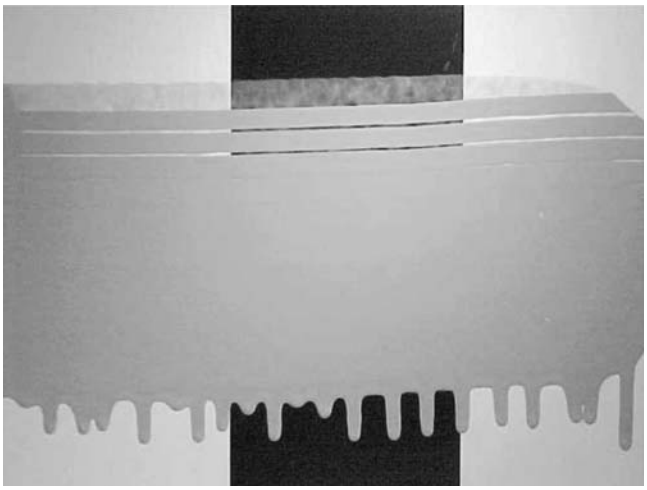

Fig. 28—Sagging evaluated by Leneta drawdown blade. Sagging is rated by the thickest paint stripe that does not show sag.

The constants n, K, and σ_0 are obtained by fitting the Herschel–Bulkley flow model to the experimental flow curve (see "Shear-Dependent Viscosity").

As with leveling, a realistic description of sagging must include not only non-Newtonian effects, but also effects of drying, geometry of the applied film, and the instantaneous rheological state of the applied film. Croll has published a review, analysis, and experimental study of sagging which examines these effects [73]. Eley and Schwartz [79] have used numerical simulation to analyze in detail the effect of rheology and substrate shape on the variation of film thickness in a drainage flow.

Measures of Sagging

A number of laboratory methods for evaluating sagging have been used, some of which measure some rheological property related to sagging behavior [80] and some of which measure sagging directly. Among the latter is ASTM D4400, in which a drawdown blade with multiple slots of graduated depths spreads paint stripes of graduated thicknesses over a nonabsorbent substrate (Leneta drawdown bar and sag chart). The chart is suspended vertically and the paint stripes allowed to flow under gravity. Sag is rated according to the thickest stripe that does not show sag (Fig. 28). A similar but somewhat simpler test involves the use of a wire device that scribes two lines, of 1/8 and 1/4 in. (0.32 and 0.64 cm) width across a 3-wet-mil paint stripe, which is then hung vertically, and sagging is visually evaluated on the dry paint film.[11] The method is illustrated in Patton [81]. Another device that has apparently met with some success is the so-called "sagging balance" [82], which uses an electronic balance to measure the shift in mass accompanying drainage of a coating applied to an inclined plate.

Sagging is, of course, driven by gravitational shear stress. The magnitude of the sagging shear stress depends solely on the wet film thickness and density [Eq (55)]. The resulting shear rate of sagging is determined by the rheology profile of the paint in question. It is imprecise to attempt to predict sagging from viscosity measure-

[11] Federal Test Method 4493, September 1965.

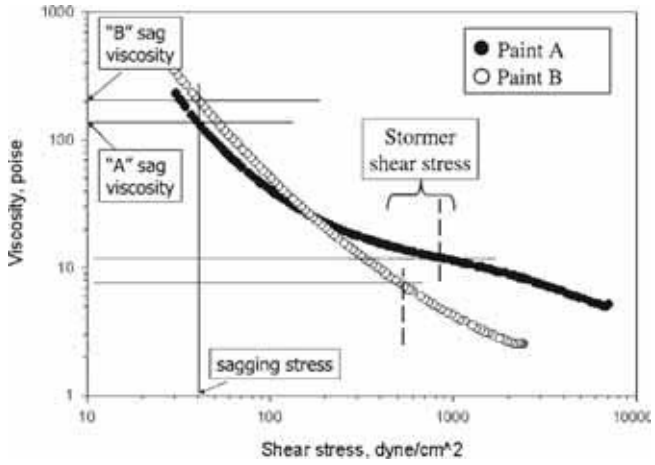

Fig. 29—Illustration of how to obtain the viscosity governing sagging from flow curve data. The gravitational shear stress driving sagging is indicated for a 6-mil wet film thickness. This stress intercepts the flow curves for paints A and B at the viscosities resisting drainage flow. "B" is higher than "A" at sagging stress and so would sag less. Stormer® viscometer shear stresses and corresponding viscosities are also indicated, and show the reverse order.

ments at an arbitrary "sagging shear rate" and may lead to incorrect estimates of relative sagging. The proper way to predict relative sagging tendency is to plot viscosity as a function of shear stress rather than shear rate as in Fig. 24. Shear stress levels corresponding to the pertinent wet film thickness can be calculated, and the magnitude of the viscosity controlling sagging, determined from the graph. Fig. 29 compares two paints in this manner, with indicated gravitational shear stress levels corresponding to a wet film thickness of 12 mils. The dashed lines in Fig. 29 indicate the approximate shear stress of the Stormer® paddle viscometer for the two paints. At the Stormer shear stress (approximately like hand stirring), the viscosity of A is higher than B (12 vs. 7.5 P). This difference is easily felt when hand stirring the two paints. However, at the sagging shear stress of about 40 dyn·cm^{-2} paint B is over 60 % higher in viscosity, and should therefore sag less than A, which is observed experimentally.

LEVELING

The mechanics of coating application generally cause the applied coating layer to be initially rough and consequently of varying thickness. Uniform film thickness is desired both for reasons of appearance (color and hiding uniformity) and for substrate protection (necessary minimum film thickness). The process of smoothing of the initial rough surface is called *leveling*. Adequate leveling is of obvious critical importance to the success of a protective or decorative coating. Hence, a large number of studies of the subject have been published (e.g., Refs. [1,41,83–91]), but the role of rheology and other factors in the leveling of paint films is not fully understood. One might expect leveling to correlate reasonably well to low-shear viscosity. However, factors such as viscoelasticity, time dependence, volatilization, wicking, and surface tension gradient flows make leveling a complex process. The leveling and film formation of a paint layer is so complex that, in the opinion of this author, only computer modeling has the potential to provide a wholly

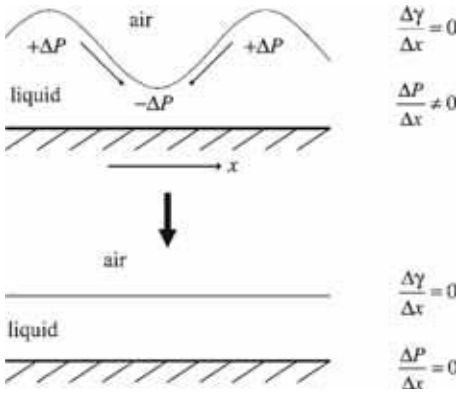

Fig. 30—Surface tension-driven leveling. Curvature of liquid surface creates capillary overpressures and underpressures ΔP. There is no surface tension gradient along the film coordinate ($\Delta\gamma/\Delta x = 0$). Pressure is not uniform, however ($\Delta P/\Delta x \neq 0$), and drives fluid flow toward leveling of surface height variations.

satisfactory method of analysis and prediction (see, for example, Eley and Schwartz [79,87]). However, such modeling capability is not readily available to most practitioners, so we will review some of the analytical models of leveling. These can provide at least a qualitative understanding of the role of rheology and other factors in leveling.

The mechanism of leveling is illustrated in Fig. 30 for a liquid without surface tension gradient ($\Delta\gamma/\Delta x = 0$), having a sinusoidal surface profile. The sum of all surface tension vectors in the curved surface produces a net force downward at the "peaks" and upward in the "valleys," the liquid-air interface acting as if it were a stretched elastic membrane. Forces due to liquid surface curvature are called *capillary forces* and result in capillary pressure variations within the liquid layer ($\Delta P/\Delta x \neq 0$). Thus, leveling is driven primarily by capillary pressure gradients due to local surface curvature, under conditions of uniform surface tension. Liquid is "pumped" from the peaks into the valleys, ultimately producing a level surface. For thin films, gravity is of negligible effect on leveling unless a critical roughness wavelength is exceeded. For a typical paint, the critical wavelength is of the order of 1 cm [93].

The quantitative prediction of leveling from physical properties requires the use of some mathematical model of the process. Smith et al. [1] derived such a model by a linear lubrication approximation-type analysis, assuming a uniform sinusoidal surface profile. (The Los Angeles Paint Club obtained a similar equation in 1953 [94] for surface roughness approximated by semicircular arcs.) Orchard later [95] developed a complicated expression for the leveling of a more realistic, arbitrarily rough surface profile in terms of a Fourier series. However, the expression simplifies considerably when the coating thickness is assumed to be small relative to the roughness wavelength. Assuming a single sinusoidal wavelength (which is a reasonable approximation since the leveling behavior will be dominated by the longest wavelength), the Orchard equation is

$$\ln \frac{a_t}{a_0} = -\frac{16\pi^4 h^3 \gamma t}{3\lambda^4 \eta} \tag{62}$$

for constant surface tension γ and viscosity η. The equation says that the ratio of the surface wave amplitude a at time

t to its initial amplitude a_0 decays exponentially with time, and the rate of decay depends on the coating layer thickness h to the third power and inversely on the wavelength of the surface roughness λ to the fourth power. For roughness geometry other than sinusoidal, the constant term $(16\pi^4/3)$ will take other values.

The Orchard equation is only an approximation to the leveling behavior of most real paints because it assumes Newtonian fluid behavior and neglects time-dependent effects (and other effects such as surface tension gradients [85]). Time-dependent effects include thixotropy and changes in rheology from loss of solvent due to drying or to "wicking" (absorption) of the liquid phase into a porous substrate. Nevertheless, the Orchard model conveys the important influence of film geometry and physical properties on leveling rates, and allows estimation of the order of magnitude of effects of changes in these variables. For example, it should generally hold, despite complicating factors, that doubling the wet film thickness will increase the leveling rate eight-fold. However, a more realistic description is warranted, taking into account other film properties and processes that affect leveling significantly. A step was taken by Murphy [96] (see also Refs. [85,84]), who rederived the Orchard equation for pseudoplastic paints assuming power law behavior (see "Shear-Thinning Fluids"), obtaining

$$a^{(n-1)/n} = a_0^{(n-1)/n} - \frac{n-1}{2n+1}\left(\frac{\gamma}{K}\right)^{1/n}\left(\frac{2\pi}{\lambda}\right)^{(3+n)/n} h^{(2n+1)/n_t} \qquad (63)$$

This expression contains the power law coefficients, K and n, all other terms retaining the same definitions as above. Note that the leveling rate increases as the power law exponent, n, decreases (i.e., as the paint becomes more shear thinning). As expected, the leveling rate decreases with increasing K (consistency). Lu [55] found the Murphy equation valid for correlating the change of brushmark amplitude with time for systems where the leveling was clearly dominated by the viscosity. However, the Murphy equation still assumes that viscosity depends only on shear rate and that surface tension does not change during the leveling process. In reality, viscosity and surface tension will both change due to evaporation of the volatile phase of the coating or to wicking. The Murphy equation may be modified to take account of time-dependent viscosity increase by including a time-integral expression for the viscosity

$$a^{(n-1)/n} = a_0^{(n-1)/n} - \frac{n-1}{2n+1}\gamma^{1/n}\left(\frac{2\pi}{\lambda}\right)^{(3+n)/n} h^{(2n+1)/n}\int_0^t\left(\frac{1}{\eta(t)}\right)dt \qquad (64)$$

where $\eta\ (t)$ is some time function of viscosity relating effects of thixotropy, drying, wicking, etc. The effect of time-dependent viscosity on leveling is dramatic, as shown in Fig. 31. Here, for two different paints, the decay of surface amplitude is calculated using Eq (63) and (64), together with an experimentally determined expression for the increase of viscosity with time due to drying. Camina [84] reported that the viscosity of a drying paint increases exponentially in the initial stages. Therefore, an expression such as the following would fit drying-viscosity data

$$\eta(t) = \eta(0)e^{kt} \qquad (65)$$

where $\eta(0)$ is the viscosity before drying has begun, k a drying rate constant, and t the time. Such an expression can be inserted into Eq (64) in place of $\eta(t)$ and integrated[12] to calculate the leveling curve for a paint whose viscosity is increasing with time due to solvent loss.

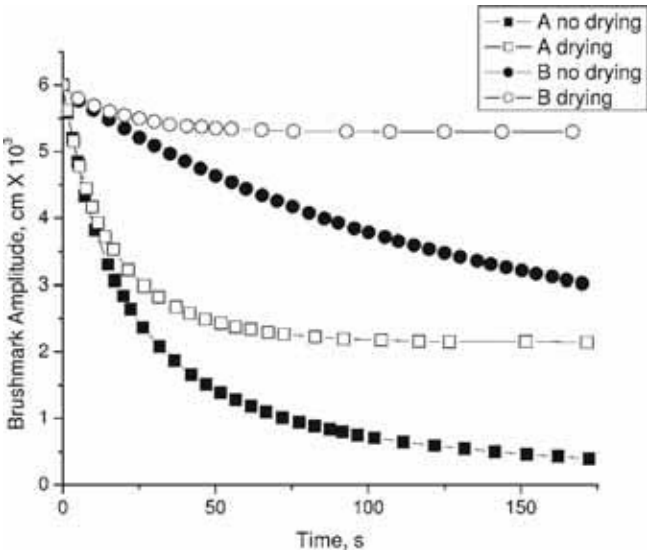

Fig. 31—Calculated brushmark leveling for two paints, with and without effects of drying. Curves calculated using Eqs (64) and (65): ○—Paint A, with drying; ●—Paint A, without drying; □—Paint B, with drying; ■—Paint B, without drying.

Quach [93] has discussed and summarized the shortcomings of various laboratory methods of leveling evaluation. As noted by Quach, much work on leveling has been done without adequately taking into account the numerous interacting subprocesses whose final result is the dried film profile. An additional important factor dealt with experimentally and theoretically is the influence of surface tension gradient-driven flows (Marangoni flows) [86,97,98]. Surface tension gradients may arise due to a number of causes during film formation and can have consequences for the course of film leveling, among other things. Figure 32 illustrates the mechanism of surface tension gradient-driven flow, which can result in the deleveling of an initially level liquid layer. Local surface tension gradients can develop due to differential solvent evaporation or to temperature gradients (or other causes). This results in a surface flow from regions of low surface tension toward regions of high, in an attempt to reach surface equilibrium. The moving surface "drags" subsurface liquid along, creating a bulk flow. This is the Marangoni effect. In the case of differential evaporation, the driving force for Marangoni flow is a shear stress σ_s tangent to the film surface, given by

$$\sigma_s = \frac{\partial\gamma}{\partial[S]}\frac{\partial[S]}{\partial x} = \frac{\partial\gamma}{\partial x} \qquad (66)$$

where $\partial y/\partial\,[S]$ is the dependence of surface tension on solvent concentration and $\partial[S]/\partial x$ is the solvent concentration gradient (x is the coordinate along the substrate). Hence, the surface tension gradient $\partial\gamma/\partial x$ drives the flow. For the case where Marangoni flow is driven by thermal surface tension gradients, replace $\partial[S]$ by ∂T in the above. If sur-

[12] Provided that the viscosity during drying is measured at unit shear rate, K in Eq (63) becomes η in Eq (64).

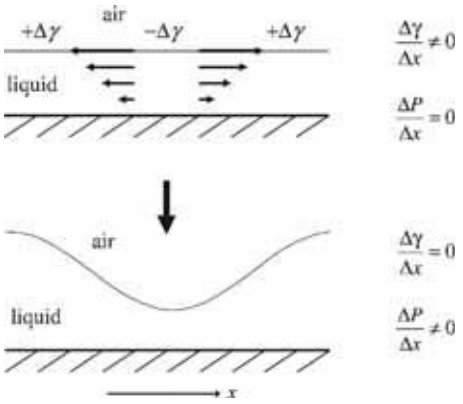

Fig. 32—Deleveling by Marangoni (surface tension gradient-driven) flow. Surface tension gradient ($\Delta\gamma/\Delta x \neq 0$) drives surface flow, resulting in bulk flow and de-leveling of initially level surface.

face tension gradients persist until the film is incapable of reflow, an appearance defect will result. Overdiep [86] demonstrated (for solvent-based paints) that Marangoni flows initially enhance the leveling rate, but can produce a "rebound" effect that ultimately worsens film roughness. Wilson [98] recently modeled this behavior by a linear perturbation analysis. Other authors have discussed the importance of Marangoni flows for waterborne, cosolvent-containing coatings [87,99].

The role of viscoelasticity in leveling has been a subject of some debate, with some authors concluding that elasticity enhances leveling [100] and some that it retards leveling [41,101]. The evident link between elasticity and the underlying structural rheology for coatings (see "Viscoelasticity and Industrial *Processes*") suggests the presence of a gel-like structure of some sort in systems possessing significant elasticity. Such a structure would be expected to inhibit flow at low stress levels so that coatings that exhibit elasticity should also show poorer leveling. The leveling behavior of viscoelastic systems has been modeled by Keunings and Bousfield [41], where the presence of viscoelastic relaxation shown to retard leveling. The leveling rate α as a function of the Newtonian leveling rate α_{Newt} was shown to be

$$\alpha = \frac{\alpha_{Newt}}{1 + \lambda\alpha_{Newt}} \tag{67}$$

where α = rate of change of roughness amplitude (s^{-1}), and λ is the elastic stress-memory time constant (or relaxation time) (see *Viscoelastic Models*). In Eq (67), the Newtonian leveling rate is always positive, hence elastic "extra stress" ($\lambda > 0$) always retards leveling. Interestingly, if surface tension gradients are present, α_{Newt} may actually become negative (i.e., deleveling). In such cases, late-developing elasticity will be of benefit by retarding the de-leveling. Table 4 shows the results of a calculation similar to that of Keunings adapted for the case of a typical paint. It is seen that, for λ =100 s, the leveling rate dramatically decreases and the leveling half-time increases (by a factor of 3,500), relative to the Newtonian ($\lambda = 0$) values.

Measures of Leveling

Visual evaluation of leveling is common practice. However, it is generally agreed that visual rating is subjective, and leveling rankings are often found to be operator-dependent. Numerous objective methods and standards have been published. Quach [93] discussed aspects of both scientific and laboratory practical studies of leveling. For the latter, special drawdown blades have been used such as the NYPC leveling test blade (ASTM D2801: now withdrawn—no longer an ASTM method), which has five pairs of notches over a range of depths. Leveling is judged by the flowing together of adjacent paint stripes. This method has been criticized by Quach and others [29] because the paint passing through the notches experiences a varying shear rate with notch depth, resulting in a different shear history for each stripe, and because the shear rate achieved is unrealistically low. The latter test has been superseded by ASTM D4062, based on a grooved drawdown rod. In this method, the paint is presheared, simulating brushing shear rates, by ejection from a syringe and 15-gauge needle prior to drawdown. The leveling quality is then estimated by visual comparison of the dried film with plastic leveling standards viewed against oblique lighting.

Kornum [102] gives a good discussion of issues of measurement under test conditions approximating real paint processes, including leveling. Dodge [29] also emphasizes that the best rheological test for leveling should most closely simulate the application experience of the paint. This means (1) the paint should experience shear rates/stresses of similar magnitude and duration to those of the application process, (2) the shear rate/stress should then be step-changed to values representative of the leveling process, and (3) the change of viscosity with time should then be followed under the latter conditions. This protocol is essentially identical to the "step-shear" method of characterizing thixotropic recovery described in "Thixotropy Test Methods." This kind of procedure is most easily accomplished by employing a rheometer capable of "job streaming" or "linked methods." However, the foregoing method still suffers from the limitation that the effect of drying on viscosity during the leveling period is neglected. Fig. 31 demonstrates that this can be a very significant effect. Paints "A" and "B" were commercial formulas which differed markedly in leveling performance. The increase of viscosity with time during drying of a film of typical applied thickness was measured for both and found to obey Eq (65). The latter expression was then inserted into Eq (64) as the time-integral function for viscosity (as described in the previous section) and the leveling curves in Fig. 31 were calculated. There are two curves for each paint, one showing how the paint levels without the effect of drying, and one calculated taking the increase of viscosity due to drying into account. The effect of drying is most dramatic on Paint B, where the reduction of surface roughness achieved after 3 min decreases from 50 % to 10 %.

It is established that leveling shear stress decays exponentially as leveling progresses [80]. A controlled-stress rheometer with programmable logarithmic stress ramps offers the ability to simulate the variation of viscosity with realistic shear-stress decay using variable ramp times. Leveling efficiency might then be judged by numerically integrating the fluidity over the "leveling" period

$$\Phi = \int_0^t \frac{1}{\eta} dt \tag{68}$$

The leveling might be expected to be logarithmically related to the fluidity integral Φ [103].

A very promising method for direct observation of paint leveling has been described by Klarskov [88]. It is an optical interferometric method that is simple but quite precise for real-time surface profile measurement, having a vertical resolution of a fraction of a micron. At present, unfortunately, there is no commercial instrument based on Klarskov's method.

RHEOLOGY INSTRUMENTATION

A great number of instruments have been devised to measure viscosity or "consistency" in the industrial laboratory. However, a number of them have serious design limitations that make them generally poorly suited for measurements of non-Newtonian fluids. The importance of this issue becomes apparent when it is realized that the majority of coatings and coatings components are non-Newtonian, yet many laboratories continue to use methods that are not suited for such materials. The problem with many familiar laboratory viscometers is that the flow field (trajectories of fluid elements or "streamlines") is complex and not subject to mathematical analysis. The result is that an accurate stress or strain rate cannot be calculated. Therefore, the true (absolute) viscosity cannot be known. Furthermore, the nonuniformity of the shear field causes the viscosity to vary within the test specimen for non-Newtonian materials. For complex flow fields, such an error cannot be corrected. The measurement error will be in proportion to the degree of deviation from Newtonian character. A second important deficiency of most simple viscometers is a lack of temperature, which can contribute a very significant measurement error. Nevertheless, such instruments have been in use throughout the industry for decades and no doubt will continue to be used for the foreseeable future. The approximate measurement given is somehow related by the practitioner to something believed relevant to the performance. One suspects that when the result is contradictory, as is probably often the case, it is either ignored or "worked around." We shall refer to this type of device as a "Q/C (quality control) instrument" or a "qualitative viscometer." It should be emphasized that these instruments are accurate for Newtonian or near-Newtonian materials and are generally useful as Q/C test devices even when the measurement is approximate. However, the practitioner should be alert to situations where their deficiencies can be of significance.

In years past, many coating fluids were nearly Newtonian, which accounts in part for the success of Q/C-type instruments. As alluded to before, it is very easy to characterize a Newtonian fluid. Virtually any type of flow measurement device may be used to obtain accurate information on the viscosity of such a material provided the device used is calibrated with known standard fluids and the temperature is controlled. It is not even necessary to know the shear rate of the measurement since Newtonian fluid viscosity is independent of the shear rate. Consequently, Newtonian viscosity measured by any test is valid for all process conditions (except turbulent flow). Even instruments which measure viscosity according to some arbitrary scale may be used since they may be calibrated in absolute units using Newtonian standard fluids.

A requirement for an instrument to measure non-Newtonian fluids properly is that the flow field within the test fluid be viscometric, defined as "everywhere indistinguishable from steady simple shear" [104]. Instruments which measure under such well-controlled conditions we will call "research instruments." Nonviscometric flows such as tube flow can be used for non-Newtonian fluids when necessary corrections are applied.

Q/C INSTRUMENTS

These are of three types of Q/C instruments, which are as follows: (1) efflux devices, (2) rotational devices, and (3) obstructed-flow devices (following Barnes et al. [105]).

Efflux Devices (Orifice Flow)

Efflux devices, or orifice cups, come in a variety of types, but share one principle: measuring viscosity by flow from a reservoir or cup through a restriction of some type. In most cases, the restriction is simply a hole in the bottom of the reservoir, but in some it is a short tube. These devices have the advantages of low cost, ease of cleaning, durability, and simplicity in the measurement, which is simply the time to empty (in whatever manner "empty" is defined). However, they also have a number of limitations. The first is that the flow is never viscometric. Even when the fluid exits via a short capillary tube, the length-to-diameter ratio is too small for proper tube flow to develop, so that the flow is dominated by entrance effects. In fact, the orifice cups have been described as "poor capillary viscometers." Since substantial shear stress is not developed in the exit hole, orifice cups are not suitable for very thin liquids because a significant fraction of energy is dissipated not in viscous flow, but rather to accelerate the fluid. In other words, measurements on low viscosity fluids are subject to significant fluid inertia errors. Thus, for the Ford No. 4 Cup (ASTM Method D1200), liquids with an efflux time of less than 20 s should not be used. The flow in efflux cups is stress-driven, controlled by the hydrostatic head, i.e., the fluid height in the cup. The pressure varies as the liquid drains; consequently, the shear stress and flow rate vary during the test. The viscosity of shear-thinning liquids, therefore, will increase in the course of the test, and in extreme cases such materials may not fully drain from the cup. Because the flow field is complex, the shear rate cannot be calculated, and from the previous argument will depend on the viscosity-shear stress relationship for non-Newtonian materials. For the above reasons, it must be concluded that orifice cups are really only suitable for viscosity measurements of Newtonian liquids of moderate viscosity. Non-Newtonian liquids should not be tested unless they are nearly Newtonian within the shear rate range of the test. Materials with possible yield stress (meaning any thixotropic materials) should not be tested with efflux devices. A final caution for these devices is that, unless the temperature of the cup is controlled by means of a water jacket, large errors are likely to result. Even if the test liquid is thermostatted in a water bath prior to test, it can rapidly change in temperature and viscosity when placed in a cup that is at the temperature of the room. Fig. 33 shows data for replicate measurements on a Ford #4 cup with and without temperature control. Obviously, the errors in the data taken with the standard cup would hide the real batch-to-batch differences of the

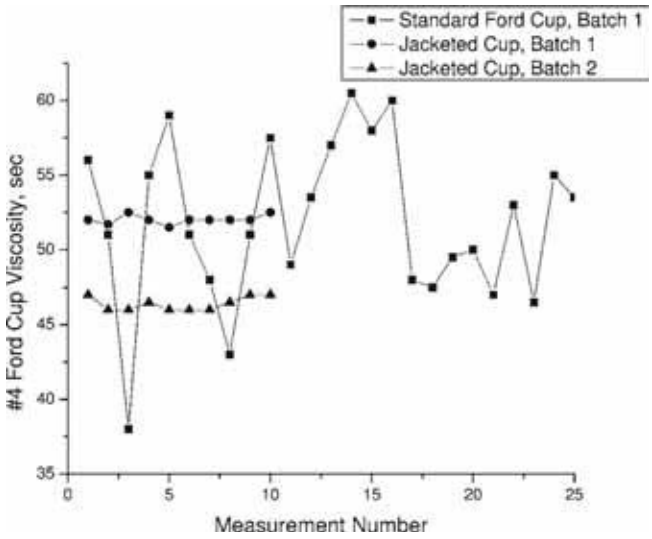

Fig. 33—Ford cup viscosity data taken with and without temperature control of the cup. Test temperature was 130°F (54°C).

product. A good Q/C test should reveal, not obscure, product variability.

Rotational Devices

STORMER® VISCOMETER

The widely-used Stormer Viscometer[13] was one of the earliest controlled-stress rotational viscometers [106]. Rotors of various geometries are available, but the "paddle" rotors, in which two small vanes are attached in offset fashion to a rotating shaft, are used exclusively for the measurement of the consistency of paints. During a measurement (in the original device), the rotation is driven by a free-falling weight attached to a string and pulley arrangement, the string being wound around a drum. The shear stress is varied by use of different weights. A counter tallies up the number of revolutions as the weight falls. After the first ten revolutions, the time required for the next 100 is measured. (Stroboscopic timers are available.) The apparent viscosity is calculated from a plot of applied torque versus rotor rpm. The measurement can also be made in terms of the weight, W, required to achieve a rotational speed of 200 rpm. The viscosity is obtained according to an arbitrary scale called "Krebs units" (KU). A conversion table of *W* versus KU is supplied. Electronic versions of the device are available (see below), which operate at constant speed rather than at constant stress. This difference may produce slightly different results as compared to the nonelectronic versions of the instrument, unless care is taken to reproduce the same conditions of measurement. As with any viscometer whose flow field is complex, an absolute viscosity (i.e., in engineering units of Poise or Pascal seconds) cannot be calculated with the Stormer for non-Newtonian fluids. The Stormer viscometer is specified in a number of standard test methods.[14]

[13] The name "Stormer" is a trademark of the Thomas Scientific Company.

[14] Test methods include ASTM D115, D562, D816, D856, D1084, D1131, D1337, and D1338 and Federal Test Methods 3011.1, 3012, 3018, 3019, 3022, and 4281.

For its purpose, i.e., to measure the in-can "feel" of paint, the Stormer is a very good viscometer—that is, the Stormer measures by stirring the paint, as the consumer would. Thus, the instrument satisfies the criterion of measuring under conditions closely approximating those of a relevant process. This justifies the use of an arbitrary measurement scale, in this case, and makes the Stormer a useful component of the paint laboratory. The only *caveat* would be not to violate the above-mentioned principle by attempting to use Stormer data to predict paint performance for a process that is far removed from the flow kinematics of the instrument.

THOMAS-STORMER® VISCOMETER MODEL ETS-1000

This instrument is an electronic implementation of the Stormer paddle viscometer by the Thomas Scientific Company.[15] Weights are done away with, as the instrument is motor-driven. A selector switch allows a digital readout to display the measured viscosity in centipoise, KU, or in grams (for comparison to the standard Stormer instrument).

BROOKFIELD DIGITAL VISCOMETER MODEL KU-1

The Brookfield Model KU-1 is likewise an electronic paddle viscometer, similar to the Stormer, by Brookfield Engineering Laboratories. A digital panel readout displays either the weight in grams corresponding to the applied motor torque or the viscosity in KU.

ICI ROTOTHINNER

The Rotothinner, originally developed by ICI Paints, is driven by a constant-speed motor and utilizes a large, disk-shaped rotor that is immersed in the sample under test. A standard steel sample container is used, which is held magnetically to a turntable. The torque transmitted through the sample rotates the turntable until a steady position is reached. (The rotary motion is resisted by a spring.) The turntable is graduated in poise units, and a pointer attached to the instrument base indicates the viscosity. The viscosity range of a given model is somewhat narrow, and measurement over a wide viscosity range necessitates purchase of separate instruments. The instrument is calibrated for use only with standard containers. There is no provision for temperature control of the specimen. For "rheologically structured" materials, the manufacturer recommends to allow up to 4 min under shear for the reading to become steady, thus providing for a more or less constant shear history. However, temperature may vary during this period due to the input of energy resulting from the 575 rpm rotor speed.

Although the instrument has a scale graduated in poise units, the shear rate of test is unknown since the flow field is not viscometric. Flow near a rotating disk can be quite complex, especially for non-Newtonian and viscoelastic materials. As a further complication the Rotothinner disk has diagonal holes bored through it, presumably to increase shear. Consequently, the apparent Rotothinner viscosity must be considered only approximate and the scale graduations arbitrary for such materials. The Rotothinner is manufactured by Sheen Instruments, Ltd. and is widely used in Europe.

[15] The Thomas-Stormer ETS-1000 is available from the Cannon Instrument Company.

Obstructed-Flow Devices

These are gravity-driven instruments in which flow is due to density differences between the test fluid and a falling object (falling ball viscometer, falling needle viscometer) or a rising bubble (bubble tube viscometer). In each case, the fluid has to flow around the moving object; hence, they are classed as obstructed-flow devices. In the falling ball and rising bubble instruments, the flow field is complex with the consequence that these devices are generally not useful for non-Newtonian fluids. The falling needle viscometer, however, possesses a well-defined flow field [105], is therefore suitable for non-Newtonian materials, and will be discussed in the section on "Research Rheometers."

FALLING BALL VISCOMETER

A ball falling in a viscous fluid will reach a constant velocity U_∞ which is dependent on the density difference of the sphere and the liquid, the diameter of the ball d and the fluid viscosity η. The viscosity of an unknown fluid may be calculated from the Stokes equation

$$\eta = \frac{(\rho_s - \rho_l) g d^2}{18 U_\infty} \tag{69}$$

where g is gravitational acceleration. This deceptively simple method has several drawbacks, however. For one, the Stokes solution is only valid for low Reynolds numbers (viscous forces controlling, rather than fluid inertia, i.e., slow flow), and for low-viscosity fluids the ball density must be small enough to produce appropriately slow rates of fall. For another, a wall correction may be needed to account for the interference of the container wall with the flow field of the ball and hence its falling rate. Perhaps the greatest difficulty, however, is the fact that the flow field around a moving sphere is complex, and when the fluid is non-Newtonian the complexity becomes mathematically intractable. Therefore, for non-Newtonian fluids, the falling-ball apparatus will not yield absolute viscosity, and the results would not be expected to correspond with those from an instrument having viscometric flow geometry. A solution to the above problems is provided by a relatively new instrument called the falling needle viscometer (see below).

Rising-Bubble Viscometers

If certain flow field assumptions are made for a rising air bubble in a liquid, the viscosity of the liquid can be calculated from [49]

$$\eta = \frac{1}{3} \frac{\rho g R^2}{\nu} \tag{70}$$

where ρ is the liquid density, R is the radius of the air bubble, and v is the rising velocity. However, the calculation is only approximate because the air bubble shape often deviates from the assumed sphericity due to buoyancy. Furthermore, if the liquid phase were non-Newtonian, significant errors would result for which there is no correction available.

The Gardner-Holdt bubble tubes provide a rapid means of estimating the kinematic viscosity (see "Capillary Viscometers") of transparent liquids such as varnishes and resins using the rising bubble principle. These consist of a series of sealed glass tubes containing mineral oils comprising a range of standard viscosities. The test liquid is placed into a similar tube (ensuring the contained air bubble is the same volume) and thermostatted in a water bath. The test material and a rack containing the standard tubes are inverted, and the viscosity of the test specimen is identified according to the letter (or sometimes number) designation of the standard tube whose rate of bubble rise is nearest the same. Interpolation between the standards is sometimes done. Bubble tubes are disposable, easy to use, and the results can be converted to kinematic viscosity by means of tables. Bubble tubes can also be used to measure resin color. For process resins nearing the gelation point, the bubble can display a pointed "tail," or pronounced "inverted teardrop" shape, an indication of the onset of viscoelasticity. As a reference for the use of the Gardner-Holdt method, see ASTM D1545.[16]

RESEARCH RHEOMETERS/VISCOMETERS

Research-quality rheometers are mainly of two types: rotational rheometers and efflux rheometers. Rotational rheometers employ steady (uniform) shear, oscillatory shear, and transient (time-dependent) shear experiments of various types. Efflux rheometers extrude the fluid through a small-gap orifice, which can be a capillary tube, a slit, or an annulus (concentric cylindrical-walled tube). The flow in these devices is well-defined and data can be obtained in absolute or engineering units for non-Newtonian fluids. Summaries of instrumentation and methods are found in Refs. [107–109]. Although dated, Van Wazer's book is still a useful source [49]. Appendix A lists vendors of research rheometers and viscometers.

Rotational Instruments

CONTROLLED STRESS AND CONTROLLED RATE

There are two basic types of rotational viscometers, which work in the following ways: (1) apply a controlled rotation rate and measure the opposing viscous torque or (2) apply a controlled torque and measure the resulting rate of rotation. In the first case, which may be termed "controlled-strain" or "controlled strain rate," the applied angular velocity is the independent variable and the viscous drag torque the dependent or measured variable. In the second case, termed "controlled-stress," the applied torque is the independent variable and the measured angular velocity the dependent variable. Examples of controlled strain rate instruments include the Wells-Brookfield Cone and Plate Viscometer, the Haake RotoVisco 1, and the TA Instruments ARES. Instruments of the controlled-stress type include the TA Instruments ARG2, the Reologica Stresstech HR, the Thermo Haake Rheostress 600, and the Physica MCR-series rheom-eters. See "Appendix" for a list of instrumentation vendors.

The choice between the two types of instruments depends on the material under test and the intended experiments. In terms of performance, controlled-stress (CS) instruments can measure much lower angular velocities than can controlled-strain-rate (CR) instruments, but CS instruments tend to be more limited at the high angular velocity and oscillation frequency end. Both CS and CR

[16] Additional standard test methods using bubble tubes are ASTM D803, D1131, and D1725 and Federal Test Method 4271 (141-a).

instruments have inertia issues affecting the accuracy at high frequencies or for rapid accelerations. In the case of CS, the issue is measurement system inertia and is correctable; for CR the problem is torque measurement system resonance and is not correctable. CS is well suited to measuring long relaxation times because of the stability of the applied torque [110].

CR instruments impose a shear-rate sweep while measuring the drag-torque response of materials. Structured fluids tend to be shear-sensitive (more precisely, strain-sensitive). Consequently, as strain increases exponentially under a linear strain-rate sweep protocol, fluid structure tends to collapse rapidly, with the result that relatively few data points are obtained to provide information on structure. In contrast, CS devices use linear (and logarithmic) rates of stress increase, an intrinsically "gentler" mode of deforming materials, which allows materials to "obey their own rules" of stress-strain response, thus resolving the maximum amount of information. CS instruments are especially useful for characterizing structured fluids, such as paint, printing ink, adhesives, ceramic slips, coal slurries, cement, pigment and colorant dispersions, drilling muds, medicines, foodstuffs, cleaners, personal care products and cosmetics, solder pastes, etc. This is particularly true where materials exhibit yield behavior. CS instruments can, in principle, directly measure the stress at the onset of yield (see "Plastic (Yield) Behavior"), avoiding errors associated with extrapolation or curve-fitting methods (see *Yield Stress Test Methods*).

CS and CR instruments each do their own version of a transient experiment: creep for CS and stress relaxation for CR. The stable torque and high strain resolution capabilities of CS mean creep experiments can be used to probe very slow relaxation processes. A modified creep method—a programmed series of small torque increments—can be used for determining the first Newtonian plateau down to very low shear rates, e.g., region I of the equilibrium flow curve (see "Shear-Thinning Fluids"). A limiting factor in the accuracy of such methods, however, is the ability to minimize or correct for spurious air bearing torque.

INERTIA CORRECTION

It can be particularly important for rotational rheometers of the controlled-stress type to correct the data for inertia error. If the test fluid is low in viscosity, and/or the test rotor has a large moment of inertia, and/or the acceleration is too high (short ramp time), a significant portion of the applied torque is dissipated not viscously, but in the acceleration of the rotor. A correction for this error has been published by Krieger [111]. Some commercial controlled-stress instruments now feature on-line inertia correction.

Brookfield Viscometers

BROOKFIELD SYNCHRO-LECTRIC

The Brookfield Synchro-Lectric viscometer utilizes a set of spindles or disks as the rotor/sensor, which are rotated in the test fluid at selected rpm, so that the apparent viscosity may be measured at several shear rates to obtain a flow curve. Its advantages include low cost, simplicity of use, ease of cleaning, and durability. The instrument is in wide use throughout the industry and is the basis for ASTM D2196 and a number of other ASTM test methods.[17] It is included here in the list of "research quality" viscometers because the viscosity can be reported in absolute units over a range of shear rate, although often it is not (see below). Its limitations include the latter fact, plus that temperature control is not integral to the instrument. The Synchro-Lectric is available with digital output, automatic viscosity calculation, and computer-interfaced versions with analysis and graphing software.

Brookfield spindle viscometer measurements suffer from the use of arbitrary or nonfundamental units in reporting the result. Even though the viscosity is reported in absolute units (cP or mPa·s), the shear rate is not. Thus, both the spindle speed (rpm) and the spindle identity must be reported along with the measured viscosity. The measured viscosity can be different at the same rpm if a different size spindle is used. Without knowing the actual shear rate of measurement, an absolute flow curve cannot be constructed from the results. The true flow curve is desirable for several reasons, among them the possibility of comparison with results from other instruments, the quantitative description of the sample rheology by use of mathematical flow models and the subsequent application of such models to predict paint performance (see "Leveling" and "Sagging" for example). Methods for calculation of the corrected shear rate for Brookfield RVT spindles were given by Williams [112] and also Pierce [113]. Smith [85] has given a simplified method. (See also Ref. [22], pp. 28–31.) Some of the foregoing issues are at least partially resolved with certain accessories available from Brookfield. These include options that have small-gap bob-in-cup geometry and temperature control, e.g., the small-sample adapter.

WELLS-BROOKFIELD CONE AND PLATE VISCOMETER

Brookfield also offers an instrument possessing a well-defined geometry and good temperature control—the Wells-Brookfield cone and plate viscometer. Its operation and appearance are very similar to the Synchro-Lectric, except the lower end has been modified to mount a cone and plate geometry with integral temperature control via a water jacket. Because the true shear rate can be calculated from the cone geometry and rpm, the viscosity of non-Newtonian materials can be measured in absolute units and an equilibrium flow curve determined. This instrument, therefore, is recommended over the standard Synchro-Lectric for routine viscosity measurement.

BROOKFIELD DV SERIES RHEOMETERS

The DV series of viscometers is basically an enhanced spindle-disk system offering programmability, a range of rotation speeds and computer interface and control capability.

BROOKFIELD CAP 2000 VISCOMETER

The Brookfield CAP 2000 multispeed digital cone-plate viscometer is similar to the ICI cone and plate viscometer, but represents an improvement in that it is capable of variable shear rate measurement (10 to 12,000 s^{-1}). It also provides a digital display of viscosity and temperature as well as a

[17] These include ASTM D115, D816, D1076, D1084, D1286, D1337, D1338, D1417, D1439, D1638, D1824, D2364, D2393, D2556, and D2669 and Federal Test Method 4287.

data interface to a personal computer or data logger with applications software.

ICI CONE AND PLATE VISCOMETER

The ICI cone and plate viscometer is a relatively high shear rate instrument capable of absolute viscosity measurement. It is normally sold in a room-temperature, single-speed configuration. Temperature control is integral to the instrument, but there is no provision for control of solvent loss from the sample. This can be improvised, if desired. A high-temperature version is available, which is useful for resin melt viscosity measurement. The chief use of the instrument has been the measurement of viscosity at a shear rate of 10,000 s^{-1} (at 50 Hz alternating current) or 12,000 s^{-1} (at 60 Hz ac) for the prediction of brushability. (See ASTM method D4287, titled "High-shear viscosity using a cone and plate viscometer.")

FALLING-NEEDLE VISCOMETER

This is an "obstructed-flow" device that utilizes a long, slender rod or "needle" as the falling object. In so doing, it overcomes the objections to the falling ball viscometer while retaining the latter's simplicity of operation and relatively low cost [114]. The needle is hollow (allowing a wide range of needle densities) with hemispherically capped ends. End effects due to the finite needle length are mathematically correctable. This geometry produces a well-behaved flow field known as "annular-ducted flow," with the central tube (needle) moving at a constant (terminal) velocity. Because of the well-defined flow field the true velocity gradient between the needle and container wall can be obtained, and the instrument therefore is suitable for measurements of non-Newtonian fluids [115]. The falling-needle viscometer may be useful for determination of very low shear stress or shear rate behavior of non-Newtonian fluids, for example the zero-shear viscosity (region I of Fig. 3) and measurement of yield stresses [116].[18] Fig. 34 compares first- and second-run flow curves of a semigloss paint, obtained on a rotational rheometer, with data points obtained from the Irvine-Park Falling Needle Viscometer (FNV). The agreement is quite good with the "up" curve of the second run, indicating that the FNV experiment imposes enough shear on the sample during the measurement that the results correspond to a pre-sheared system rather than to a previously unsheared system. This was found to be a consistent result for several paints. For highly thixotropic paints, the result was in between the first- and second-run flow curves.

CAPILLARY VISCOMETERS

Capillary tube flow is a classical viscometric method that is useful for coatings in two main ways. Capillary viscometry is the method of choice for measurement of intrinsic viscosity (ASTM Method D446 and D2162) (see also "Dispersion Rheology") and also for the measurement of very high shear rate rheological properties (see below).

For fluid flowing through a tube, the shear stress at the tube wall is

$$\sigma_w = \frac{\Delta PR}{2L} \tag{71}$$

[18] A new ASTM method for falling-needle viscometry is D5478.

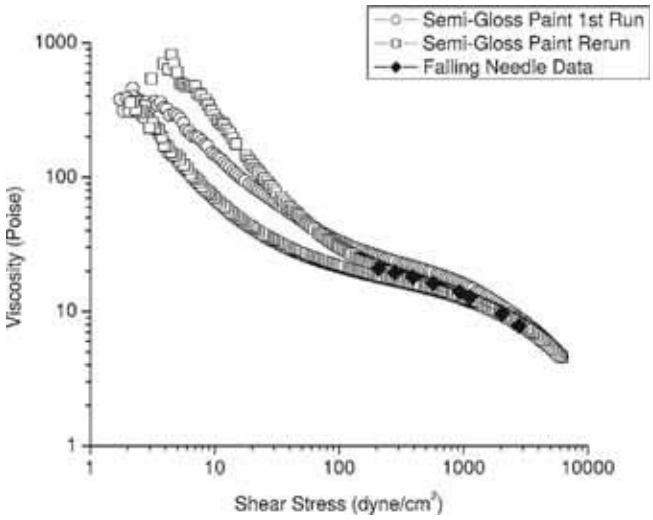

Fig. 34—Comparison of Falling Needle Viscometer® data with that from a rotational controlled-stress rheometer

where ΔP is the decrease in pressure occurring over tube length L of radius R. The shear rate at the tube wall for a Newtonian fluid is given by

$$\dot{\gamma}_w = \frac{4Q}{\pi R^3} \tag{72}$$

where Q is the volumetric flow rate ($cm^3 \cdot s^{-1}$). The viscosity is then

$$\eta = \frac{\sigma_w}{\dot{\gamma}_w} = \frac{\pi R^3 \Delta P}{8LQ} \tag{73}$$

which is the well-known Hagen-Poiseuille equation. For pressure-driven capillary flow, particularly for high-shear measurements, a correction to Eq (73) is required because the fluid undergoes a large acceleration as it enters the capillary. Therefore, the acceleration of the fluid accounts for part of the energy loss represented by the pressure drop ΔP. As a result, the calculated viscosity will be too high and a subtractive term or kinetic energy correction is necessary

$$\eta = \frac{\pi R^4 \Delta P}{8LQ} - \frac{m\rho Q}{8\pi L} \tag{74}$$

where ρ = fluid density and m is a constant equal to unity for Newtonian fluids. For non-Newtonian fluids obeying the power law (see "Shear-Thinning Fluids"), m is calculated from

$$m = \frac{3(3n+1)^2}{(4n+2)(5n+3)} \tag{75}$$

where n is the power law exponent. Various additional corrections for capillary flow are described in van Wazer [49].

The pressure head ΔP can be created two ways: By pressurizing the delivery vessel or by relying on a gravitational hydrostatic head to drive the flow through the capillary. In the latter case, the density of the fluid becomes an important part of the measurement because the rate of flow will depend both on the fluid's viscosity and on the magnitude of ΔP, which now depends on the fluid density ρ and on the height of the fluid above the capillary, h ($\Delta P = \rho g h$).

The fluid density is taken into account by the kinematic viscosity, defined as

$$\nu = \frac{\eta}{\rho} \tag{76}$$

That is, the kinematic viscosity is equal to the shear viscosity divided by the density. The viscosity obtained from gravity-driven capillary flow is in units of stokes (stoke = $P \cdot g \cdot cm^{-3}$). The absolute shear viscosity can then be calculated from $\eta = \nu\rho$.

The velocity profile in tube flow is parabolic in shape for Newtonian liquids [as can be proven by integration of Eq (72)], with the maximum shear rate at the walls and zero shear rate in the tube center. For non-Newtonian fluids the velocity profile is nonparabolic and of complex shape. Because the shear rate in tube flow is nonuniform, the viscosity of non-Newtonian materials will vary across the diameter of the tube. Non-Newtonian fluid measurements may be made accurately only if the Weissenberg-Rabinowitsch correction is applied [117], which corrects for the variations in viscosity across the capillary arising from the nonuniform shear field

$$\eta = \eta_a \left[1 - \frac{1}{4} \frac{d(\log \eta_a)}{d(\log \sigma_w)} \right]^{-1} \tag{77}$$

where η_a is the uncorrected apparent viscosity.[19] The second term inside the brackets is obtained by calculating the slope of a log-log plot of the measured viscosity versus wall shear stress.

Tube flow is inappropriate for materials with yield behavior. Reviews by Schoff [108,109] describe the application of capillary viscometry to coatings.

HIGH-SHEAR CAPILLARY RHEOMETRY

It has been claimed by some that the measurement of very high shear rate viscosity is not necessary because it may be estimated from moderate-shear data. This is true to an extent, especially if one can obtain an adequate description of the general flow curve by use of one of the flow models containing the high-shear limiting Newtonian viscosity η_∞ (e.g., the Sisko, Cross, or Carreau models). If a good enough fit to experimental data is obtained, the latter models can be extrapolated to predict viscosity beyond the experimental range of shear rate, with caution. The simple power-law models should not be used for estimation of high-shear viscosity since they predict unrealistic high-shear behavior (see "Shear-Dependent Viscosity"). However, under the best of circumstances, data should be extrapolated no further than about a decade of shear rate. This means that, in general, shear rates of only about 10^5 s^{-1} can be reached, even by extrapolation methods. It should be pointed out here that the onset of shear thickening (region IV, Fig. 3) cannot be predicted by extrapolation, yet it can cause disastrous consequences in high-shear application processes. In any case, for precise comparisons of materials, extrapolation will be unsatisfactory. There are several industrial processes which involve shear rates of 10^5 to 10^6 s^{-1}. These include airless spray and reverse rollcoating, for example. It will be difficult to resolve performance problems of coatings exposed to such high shear without direct experimental measurement under the appropriate deformation conditions. Such severe conditions of shear can cause a fundamental change in a material, such as gross coagulation of an emulsion, with a possible deleterious effect on rheology and hence on postapplication film formation behavior. It is recommended, therefore, to characterize by high-shear rheometry materials that must be exposed to high-shear processing.

There are some commercial high-shear viscometers which use small-gap bob-in-cup geometry. Problems with this geometry include poor temperature control due to viscous heating and a tendency toward flow-field instabilities. Capillary viscometry has some advantages in both regards. The very short residence time in the capillary at high flow rates minimizes temperature rise, and, for length-to-diameter (L/D) ratios of 50 or greater, entrance effects are negligible and the flow field will be essentially uniform.

By use of short, small-diameter capillaries and high pressures, shear rates of approximately 10^6 s^{-1} are achievable for fluids in the range of viscosities typical of paints [118]. At this writing, however, we are unaware of any commercial capillary rheometers suitable for high-shear rate measurement of coatings fluids other than the Paar-Physica HVA-6.

Rank Pulse Shearometer

This instrument is a relatively inexpensive and simple viscoelastometer. A fixed-frequency acoustic wave pulse is passed through a test sample and the signal detected by a receiving transducer. The propagation velocity v is measured from the signal transit time and used to calculate the shear elastic modulus according to

$$G' = \rho v^2 \tag{78}$$

The signal wave is of high frequency but very small amplitude (10^{-4} rad), so that weak gels are not disturbed (the induced strain will likely be within the linear viscoelastic regime). Because of the high frequency used, the measured shear modulus corresponds to the plateau modulus G_∞ (see "Viscoelastic Models"). This gives a useful measure of the gel strength of even weak gels and has an advantage in this regard over instruments which subject the sample to uncontrolled shear upon closure.

RHEOMETRY

Rheometry is the experimental aspect of rheology. A rheometer is an instrument that measures some rheological property, or material function, such as the viscosity as a function of shear rate or shear stress. Normally, a curve will be produced representing the functional dependence of the measured property. A viscometer, in contrast, will generally measure viscosity at a single (sometimes even unknown) value of the shear rate (or shear stress), or perhaps over a limited range of values. These types of devices are typically found in the industrial quality control or formulation laboratory, and have been discussed in earlier sections. This

[19] The "apparent viscosity" is simply the quotient of the apparent (or experimentally measured) shear stress and the apparent shear rate. The true values of the foregoing, however, may be different from the apparent, as for example for flow fields where the shear rate varies across the field and must be corrected for non-Newtonian effects, or where inertia errors are involved.

section will focus on techniques for the use of rotational rheometers to characterize fluids with complex rheological properties.

Rotational Rheometry

Simple shear deformation was defined previously for a fluid confined between a stationary surface and a moving surface that are in parallel, rectilinear motion (i.e., a "sliding plate" rheometer). There are, however, very few rheometric instruments that utilize this test geometry. This is due to the fact that it is not a practical geometry, because either the experiment must be rather short in duration or one of the shear faces must be very long. This predicament is solved by using rotational motion to shear a material between, say, a fixed plate and a rotating disk. The majority of commercial rheometers operate in this way, using a variety of rotating fixtures or geometries, mainly:[20]

1. cone and plate
2. parallel plate
3. concentric cylinder (bob and cup).

Detailed descriptions of these standard geometries can be found in the referenced monographs [22,45,107,119].

There are three principal rheometric techniques typically used for *rotational rheometers,* discussed below.

1. Steady shear (large strain)
   a. Equilibrium viscosity measurement
   b. Non-equilibrium viscosity measurement
   c. Normal stress measurement.
2. Creep (medium strain)
3. Oscillation (small strain).

Steady Simple Shear (Equilibrium Flow)

Steady simple shear involves a uniform flow field in which the shear rates and stresses are independent of position. Not all rheometer test geometries meet this criterion exactly, but they do generally satisfy the requirements of *viscometric flow,* defined by Dealy [120] as a flow field that is "everywhere indistinguishable from steady simple shear." Viscometric flow is a necessary requirement in order to properly measure the viscoelastic material functions.

Some rotational rheometers utilize steady-shear equilibrium viscosity measurements to characterize flow behavior by means of a series of shear rate steps. If, for example, a constant torque is applied to a specimen until a constant shear rate is observed (after inertial and structural relaxation effects have equilibrated with time), the system is undergoing *steady simple shear* and the *steady-state viscosity* or *equilibrium viscosity* can be measured. (Even with thixotropic materials, one should generally be able to observe a steady-state viscosity value eventually.) An equilibrium flow curve (as in Fig. 3) can be generated in this way.

Time-Dependent Materials: Nonequilibrium Flow Curve

As mentioned, one can construct a curve of equilibrium viscosity versus shear rate or shear stress by a series of step-equilibrium experiments. However, the *nonequilibrium flow curve* is less time-consuming experimentally and perhaps more informative with regard to the processability of time-dependent materials. The nonequilibrium flow curve is obtained by recording the viscosity while either the angular velocity or the torque is "ramped"—i.e., increased with time (usually followed by a decreasing torque or velocity ramp) [Fig. 9A]. Time-dependent effects such as *hysteresis* can be seen in this way [Figs. 9B and 24]. The collapse of structure can be seen, but which is lost in an equilibrium measurement. Fig. 24 (solid circles) shows a flow curve for a structured fluid, measured by a stress-ramp procedure, with the upper curve corresponding to the increasing-stress ramp and the lower curve the decreasing-stress ramp.

SHEAR HISTORY EFFECTS: SAMPLE MOUNTING AND CONDITIONING

A great many industrial and commercial fluids possess time-dependent rheology, usually thixotropy, but occasionally anti-thixotropy (see "Time-Dependent Fluids"). Time-dependent materials pose a special set of challenges to the experimentalist, and it is easy to make mistakes in characterizing them. For time-independent systems, the pre-experiment shear history is of no consequence. In contrast, the shear history of time-dependent materials prior to the experiment can greatly influence the results.

Both the degree of deformation in mounting a sample and the time lapse since mounting will determine the rheological state of a time-dependent material, and hence the experimental result. Failure to take account of this issue often leads to poor repeatability of data on such systems. Some approaches to the control of the shear history problem are:

1. Controlling the rate of closure of the platens in a parallel plate or cone-plate experiment (e.g., exponentially decreasing closure rate)
2. Allowing a rest time for the sample after mounting (limited by evaporation and productivity issues)
3. Giving a controlled shear history to the sample, e.g., preshearing the specimen for a set period, then initiating the experiment immediately on cessation of shear. (An up-down ramp cannot be applied in this case, since the sample would begin to recover in an uncontrolled way concurrent with the initial low-shear ramp onset. Instead, a series of step reductions from high shear can be applied, with the time delay between steps being varied, in order to simulate the effects of varying degrees of structural recovery [121].

Method (1) reduces the strain rate (but not the strain) that the sample experiences as the instrument gap closes, but will be limited in its effectiveness because practical rates of closure (and the coupled deformation) are likely to be significant in terms of their effect on the specimen's structural integrity. Furthermore, depending on the geometry (e.g., cone and plate) the strain may not be uniform. Method (2) is limited by the time one can afford to wait for structure recovery. It is not uncommon for a material to require hours in order to regain its "rest-state" condition. The use of an arbitrary rest time is a compromise that provides a practical (if not ideal) method of characterizing thixotropic materials. Method (3) is somewhat arbitrary, too, in that it is not known *a priori* at what shear stress or shear rate or for how long a material must be preconditioned in order to achieve adequate or consistent structural breakdown. Whatever the method chosen, it is important to

[20] Another principal test geometry used in steady shear flow is tube flow or capillary rheometry. Its use is somewhat limited outside of the characterization of polymer melts, and will not be further discussed here.

adhere strictly to a constant protocol if results are wanted on a comparable basis.

RAMP METHODS

Many rotational rheometers are able to apply a time-based ramp of torque or angular velocity for purposes of flow curve measurement. Some allow a choice of a linear time-based ramp or one that is logarithmic with time. The latter method spaces the data points very close together in the beginning of the ramp, which increases the amount of information obtained at low shear rates and stresses. For time-dependent systems, it is important to keep both the pre-experiment shear history and the experimental protocol constant, in order to assure valid comparison of materials. This means keeping the following experimental settings the same for a given series of experiments:

1. Sample preconditioning
2. Choice of linear or log time-based ramp
3. Ramp duration
4. Initial and maximum shear stress (or shear rate)
5. Duration of any "hold-time" at ramp maximum.

TRANSIENT METHODS

Transient methods are non-steady state, i.e., the stresses, strains and material properties are not at equilibrium, and it is their behavior as a function of time that is being studied, as they move toward equilibrium. Transient methods include:

1. Step shear stress (creep and recovery)
2. Step shear strain (stress relaxation)
3. Step shear rate (thixotropic recovery)
4. Startup of flow. The first two methods have been briefly discussed in the section on "Elastic Liquids." The third method was described in the "Time-Dependent Fluids" section. The last method will not be discussed here. For more detail on creep methods see Ref. [122].

Oscillatory Shear

If, instead of applying a stress (or, interchangeably, strain)[21] in a constant direction, the direction of the strain undergoes cyclic reversal, then the specimen is subjected to oscillatory deformation, sometimes also referred to as a dynamic test. Most commercial rheometers are capable of oscillatory shear using a variety of test geometries. Oscillatory testing is normally done in the linear viscoelastic regime (LVER), where the stress and strain are related by a linear differential equation. The usual practice is to employ sinusoidal variation of strain or stress. Testing modes in oscillation include:

1. Torque sweep or strain sweep at constant frequency
2. Frequency sweep at constant strain
3. Time or temperature sweep at constant frequency and strain.

Oscillation is a convenient way of characterizing medium to short time-scale response of viscoelastic materials. The employment of small strains (below the critical strain limit of the LVER) at low frequencies is a reasonable simulation of the physical state of a newly applied coating layer in the process of film formation. Hence, the low-frequency linear viscoelastic properties of coatings are of interest in understanding this phase of coating performance, especially if measured subsequent to a high-shear, high-strain experience.

[21] Note that it is immaterial whether the independent variable is the stress or the strain, for oscillatory linear viscoelastic measurements. Wherever the discussion mentions "stress," one may equally well read "strain."

TORQUE SWEEP/STRAIN SWEEP

Torque sweep on a controlled-stress rheometer or strain sweep on a controlled-strain-rate rheometer are used to determine the strain-sensitivity of the viscoelastic parameters, and thus determine the *critical strain* γ_{cr}, which is the strain limit of linear viscoelastic response. Above the critical strain, the fluid microstructure responsible for elastic response begins to break down. The elastic modulus G' is a sensitive indicator (more so than the dynamic viscosity) of the breakdown of structure, and is often used to determine the critical strain. The experiment is done by applying a constant frequency (e.g., 1 Hz) while increasing the torque gradually, so that the strain amplitude steadily increases. G' will be constant within the linear viscoelastic regime. The critical strain is sometimes arbitrarily chosen as the point where G' has fallen by 10 % (Fig. 35). The strain is then held constant at the critical value for subsequent frequency sweep experiments, ensuring that the deformation remains within the linear regime. It should be noted, however, that the critical strain is not a single value for a given material but will decrease as the oscillation frequency decreases, a consequence of the superposition of viscous and elastic deformation responses in a viscoelastic material.

Polymeric systems can have quite large critical strains (>10 %), while γ_{cr} for colloidal systems can be quite small (<10 %). The critical strain value is a measure of the "brittleness" or "ductility" of the microstructure, and an indicator of the relative length scale of the forces responsible for the elastic behavior. Difficulty is often encountered in finding the linear regime for thixotropic materials composed of flocculated or associated particles, because the structure is rather "brittle," attractive forces are short-range, and the critical strain is consequently small.

FREQUENCY SWEEP

In a frequency sweep experiment, the oscillation frequency is steadily increased, while the strain is held constant below the critical value. Typically, the frequency is swept logarithmically with time, so that the discrete frequency points are linear on a log axis. A typical plot of viscoelastic

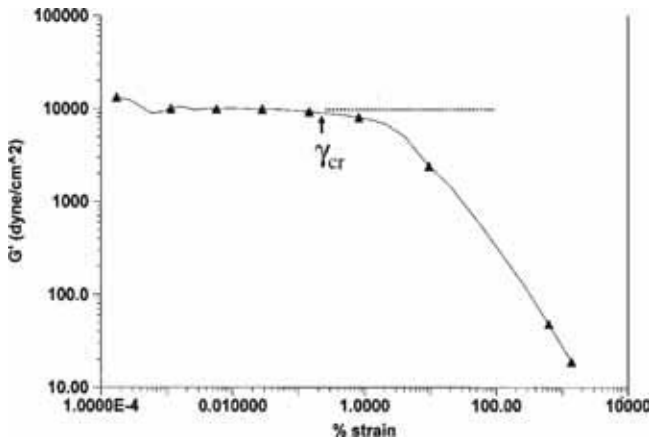

Fig. 35—Illustration of torque-sweep (strain-sweep) data and the location of the critical strain γ_{cr} for oscillatory shear testing.

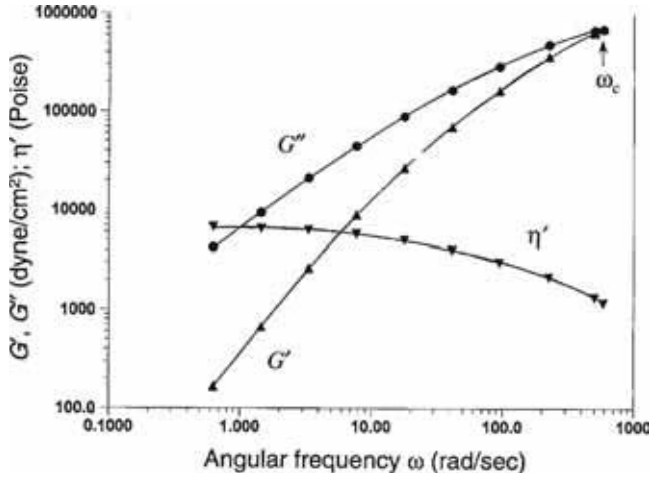

Fig. 36—Typical dependence of the viscoelastic parameters on frequency in a frequency-sweep experiment. Crossover frequency ω_c is indicated.

functions for a frequency sweep experiment is shown in Fig. 36. G' and G'' normally increase with frequency while η' decreases with frequency, trends which can be understood by examination of the mechanical models' response. As pointed out in "Elastic Liquids," values for the viscoelastic functions can be obtained from frequency-sweep data, e.g., the frequency ω_c where G' and G'' cross equals the inverse of the relaxation time (Maxwell model). A gel is distinguished by having a nearly constant value of G' with frequency.

TIME OR TEMPERATURE SWEEP

A time sweep at constant frequency is used to characterize recovery of structure after shear, e.g., for a thixotropic material (see "Time-Dependent Fluids"). Emulsion stability can be indicated by temperature sweep experiments at constant frequency [123]. An oscillatory temperature sweep is an excellent way to characterize the chemical advancement of thermosetting polymers, a technique used in a subdiscipline known as chemorheology (study of the rheology of chemically reacting systems) [60,124].

EXPERIMENTAL PROTOCOL

Similar to the discussion of shear-history effects above, the rheological state of a specimen is of concern, with an eye to obtaining repeatable results. Consequently, the following series of experimental steps is recommended:

1. Specimen should be prior-sheared in steady shear at an arbitrary high shear rate or stress value, to put the specimen in a low-structure state;
2. A constant-frequency small-strain oscillatory time-sweep step should be immediately begun, following the structural recovery to a constant-property state, if possible;
3. Once the specimen has recovered to equilibrium properties, either of two experiments can be done:
   a. Oscillatory frequency-sweep experiment, or
   b. Steady-shear flow curve ramp experiment.

The above protocol is a logical sequence that permits tests to be done on a specimen that is in a repeatable rheological state.

APPENDIX

List of Rheometer/Viscometer Suppliers

Anton Paar USA Inc.
10215 Timber Ridge Drive
Ashland, VA 23005
Ph: 804-550-1051
Fax: 804-550-1057
E-mail: info.us@anton-paar.com
www.anton-paar.com

Brookfield Engineering Laboratories, Inc.
11 Commerce Boulevard
Middleboro, MA 02346
Ph: 508-946-6200 or 800-628-8139
Fax: 508-946-6262
E-mail: sales@brookfieldengineering.com
www.brookfieldengineering.com

BYK-Gardner USA 9104
Guilford Road
Columbia, MD 21046
Ph: 301-483-6500
Fax: 301-483-6555
www.byk.com/instruments/
E-mail: info.BYK.GardnerUSA@altana.com

Cannon Instrument Company
P.O. Box 16
2138 High Tech Road
State College, PA 16804-0016
Ph: 800-676-6232
Fax: 814-353-8000
E-mail: sales@cannoninstrument.com
www.cannoninstrument.com

Malvern Instruments, Inc.
117 Flanders Road
Westborough, MA 01581-1042
Ph: 508-768-6400
FAX: 508-768-6403
E-mail: info@malvernusa.com
www.malvern.com

Reologica Instruments, Inc.
231 Crosswicks Road
Bordentown, NJ 08505
Ph: 609-298-2522
Fax: 609-298-2795
E-mail: info@reologicainstruments.com
www.reologicainstruments.com

Stony Brook Scientific
1055 West Germantown Pike
Norristown, PA 19403
Ph: 610-635-1740/888-889-7764
Fax: 610-635-1780
E-mail: info@stonybrooksci.com
www.stonybrooksci.com

TA Instruments, Inc.
109 Lukens Drive
New Castle, DE 19720
Ph: 302-427-4000
Fax: 302-427-4001
E-mail: info@tainstruments.com
www.tainst.com

Thermo Scientific
(Haake Rheometers/Viscometers)
Ph: 800-258-0830
www.thermo.com

Thomas Scientific
99 High Hill Road
P.O. Box 99
Swedesboro, NJ 08085-0099
Ph: 856-467-2000
Fax: 800-345-5232
E-mail: value@thomassci.com
www.thomassci.com

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Surface Energetics

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Nomenclature

a	=	**Integration limit, distance from surface into bulk of material, Eqs (3) and (6)**
a	=	Subscript for advancing contact angle
A	=	Surface area
A	=	Subscript indicating adhesion, Eqs (12), (13), (31), and (32)
b	=	Variable in Eq (25), the difference in maximum and minimum diameters in elliptical orifice
c	=	Constant in Eq (33)
c	=	Surfactant concentration
c_i	=	Concentration of species i
c_{i0}	=	Concentration of species i in the bulk
C	=	Subscript indicating cohesion, Eqs (11) and (13)
D	=	Diffusion coefficient
E	=	Surface elasticity
f	=	Correction factor, Eq (22)
f	=	Fractional surface area, Eq (15)
F	=	Pull-off force, Eq (31)
g	=	Acceleration of gravity
G	=	Gibbs free energy
h	=	Variable defined in Eq (9)
h	=	Height in capillary rise measurements
h	=	Width of falling film in curtain coating, Eqs (36)–(38)
i	=	Index identifying species i
j	=	flux of adsorbing and desorbing species
k	=	Wave number = $2\pi/\lambda$ (λ = wavelength, see below), Eq (27)
l	=	Subscript indicating liquid phase
l	=	Length of capillary pore path in Eq (23)
$\mathbf{n}$	=	Normal vector to surface, Eq (3)
n	=	Exponent in Eq (4)
n	=	Most probable number of drops from breakup of charged drop, Eq (31)
n_i	=	Number of moles of component i, Eq (2)
p	=	Pressure
$\mathbf{p}$	=	Pressure tensor in the bulk phase, Eq (3)
$\mathbf{p}^T$	=	Tangential pressure tensor, Eq (3)
$\mathcal{P}$	=	Perimeter length
$\mathcal{Q}$	=	Liquid flux, volume/second
q	=	Charge on drop
r	=	Variable in Eq (25), sum of maximum and minimum radii in elliptical orifice
r	=	Radius
r	=	Roughness ratio, Eq (14)
r	=	Subscript for receding contact angle
r	=	Average pore size in rate of penetration into powder measurements, Eq (34)
R	=	Ring radius in Du Nouy ring surface tension measurement
R	=	Diameter of probing tip in direct force AFM measurements, Eqs (31) and (32)
R_1, R_2	=	Principal radii of curvature
s	=	Subscript indicating solid phase
S	=	Entropy
S	=	Subscript indicating spreading, Eq (13)
T	=	Temperature
T_c	=	Critical temperature
u	=	Velocity, Eqs (26) and (26*a*)
x	=	Distance from surface in Eq (6)
v	=	Index indicating vapor phase
v	=	Velocity, Eq (25)
V	=	Volume
W	=	Weight
W	=	Work, Eqs (11)–(13)
Y	=	Subscript for Young's contact angle
γ^0	=	Liquid surface tension at $T = 0$
γ	=	Liquid surface tension

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Γ, Γ_i	=	Surface excess concentration, of *i*th species
δ_f	=	Final film thickness in dip coating
Δ	=	Difference
ε	=	Dielectric constant
η	=	Viscosity
θ	=	Contact angle
λ	=	Wavelength
μ_i	=	Chemical potential of species *i*
π	=	3.141 59
ρ	=	Density
ω	=	Frequency
0	=	Subscript indicating zeroth or bulk phase, or reference value

INTRODUCTION

SURFACES ACT AND PERFORM DIFFERENTLY FROM the bulk material because they have two distinct properties that do not exist in the bulk. First, the unbalanced forces on molecules or atoms at the surface cause it to have excess free energy when compared to the bulk [1] (i.e., they are in a higher state of potential energy). This excess energy per unit area is the thermodynamic cost of forming a new surface; it has the units of energy/area or force/length. The latter units are those of tension, and the surface excess free energy is often known as surface tension and can be measured for liquids as such. (A more detailed discussion of this excess free energy identified with a surface, including the thermodynamic definition of surface tension, is given below.) Second, there is a preferred direction normal to the surface that can be defined in the mechanical definition [2] of surface tension. This directional effect of surfaces can be observed in molecular directionality in adsorption phenomena, surface area minimization by surface tension effects, and molecular ordering in Langmuir-Blodgett films deposited from ordered mono-molecular layers (monolayers).

Since the first version of this chapter was published in 1995, there has been a significant increase in the attention given to surface and interfacial effects, including those in organic coating systems [3]. Much of this interest has been due to the increasing importance of science at the nanoscale. When one approaches nanometer dimensions, surface effects begin to predominate, and careful consideration must be given to surface energetics [4]. For this reason, we have revised and updated this chapter into its present form. Much of what was stated in the first version remains true, but more recent research has yielded additional knowledge regarding the science of surfaces. Scanning tunneling microscopy, atomic force microscopy [5], and a broad range of new characterization tools that greatly enhance our capabilities to characterize and visualize surfaces at nm dimensions have become everyday tools for scientists and engineers working in many fields.

Surfaces occur only when the energetic cost of creating an interface between two dissimilar materials or phases is satisfied. Thus, there are no stable interfaces between gases, nor among phases in a material above its critical point. However, surfaces can occur between gas and liquid (g/l), liquid and liquid (l/l), gas and solid (g/s), liquid and solid (l/s), and solid and solid (s/s) phases. An example of a g/l interface is the surface of an open, unfrozen body of water. Because a liquid surface cannot support a stress, its surface energy phenomena can be analyzed directly by equilibrium thermodynamics. For a solid, object history will affect the properties of the surface. As a result, surface energy and surface stress must both be considered in analyzing the properties of an interface [6]. Even though this is well known, there has not been as much concern given to the surface history of solids when determining their surface properties as is necessary [7].

Surface effects relative to bulk properties become more important as the surface area to volume ratio for materials becomes larger. In the simplest case, a sphere, this ratio is given by

$$\frac{A}{V} = \left[\frac{4\pi r^2}{\frac{4}{3}\pi r^3}\right] = \frac{3}{r} \tag{1}$$

In the most general case, one can estimate that the surface to volume ratio for any object shape always scales as the reciprocal of some characteristic linear dimension of the object. Surface effects thus increase in importance as the size of the object being considered becomes smaller. Statistical thermodynamics and molecular dynamics considerations indicate that the range of surface effects as two to five molecular diameters [8]. Simple arguments concerning the dimensions of a [solid polymer 1/polymer 2] interface give similar estimates [9]. An interesting feature of this type of analysis of surface effects and their ranges is that the distance of propagation of surface effects into the bulk from a polymer adsorbed at an interface can be quite large in atomic dimensions. In effect, the interface pins one end of the polymer, removing one of its degrees of freedom, and thus making it a location of different thermo-mechanical properties than the bulk of the polymer. This is of exceptional importance when analyzing the adhesion of polymeric films to bulk substrates. The strength of the adhesive bond can be influenced by these directionality effects and can be even more important if the substrate is a plastic (polymer), since the ordering effects propagate on both sides of the interface [10]. The directionality and ordering of surrounding polymeric bulk media near an interface can extend unexpectedly large distances. Many of the properties of self-ordering systems have these effects as their origin. This will be commented upon further in the discussion of surface effects in pigment dispersion and emulsions.

Anyone dealing with coatings must realize that surface effects are very important in all stages of coating preparation, application, and utilization. Coatings are thin films with high surface-to-volume ratios. Pigments also have large surface-to-volume ratios, and their surfaces are often chemically reactive or catalyze reactions [11]. Latex polymers also occur in fine particulate form, and their use and stability depends on surface-dominated effects. Foaming, cratering, and other coating defects develop through surface-mediated events [12,13]. The wetting, coverage and adhesion of a coating to a substrate is strongly affected by

surface effects. Adsorption at surfaces of particulate materials in a coating, be they pigments or polymer particles, is controlled by the energetics of the interface between the particles and the suspending liquid.

SURFACE THERMODYNAMICS—BASICS

Liquid Surfaces

To understand surface energetics in coatings, one must first understand the basic thermodynamics of surfaces and interfaces. However, when the system under consideration contains a surface, the definition of the Gibbs free energy is modified. The defining equation for liquids is

$$dG = -SdT + Vdp + \sum_i \mu_i dn_i + \gamma dA \tag{2}$$

where G, T, S, V, p, μ_i, and n_i are the thermodynamic quantities Gibbs free energy, temperature, entropy, volume, pressure, chemical potential of component i, and the number of moles of component i, respectively, and γ and A are the surface tension and surface area. The other equations of thermodynamics can be similarly modified. As can be seen, the energetic cost of expanding a liquid surface is the γdA term. Again, the use of γ is valid only for liquid interfaces; it cannot be considered a thermodynamic quantity for solid surfaces because they store energy as surface stress and are thus not in true equilibrium [7]. Many references discuss this equation in detail (see Ref. [4], for example) Another equation for γ is the mechanical definition given in Ref. [2], also discussed by Adamson [1] and reviewed by Burshtein [14] and Navascues [15] as

$$\gamma = \int_{-a}^{+a} \left(\mathbf{p} - \mathbf{p}^T\right) d\mathbf{n} \tag{3}$$

where $+a$ and $-a$ are distances in either direction from the surface such that molecules at these positions are in the bulk phases, $\mathbf{p}$ and $\mathbf{p}^T$ are the bulk and tangential pressure tensors, respectively, and $\mathbf{n}$ is the normal vector to the surface; this is shown schematically in Fig. 1. The direction of $\mathbf{n}$ is the preferred direction of a surface referred to above. Even if it is not commonly included in introductory discussions of surface phenomena, it is important to consider Eq (3) when considering the thermodynamics of surfaces because it is the relationship between the bulk mechanical properties of the system and the almost "discontinuous" behavior of the system properties at an interface. A more recent discussion of this manner of expressing surface tension is given by Davis [16]. This expression also describes the *directionality* that an interface possesses and is very crucial to modern theories of capillarity [17].

In general, the surface tension, γ, of pure liquids decreases with increasing temperature. An approximate form of this temperature dependence is [16,18]

$$\gamma = \gamma^0 \left(1 - \frac{T}{T_c}\right)^n \tag{4}$$

where γ^0 is the surface tension at $T = 0$, T_c is the critical temperature of the material, and n is an empirical exponent, ~11/9 for organic liquids.

The other important thermodynamic relation for surfaces is the Gibbs equation. In multi-component systems, one must consider the effects of materials absorbing at the interface. When these are properly taken into account, the Gibbs equation (at constant T and p) gives

$$d\gamma = -\sum_i \Gamma_i d\mu_i \tag{5}$$

where Γi is the surface excess concentration for component i [4,19]. This equation gives the relationship between the surface tension of a fluid interface and the amounts of surface active materials (hereafter referred to as surfactants) in the solution (component i). The surface excess concentration Γi is the difference between the actual and bulk concentrations, c_i and c_{i0}, of component i and can be calculated in a manner analogous to Eq (3) as

$$\Gamma_i = \int_{-a}^{+a} \left(c_i - c_{i0}\right) dx \tag{6}$$

where x is again the direction normal to the interface and $+a$ and $-a$ are locations equidistant from the interface in the bulk of the material. Fig. 2 expresses this schematically for a single surfactant. In adsorption of materials to an interface, the local concentration in the neighborhood of the interface can be much higher (by factors of up to 10^8 or greater—see Ref. [1], Chapter 3 for further details or for a more recent version, see Ref. [20]) than that in the bulk.

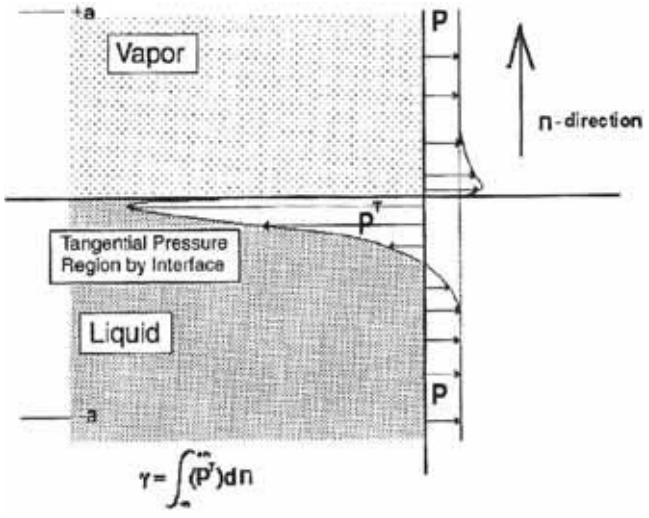

Fig. 1—Schematic of local pressure changes at surface giving surface tension.

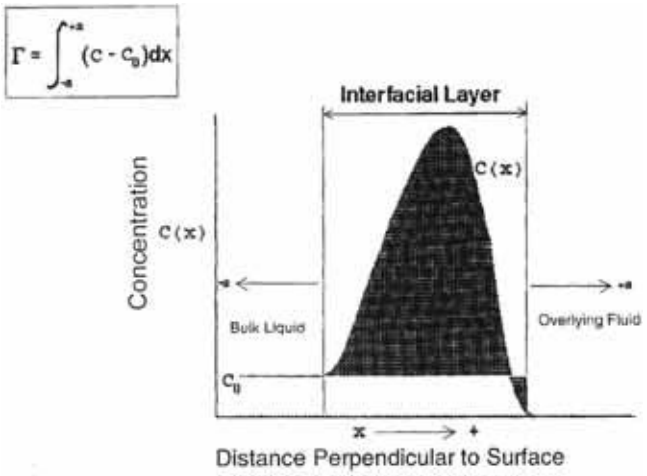

Fig. 2—Schematic of surface excess concentration as calculated as difference for bulk concentration.

The net energy of the system is minimized by the surfactant molecules adsorbing and orienting at the interface to reduce interactions between unlike molecular components. The terms often used to describe the compositional differences in surfactants are polar/nonpolar or hydrophobic/hydrophilic. Materials that act as surfactants are those that have a distinct separation of properties between different sections of their molecules, the classic example being soaps, with an alkyl nonpolar group and a [carboxylat+metal ion] polar group.

In concentrated systems of surface-active materials, especially those of low inherent solubility in the liquid phase, there exists a certain concentration where the addition of further surfactant no longer depresses the surface tension, as the surface is saturated, and the molecules of the surfactant begin to form self-ordered structures, or micelles, in the bulk liquid [21]. Micelles are aggregates of surfactant molecules that form in solution to minimize the total system energy. In water, they orient with the hydrophobic portion of the molecule directed toward the interior of the micelle, and in non-aqueous systems they have the hydrophilic end in the interior. At the surfactant concentration where micelles just begin to form, many of the solution properties also undergo rapid change; this breakpoint in surfactant solution properties is known as the critical micelle concentration (CMC) (Fig. 3). The CMC is a unique concentration for a surfactant/solvent combination at a specified temperature. The book by Rosen [22] gives an expanded discussion of surfactant behavior, and Tanford's book [23] provides further description of micellar behavior in aqueous systems. These texts also describe the complex aggregates that form in surfactant/solvent mixtures, including membrane-like structures and liquid crystals.

Micellar effects and the more general case of self organization in materials has become a very important part of recent studies in materials science. Much of what is considered under what is termed "Soft Matter" concerns itself with colloidal and surfactant behavior involving self-organized matter [3,4,9,24,25]. This still-evolving area of materials science appears to be very pertinent to the science of organic coatings [3].

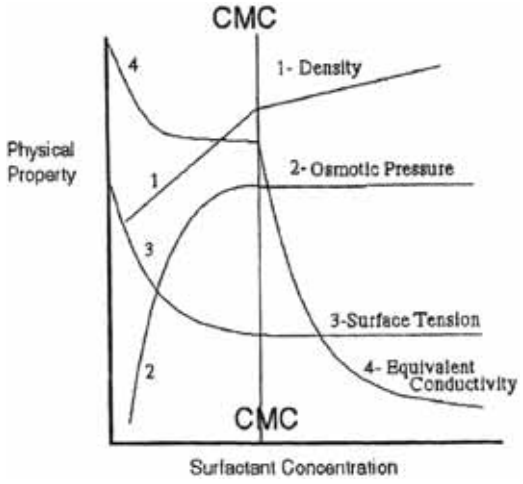

Fig. 3—Schematic of physical property changes in surfactant solution at critical micelle concentration (CMC).

As Gibbs first noted, the presence of a material adsorbing preferentially at an interface imparts elasticity to the surface, as it will tend to resist expansion and contraction. This surface elasticity is given by

$$E = \frac{d\gamma}{d\ln A} = -\frac{d\gamma}{d\ln \Gamma} \tag{7}$$

where A is the surface area. This elasticity is the resistance to disturbance of a film by the presence of a surfactant. The effects of this surface elasticity have been reviewed with respect to liquid films and liquid threads [26]. Recent reviews of surface elasticity discuss this effect in surfactant solutions [25,27], furthermore, an examination in coating application processes emphasizes the importance of dynamic effects in such processes [28]. Surface elasticity measurements have been used to characterize the properties of monomolecular layers at surfaces [29]. If a soluble surfactant diffuses to the surface (see below, "Dynamic Properties of Liquid Surfaces"), it will reduce the surface elasticity, effectively short circuiting the surface tension changes by surface replenishment [30–32]. In these cases, Eq (7) should be modified to read

$$E = \frac{-(d\gamma / d\ln \Gamma)}{\left[1 + (h/2)(dc/d\Gamma)\right]} \tag{8}$$

where c is the surfactant concentration and h is given by the relationship

$$h = 2\sqrt{\frac{D}{\omega}} \tag{9}$$

where D is the surfactant diffusion coefficient, and ω is the frequency of the surface motion [31]. Surface elasticity effects are a major consideration in foam stability [33] and where there are rapid surface area changes and creation of new surfaces [34].

Liquid/Solid Interfaces: Wetting and Contact Angles

When a liquid comes into contact with a solid, a three-phase contact, or wetting, line develops between the liquid, solid, and vapor. Three interfaces are generated; thermodynamic equilibrium exists when the total interfacial energy, the excess energy attributed to the solid-liquid, solid-vapor, and liquid-solid interfaces, is minimized. The liquid-vapor interface forms a characteristic angle tangent to the solid surface as a result [35]. This contact angle is often used to determine the surface excess energy, or surface tension, of the solid-vapor interface through Young's equilibrium equation [4,36]:

$$\gamma_{sv} = \gamma_{sl} + \gamma_{lv}\cos\theta \tag{10}$$

Here, γ_{sl}, γ_{sv}, and γ_{lv} represent the solid-liquid, solid-vapor, and liquid-vapor surface tensions, respectively, and the contact angle is measured between the solid-liquid and liquid-vapor interfaces. The equation is applicable to any solid surface when γ_{sl} and γ_{lv} are known and θ is measurable; issues such as roughness and chemical heterogeneity will be revisited later [24,37]. Often γ_{sl} is unknown; here, two measurements using different liquids of known γ_{lv} gives two equations with two unknowns and γ_{sv} is

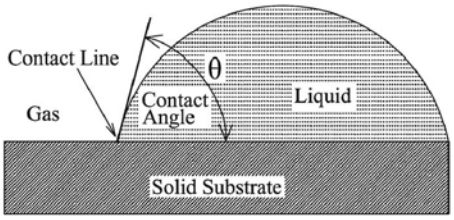

Fig. 4—Schematic of contact angle in G/L/S system.

solved algebraically. Fig. 4 shows the measured contact angle between the three phases. Further derivations and applications of Young's equation are discussed in the review by Churaev and Sobolev [38]. The case where the "substrate" is an immiscible liquid is discussed in Chapter 13 of Ref. [4].

A contact angle describes the wetting behavior of a liquid for a given solid. Complete wetting, or a contact angle of zero, occurs when the liquid spreads spontaneously over the substrate. In this case γ_{lv} is lower, or more favorable, than γ_{sv} and the liquid displaces the air in contact with the solid surface. Any contact angle greater than zero causes the liquid to not wet the solid, or to bead up and form a sessile drop. From Young's equation the relation between γ_{sv} and γ_{sl} determines the shape of the drop such that the contact angle is less than 90° when $\gamma_{sv} > \gamma_{sl}$ and 90° when $\gamma_{sv} < \gamma_{sl}$. Fig. 5 lists the possible scenarios for wetting. The work of spreading, W_S, is a measure with which a liquid favors spontaneously wetting a solid. This value is the difference between the work of adhesion, W_A, and work of cohesion, W_C, for the solid-liquid interface [39].

$$W_C = 2\gamma_{sl} \tag{11}$$

$$W_A = \gamma_{sv} + \gamma_{sl} - \gamma_{lv} \tag{12}$$

$$W_S = W_A - W_C = \gamma_{sv} - (\gamma_{sl} + \gamma_{lv}) \tag{13}$$

A positive spreading coefficient indicates the liquid possesses sufficient excess energy in the liquid to spread

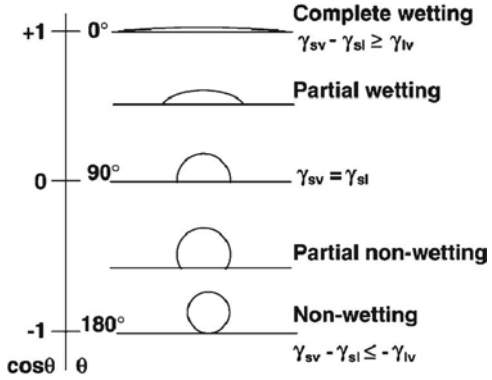

Fig. 5—Schematic of the possible scenarios for wetting. (*Image duplicated from Fig. 4 of Ref. 37*). Reprinted from *Advances in Colloid and Interface Science*, Vol. 133, Kumar, G. K., Prabhu, N., "Review of Non-Reactive and Reactive Wetting of Liquids on Surfaces," pp. 61-89, 2007, with permission from Elsevier.

spontaneously under equilibrium conditions, whereas a finite contact angle is formed for W_S less than zero [40,41].

The surface energy of a substrate is the determining factor in the degree of wetting that occurs. Polarity, which often describes affinity to water, has also been discussed as a basis for predicting extent of wetting and is dependent on the nature of the substrate [42]. Low surface energy, hydrophobic solids such as hydrocarbons or fluorocarbons are not easily wet and form high contact angles with most pure solvents or solutions; poly(tetrafluoroethylene), or Teflon®, is an extreme example of this. Superhydrophobicity and supero-leophobicity describe solid materials whose contact angle with water and organic liquids, respectively, is larger than 150° [43]. Also unique to these surfaces is that they have near-zero contact angle hysteresis, or the difference between the advancing, θ_a, and receding, θ_r, contact angles [44]. Materials of this nature have been the subject of extensive research within the last decade, especially in areas including stimulus-response chemistry, biologically inspired synthesis, and hierarchical structuring [45]. Substrates with these properties are of great interest and are considered for a variety of possible uses such as self-cleaning and self-healing applications. Additional publications concerning these topics and the chemical and topographical sources of their extreme contact angles are found in Refs. [42–54].

High surface energy materials include metals and metal oxides that form low contact angles and are easily wet. When coating these materials, caution should be taken during surface preparation; oils and low surface energy impurities readily adsorb and have the effect of lowered surface energy and reduced wetting. Wettability is essential in the application of coatings to polymeric or metallic substrates; the liquid must wet the surface completely to obtain good adhesion [40]. This is commonly achieved by cleaning the substrate well, or adding surfactants to the wetting liquid to depress its surface tension and reduce the contact angle to zero. Cationic surfactants are most commonly used because the surfaces to be wet generally have a negative charge [38]. Methods for measuring the extent of cleanliness, such as contact angle, have been discussed by Durkee and Kuhn [55]. Surface preparation is the single most important step in coating application to ensure substrate/coating adhesion and guarantee its protection. In addition to cleaning with detergents, physical and chemical surface pre-treatment options for altering the substrate surface energy are available; a section at the end of this chapter is dedicated to their discussion. Pre-treatments such as flame and corona are especially necessary for low surface energy polyolefin substrates such as polyethylene or polypropylene.

Adjusting the surface roughness of a substrate also affects a coating's ability to wet a substrate [40]. Substrate pre-treatments may often include sanding or other roughening techniques. Increased surface roughness promotes wetting when the contact angle is below 90° but decreases wetting for those above 90°. Roughened surfaces generally have the adverse effect of creating a hysteresis in the contact angle measurements, with the advancing drop being the larger than the receding [39]. In order to maintain the applicability of Young's equation, Wenzel developed a relation to account for surface roughness. Here, cos θ_{rough} is the measured contact angle, cos θ_{smooth} is the thermodynamic

contact angle for an atomically smooth surface, and r is the roughness ratio [37]:

$$\cos\theta_{rough} = r\cos\theta_{smooth} \quad (14)$$

$\cos\theta_{smooth}$ is also the theoretical Young's equilibrium contact angle, θ_Y. Aside from wettability, contact angle measurements are also valuable for studying the weathering and degradation of organic coatings. Wenzel's equation has been applied to polymer photodegradation; chemical bonds are broken at the surface, polymer segments are liberated, and the contact angle is decreased [56,57]. This roughening is not unlike surface pre-treatments.

Hysteresis effects also arise from compositional variations or impurities at the surface [37]. Heterogeneity in a polymer surface is almost inevitable when considering the phase separation that occurs between crystalline and amorphous regions. The Cassie-Baxter equation can be applied to chemically heterogeneous surfaces if an estimate of the partial surface area of each material is known [58]:

$$\cos\theta = f_1\cos\theta_1 + f_2\cos\theta_2 \quad (15)$$

Here, θ is the contact angle and f is the fractional surface area for the chemically homogeneous materials of respective indices. The combination of these and other variables result in contact angle measurements that are slightly ambiguous and irreproducible within small standard deviations. However, with great care, techniques such as the low-rate dynamic automated axisymmetric drop shape analysis-profile (ADSA-P) have yielded contact angle accuracy greater than 0.3° [59].

It may be of interest to determine the surface tension required of a coating to wet a given substrate. Zisman and co-workers derived a method using contact angle measurements for determining the "critical surface tension," or the energy needed for a liquid to spontaneously wet the solid surface of interest. This is the γ_{lv} value for a contact angle of zero. Experimentally it is determined by plotting the cos θ versus γ_{lv} for various liquids of known surface tension. A linear extrapolation of the data to zero contact angle, or cos θ = 1, gives the critical surface tension. Pure liquids eliminate the preferential absorption issues associated with surfactant solutions although both have been used in practice [60,61]. Caution is advised by van Oss [42] in regards to polar liquids, especially water and aqueous solutions, as they introduce interactions and error in the measurement of thermodynamic properties. Therefore, Zisman's technique should be used in situations where van der Waals forces dominate [62].

The study of deriving surface tensions from contact angles has evolved into two approaches: surface tension components and equations of state [43]. Surface tension components include the previously mentioned method by Zisman as well as major contributions by van Oss and Good, Fowkes, Owens and Wendt, and Wu and the acid–base approach; discussion and supplemental references can be found within Refs. [58,62]. The equation of state approach obtains the relation between the three interfacial tensions theoretically. As mentioned before, Zisman's technique revealed a linear trend for cos θ versus γ_{lv}; Neumann and co-workers went on to show that γ_{lv} cos θ versus γ_{lv} yielded a smooth curve representative of the solid surface

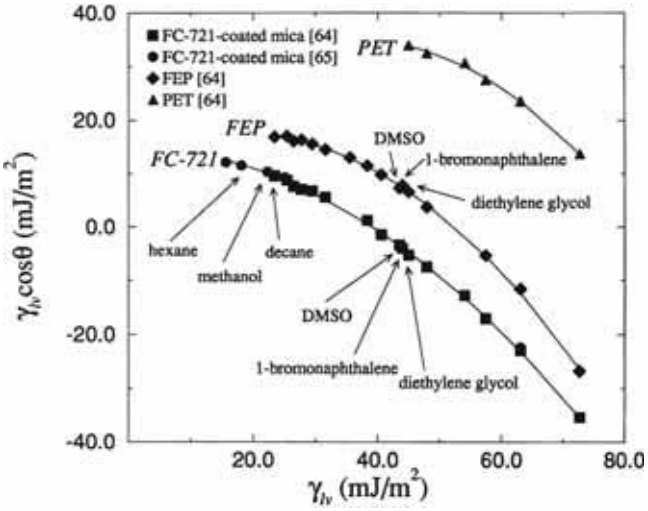

Fig. 6—Schematic of the parallel curve that suggests an equation of state, found by changing the substrate. (*Image duplicated from Fig. 2 of Ref. 61*). Reprinted with permission of John Wiley & Sons, Inc.

tension [61,63]. Changing the substrate produced a parallel, smooth curve as shown in Fig. 6; this indicated that an equation of state exists for surface tension, which is independent of inter-molecular interactions. The equation of state was developed using contact angle measurements on polymeric substrates and does not work well for polar substrates; other criticisms also persist as indicated in the publications by Morrison [64] and Janczuk et al. [65]. One main advantage of this approach is that it alleviates the deviations seen in the Fowkes equation for large liquid and solid surface tension differences.

DYNAMIC PROPERTIES OF LIQUID SURFACES

Fresh surfaces in liquid solutions have an initial surface tension unlike their equilibrium value. Considerations of this are necessary in manufacturing processes, such as coating application, where fresh surfaces are formed. The instantaneous γ_{lv} is characteristic of the bulk solution and approaches an equilibrium surface tension, γ_{eq}, as a function of time, $\gamma(t)$. The time-dependent behavior associated with fresh liquid interfaces is referred to as dynamic surface tension (DST) in the literature; this is represented by Eq (16):

$$\gamma_{eq} = \lim \gamma(t) \quad \text{for} \quad t \to \infty \quad (16)$$

A minimized free energy conformation is approached as a result of adsorption of surface active agents, or surfactants, at the liquid/vapor interface. Aside from fresh surfaces, changes in the surface area of an existing interface or bulk surfactant concentration also tend toward a new γ_{eq} and are applicable to DST models [66]. For additional details on the state-of-art, refer to the reviews by Miller et al. [67] and Eastoe and Dalton [68] for air-water interfaces and Ravera et al. [66] for liquid-liquid interfaces.

By the end of the 19th century, researchers recognized that instantaneous γ_{lv} differed from γ_{eq}; however, it was not until 1946 that a quantitative model was published [69]. Utilizing Fick's equations, Ward and Todai [69] proposed the first analysis to support the theory that surfactant

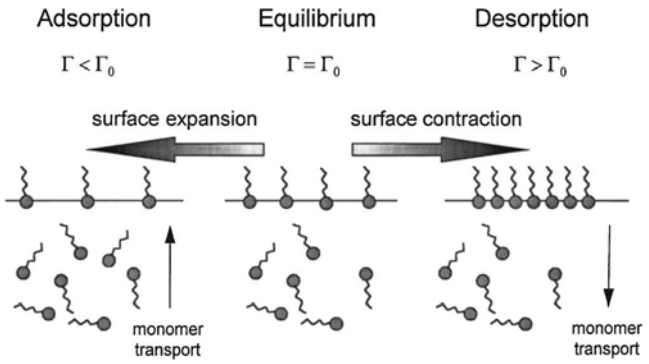

Fig. 7—Schematic of surfactant flux and surface excess concentration with regard to liquid surface area. (*Image duplicated from Fig. 1 of Ref. 68*). Reprinted from *Advances in Colloid and Interface Science*, Vol. 85, Eastoe, J., Dalton, J.S., "Dynamic Surface Tension and Adsorption Mechanisms of Surfactants at the Air-Water Interface," pp. 103–144, 2000 with permission from Elsevier.

molecules were driven to the interface by diffusion processes. The work also includes definition of the subsurface, the region a few molecular diameters below the interface, which regulates adsorption to the interface. Initially the surface excess is zero and each molecule in or reaching the subsurface subsequently diffuses to the interface, represented as the adsorbing flux, j_{ads}. Over time, the number of occupied surface sites increases and adsorption is no longer automatic. The desorbing flux, j_{des}, or back diffusion to the subsurface becomes significant as the system continues towards equilibrium. The surface excess concentration, Γ, over time is the result of balancing the flux of surfactants to and from the interface, respectively.

$$d\Gamma/dt = j_{ads} - j_{des} \tag{17}$$

Fig. 7 shows how the surfactant flux and F adjust to changes in the liquid surface area where Γ_{eq} is the equilibrium surface excess concentration. Significant contributions to the DST models were later made by Sutherland [70], Hansen [71], and Miller and co-workers [67,72]. References [28,29] discuss the importance of dynamic effects in relation to micellar solutions.

Two models persist for DST; they are the diffusion-controlled model and the mixed kinetic-diffusion model. In the diffusion-controlled model, diffusion to the subsurface is the rate-limiting step followed by a fast adsorption to the interface as theorized for short-time scenarios. On the contrary, the mixed kinetic-diffusion model assumes the transfer of surfactant molecules from the subsurface to the interface to be the rate-limiting step. Also, there is an energy barrier for adsorption which is possibly related to the number of available sites for adsorption or increased surface pressure [68]. Comparatively, the diffusion-controlled model contains one kinetic parameter, that is diffusion, D, whereas the mixed kinetic-diffusion model contains an additional parameter for the adsorption energy barrier denoted by β [73]. Once a surfactant molecule has adsorbed at the interface, additional reorientation and relaxation further minimizes the surface excess energy, or surface tension.

Both models are used experimentally in association with a chosen adsorption isotherm to measure γ_{eq} and Γ_{eq} for surfaces of interest. Experimental techniques for measuring DST are explained in the following section along with those for static surface tension. It must be understood that DST is interested in solution, particularly surfactant solutions, and the appropriate measurement should reflect this. For example, the Wilhelmy Plate method is appropriate for solutions whereas Du Nuoy ring is reserved for pure liquids. DST is especially important in coating application and all other processes that generate fresh surfaces [35,74]. Wetting in thin film spreading [75] and the dynamics effects of contact angles on moving substrates [76] are also pertinent. Schunk and Scriven [28] review the dynamic effects of surfactants in continuous application processes and give an extensive bibliography. More recent studies of dynamic wetting effects include wetting phenomena at structured surfaces, and surfaces of variable composition [77,78].

MEASUREMENT OF THE SURFACE TENSION OF LIQUIDS

Introduction

There are many ways of measuring surface tension, but in essence, they are all related to two effects of capillarity. The first effect is the excess pressure due to surface tension at a curved interface. The Young–Laplace equation describes this as

$$\Delta p = \gamma\left(1/R_1 + 1/R_2\right) \tag{18}$$

where Δp is the excess pressure due to the curved interface, and R_1 and R_2 are the two principal radii of curvature of the interface. In the case of a sphere of radius r, where the radii of curvature are both equal to r, this equation reduces to

$$\Delta p = 2\gamma/r \tag{19}$$

The other capillary effect is that the surface tension of a liquid exerts a force upon a solid body immersed in it equal to the surface tension times the perimeter of that body times the contact angle the liquid makes with the solid. If one is using a balance, one can write

$$\Delta W = \mathcal{P}\gamma\cos\theta \tag{20}$$

where $\mathcal{P}$ is the perimeter of the solid, θ is the contact angle of the solid-liquid interface, and ΔW is the extra force on the solid body due to surface tension. These two effects yield—together with various modifications of geometry, etc.—many methods to measure static and dynamic surface tension. The most widely used methods are described in the following sections.

It should be noted that all surface tension measurements require the cleanliness of all apparatus and the purity of all materials. Organic impurities in aqueous systems will have drastic effects in reducing the surface tension values measured. The concentration levels necessary to alter surface tension measurements can be as little as 10^{-8} *M*. Trace amounts of impurities on solid apparatus surfaces can alter contact angles and, as will be shown, the measured surface tension values. All water used in surface tension measurements should be at least double distilled, and often the presence of a strong oxidizing agent in one step of the distillation ensures that trace surfactants are removed. The water should be used fresh, as surface active

impurities can be leached from glass and plastic containers. The same holds true for all solvents used in surface characterization studies.

Static Surface Tension Measurements

Certain surface tension measurement methods work well only in a static system. These methods must thus be used on systems where there is no formation of fresh surfaces, or with pure liquids.

Capillary Rise

Within a small capillary tube, there exists a pressure on a liquid relative to the pressure on a large vessel of the liquid. Using Eq (19) and allowing for the contact angle between the liquid and the capillary, we have at equilibrium between the force of gravity and the capillary pressure

$$\Delta\rho g h = \frac{2\gamma\cos\theta}{r} \tag{21}$$

where Δp is the density difference between the liquid and air, g is the acceleration of gravity, h is the height of the capillary rise, and the rest of the terms are defined above. This equation allows one to measure the surface tension from a simple measurement of the height of the rise of the liquid in a capillary of known radius and contact angle with the test liquid. This method is shown schematically in Fig. 8. As a measurement technique, it has remained largely unchanged since its inception, with only the addition of computer-aided analysis of the instrument.

Drop Weight

The weight of a drop when it is formed slowly is the weight just to exceed the force of surface tension times the radius of the capillary tip from which it is formed, with a correction factor required for the formation of small satellite drops. Thus, one has

$$W = 2\pi\gamma r f \tag{22}$$

where W is the weight of the drop and f is the correction factor, which is discussed in Adamson [1]. This method is simple to use and accurate if precautions are taken for cleanliness and very slow flow rates of the liquid in the formation of drops. The method is shown schematically in Fig. 9. The simplicity of this measurement, and easy availability of the equipment, results in it being a popular technique. Reference [79] provides a review of this technique.

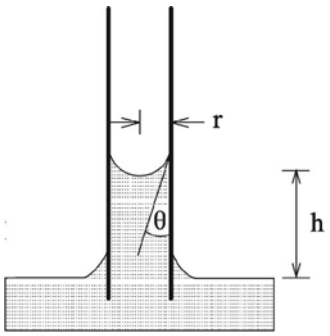

Fig. 8—Schematic of capillary rise method of measuring surface tension.

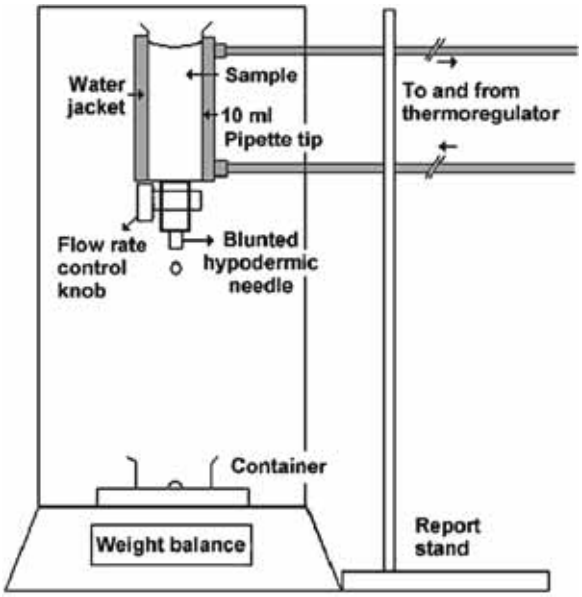

Fig. 9—Schematic of drop weight method of measuring surface tension. (*Image duplicated from Fig. 1 of Ref. 79*). "A Critical Review: Surface and Interfacial Tension Measurement by the Drop Weight Method," Boon-Beng, L., Ravindra, P., Chan, E.-S., *Chem. Eng. Comm,* Vol. 195, 2008, pp. 889–924, reprinted by permission of the publication (Taylor & Francis Group, http://www.informaworld.com).

Du Nouy Ring

Applying Eq (13) to the case where the object is a ring being pulled from the surface of a liquid, one has

$$W = W_{\text{ring}} + 4\pi\gamma R \tag{23}$$

where W is the total weight sensed by a balance, W_{ring} is the ring weight, and R is the ring radius as shown in Fig. 10. However, this formula requires a correction to be accurate and holds only for a zero contact angle between the ring and test liquid. Again, see Adamson [1] for further details. The force measured by the balance is that force just at detachment of the ring and so involves motion of the sensor; the method is thus not an appropriate technique to use in studying solutions. In general, this method is infrequently used, compared to the other options available.

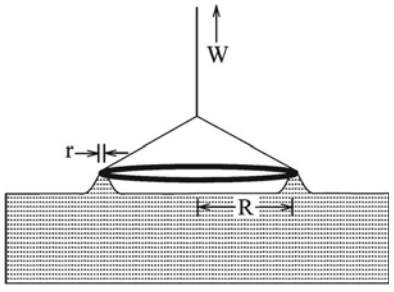

Fig. 10—Schematic of Du Nouy ring method of measuring surface tension.

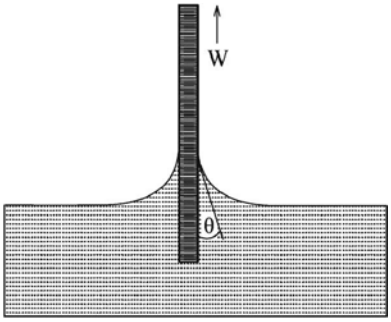

Fig. 11—Schematic of Wilhelmy plate method of measuring surface tension.

Wilhelmy Plate

If one uses a thin plate instead of a ring and measures the force exerted on the plate just touching the surface of a liquid, one has

$$W = W_{\text{plate}} + \gamma \mathcal{P} \tag{24a}$$

where $\mathcal{P}$ is the perimeter of the plate. If the liquid does not perfectly wet the plate, the expression

$$W = W_{\text{plate}} + \gamma \mathcal{P} \cos\theta \tag{24b}$$

must be used as illustrated in Fig. 11. The perimeter of the plate may be determined in practice as an experimental constant from γ measurements with liquids of known surface tension. Again cleanliness is most crucial, and a roughened platinum plate cleaned in a Bunsen burner flame is often used to create a clean plate that is wet by most liquids. Because there is no motion of the plate in the measurement, this method can be used to measure dynamic as well as static values of γ. This technique may be used as well with a rod [80] or cone [81] instead of a plate and may also be used to measure the contact angle of a liquid of known surface tension against a specific plate, fiber, or cone-shaped substrate (see later in this chapter under "Contact Angle Measurements"). Also, the method does not require corrections as with the drop weight or the Du Nouy ring methods.

Sessile or Pendant Drop Shape Methods

If the shape of a sessile or pendant drop is measured photographically or by a digital camera, a solution of Eq (18) for the specific shape of the drop in the presence of a gravitational field can be used with the measurements of the drop profile to back calculate the surface tension of the drop. Fig. 12 gives a schematic of the method. This method works well at liquid–air or liquid–liquid interfaces and can also be used to make dynamic measurements if the camera response is continuous and rapid [82]. A variation of the drop-shape method of measurement is used wherein the drop is deformed by a centrifugal field or an electrical field. The spinning drop shape method allows very small interfacial tensions to be measured between two liquids [83].

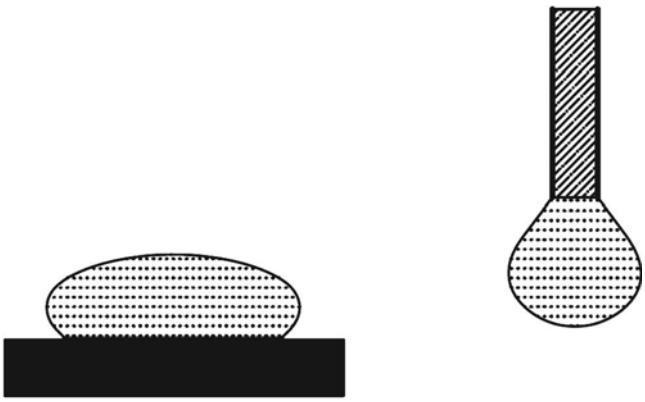

Fig. 12—Schematic of sessile and pendant drop methods of measuring surface tension.

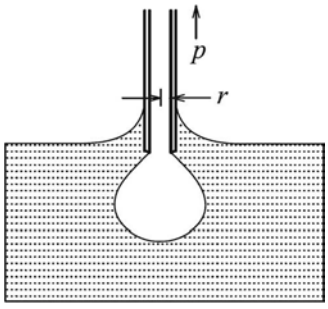

Fig. 13—Schematic of maximum bubble pressure method of measuring surface tension.

Maximum Bubble Pressure Methods

A bubble created by forcing a gas through the end of a capillary in a liquid and the maximum pressure on the resultant bubble can be used to measure surface tension by Eq (19). This measurement procedure is illustrated in Fig. 13. However, this is another measurement that requires correction, in this case for the nonspherical shape of the bubble. With rapid formation of the bubbles and accurate differential pressure measurements, the technique may be used to make dynamic measurements [84]. If capillaries of two different radii are used simultaneously and the pressure difference between the bubbles formed and the two capillaries is measured, a rapid, accurate measurement of surface tension can be made and has been used as a process monitor in emulsion polymerization [85]. This is known as the differential bubble pressure method and is illustrated in Fig. 14. This technique has been improved by the use of computers with the ADSA/ ABSA technique [86,87].

Dynamic Surface Tension Methods

When confronted with situations where fresh surfaces are formed, flow is occurring, or there are polymer solutions with long equilibrium times, it becomes necessary

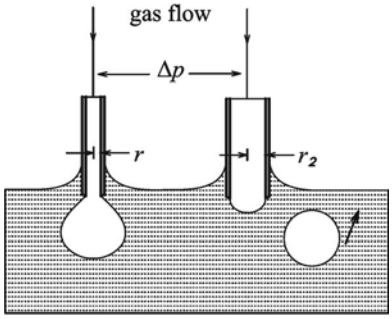

Fig. 14—Schematic of differential bubble pressure method of measuring surface tension.

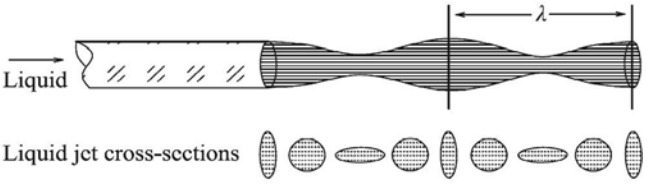

Fig. 15—Schematic of oscillating jet method of measuring surface tension.

to consider dynamic surface tension. As previously mentioned, bubble pressure, drop-shape methods, and the Wilhelmy plate method can be used for static as well as dynamic γ measurements. These methods are appropriate only for relatively slow changes in γ, and they will be discussed briefly below with literature references that discuss their use in characterizing $\gamma(t)$ effects. In addition to the already mentioned methods, other techniques have been developed to measure γ for short-time scales and fresh, rapidly changing surfaces.

Oscillating Jet

The mechanical instability of a liquid jet leaving an elliptical orifice causes the stream to oscillate about a circular shape and eventually break up into droplets, as illustrated in Fig. 15. The oscillations are periodic, and measurement of their wavelength can be used to determine γ as given by

$$\gamma_{app} = \frac{4\rho v^2\left(1+\frac{37b^2}{24r^2}\right)}{6r\lambda^2\left(1+\frac{5\pi^2 r^2}{3\lambda^2}\right)} \tag{25}$$

where ρ is the liquid density, v is the velocity of the jet, λ is the wavelength of the oscillation, r is the sum of the minimum and maximum radii, and b is their difference [1]. This dynamic measurement of γ has been considered by Vijian and Ponter [88], who give references to the earlier work of Ray-leigh, Bohr, Sutherland, Hansen, and others.

Falling Curtain

In an analysis of curtain coating, Brown [89] observed that the angle θ in the falling curtain formed by the break around a small, non-wettable obstacle could be used to measure surface tension as

$$\sin\theta = \frac{2\gamma}{Qu} \tag{26a}$$

where Q is the mass flow rate per unit orifice slit length in the curtain and u is the velocity of the liquid. This can enable one to calculate the dynamic surface tension in the falling film at the point where the obstacle intersects the falling curtain if the velocity u is greater than the "bursting velocity" of the falling sheet. A schematic of this method is given in Fig. 16. This has been considered further by Van Havenburgh and Joos [90]. Antoniades et al. [91] reconsidered the work of Brown and suggested that Eq (26), when derived correctly, should be written as

$$\sin^2\theta = \frac{2\gamma}{Qu} \tag{26b}$$

and give experimental evidence for this corrected equation.

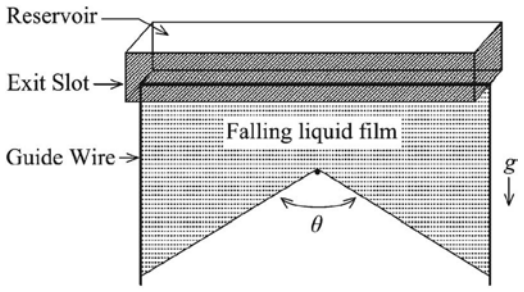

Fig. 16—Schematic of falling film method of measuring surface tension.

Capillary Waves

The properties of capillary waves, small wavelength waves on the surface of a liquid with the dominant restoring force being surface tension, can be studied to provide a measurement of surface tension, surface elasticity, and other dynamic surface properties. For clean surfaces of an inviscid liquid, Kelvin [92] determined that on a liquid of density, ρ, waves of frequency, ω, and wave number k, the surface tension is given for small wavelengths.

$$\gamma = \frac{\rho\omega^2}{k^3} \tag{27}$$

The situation for interfaces in real systems, viscous liquids with surfactants present, has been studied in detail [15,17], and the use of mechanically generated capillary waves for studying interfaces has been reviewed by Hansen and Ahmad [93]. The capillary waves generated by temperature fluctuations at a surface can be measured by laser-light scattering techniques, and these data can be used to generate very accurate values of surface and interfacial tensions [94]. Capillary wave studies can be used to study the time dependence of γ in some detail and are probably the most accurate and complete of the methods for measuring all dynamic surface properties.

The Falling Meniscus Method

The measurement of the height of a column of liquid in a tube with a small opening on top can be used to measure the dynamic surface tension of aqueous systems. The height measurement versus time may be analyzed to calculate the surface tension as a function of time. This is discussed in further detail, together with a full description of the experimental apparatus and analytical equations, by Defay and Hommeln [95].

Modified Static Surface Tension Measurements

Maximum Bubble Pressure

If one can monitor the time response of pressure to the time-dependent surface tension, one can use the maximum bubble pressure technique described above to measure dynamic surface tension [84]. The equipment required for such measurements is the same as the static maximum bubble technique plus instrumentation for time-dependent measurement of the bubble pressure. Various authors have examined the theoretical and experimental aspects of these methods [96,97].

Wilhelmy Plate

If a time-recording balance is used to monitor the force of surface tension pulling on the immersed plate, the Wilhelmy plate technique can be used for characterizing dynamic surface tension. As discussed above, the method is not useful for short times, but for slowly varying $\gamma(t)$ values. The method is used considerably with Langmuir film balances and has been applied to various other problems [98].

Other Methods

If a sensing technique that can be time resolved is coupled to a specific static surface tension measurement, $\gamma(t)$ data can be acquired. Reference [82] discusses this for drop-shape methods, and Jho and Burke [99] present a modification of the drop weight technique for $\gamma(t)$ characterization. Reference [29] discusses the general issue of characterizing surfactant effects in dynamic systems.

CONTACT ANGLE MEASUREMENTS

Introduction

Contact angle measurement remains the most common method for determining γ_{sv} or wettability. Arguments suggest, however, that θ_Y is difficult to obtain for a variety of reasons. Surface roughness results in contact angle hysteresis, as mentioned earlier, in which θ_a gives the closer fit to θ_Y. A rigid, physically smooth, and chemically homogeneous surface should be used in order to get the best approximation. Other assumptions include: the use of pure liquids to eliminate preferential adsorption effects, physical and chemical reactions do not occur between phases, γ_{lv} is higher than γ_{sv} such that a drop forms on the surface, and that γ_{sv} is constant and independent of the liquid used. The review by Kwok and Neumann [61] includes further details on contact angle measurement techniques and their interpretations.

In addition to the common contact angle measurements, a partial list of practiced solid surface tension measurement techniques not discussed here includes: solidification front techniques, sedimentation techniques, gradient theory, film flotation, Lifshitz theory of van der Waals forces, and theory of molecular interactions. All approaches share in common the assumed validity of Young's equilibrium equation. References relevant to these solid surface tension determining techniques are given in the review by Tavana and Neumann [63]. Recent work has also been done to determine contact angles at high temperatures [100] and under flow conditions [101]. This chapter includes information on direct/indirect sessile drop methods, Wilhelmy plate, capillary rise, rate of penetration, ADSA-P, and atomic force microscopy (AFM).

Direct Measurement of Contact Angle by Sessile Drop

The common contact angle measurement is also known as the sessile drop measurement and refers to optical techniques for determining contact angles [102]. These include contact angle goniometry of the drop profile using a photograph or digital video image, see Fig. 17. The drop must be small enough that gravitational forces have insignificant effects on the drop shape; therefore, magnification is necessary either using a digital image or goniometer-fitted microscope. Once the contact angle is known, Eq (10) can be used to calculate the surface tension of the solid if desired. Often

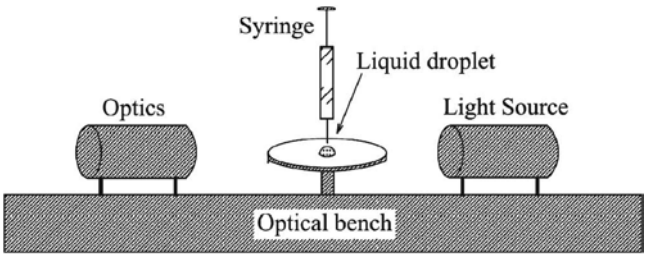

Fig. 17—Schematic of contact angle goniometer.

experimentation with two different liquids is necessary to obtain two equations with two unknowns and solve for γ_{sv} algebraically.

The contact angle measured by this method is referred to as the equilibrium angle, θ_e, which lies between θ_a and θ_r but nearer to the former and is not necessarily equal to θ_Y. It may be desirable to know the values for θ_a and θ_r; this is accomplished by slowly adding or removing liquid from the sessile drop until the maximum and minimum contact angles are recorded, respectively [63]. Differences of 5° to 20° are common between the two angles. The method was first performed by Zisman and co-workers using a thin platinum wire to add liquid and a fine glass capillary to remove liquid [63]. Later, Good and co-workers [103] applied the technique using micrometer syringes.

Two similar techniques for measuring the contact angle are the captive bubble method and the tilting plate method [104]. The captive bubble method places a drop of air on the solid surface in a liquid environment instead of vice versa. The same contact angle is measured as before, however, it is now nearer to θ_r. Although this method deviates from the simplicity of a liquid drop on a surface, it assures one that the saturated vapor pressure of the liquid and the solid-vapor interface are in equilibrium [63]. The tilting plate method suspends a plate or cylinder of the solid material in a bath of liquid with known γ_{lv}. The solid is then tilted until the capillary rise on the plate is zero, such that the liquid-vapor interface is flat at the contact line. A simple goniometer scale gives the contact angle to be the plate's displacement from the position normal to the liquid. Placing a sessile drop on the tilted plate at this position gives a good approximation of θ_a and θ_r. Considerations must be taken when choosing the liquid used in this method as it requires appreciable quantities.

Contact angle measurements are considered to be dynamic when there is a time dependency. For example, θ_a and θ_r are found through dynamic techniques in which the drop volume is steadily increased or decreased, respectively. The key factor is that the contact line is not static; the review by Blake [105] contains theoretical information on dynamic contact angles, velocity of the wetting line, and the models that describe them.

Measurement of Sessile Drop Dimensions

Using the same drop preparation as the direct measurement, the contact angle may be calculated through trigonometric equations by measuring drop diameter and height, volume, or mass (only if the liquid is of known density to obtain drop volume). Reference [62] further explains the methods and derives the necessary equations. The technique assumes that the drop is a section of a sphere of

radius, r, such that the surface tension is satisfied by the Laplace equation

$$\Delta p = 2\gamma/r \tag{28}$$

where Δp is the difference in pressure across the liquid-vapor interface. Error is commonly associated surface heterogeneities, leading to variations in the diameter and contact angle along the drop perimeter.

Wilhelmy Plate

The equation for Wilhelmy plate method is adjusted to give the contact angle of a solid if the liquid surface tension is known. Eqs (29a) and (29b) both satisfy the solution of this method.

$$\cos\theta = \Delta W/\gamma\mathcal{P} \tag{29a}$$

$$\sin\theta = 1 - \left(\rho g h^2/2\gamma_{sl}\right) \tag{29b}$$

As before, the surface tension of the solid is determined from the Young equation using this contact angle. This is the static Wilhelmy plate method; information on the dynamic method is given above and by Erbil [62].

Capillary Rise Method

The capillary rise method is also used to determine contact angles:

$$\cos\theta = \Delta\rho r g h/2\gamma_{sl} \tag{30}$$

Automated Curve-Fitting Approaches

In an effort to enhance the reliability of contact angle measurements, curve-fitting programs have been developed to analyze the profile of a sessile drop by transferring the image to a computer for digitizatiion and analysis [58]. The first such approach ADSA-P by Neumann and co-workers [106,107]; adjustments have consistently been made to improve its applicability as a high-accuracy technique. Assuming that the profile is both Laplacian and axisymmetric, an integration of the Laplace equation gives the contact angle [104]. The method is used as a low-rate dynamic technique to measure the advancing and receding contact angles [61]. A similar approach, the automated polynomial fitting, was proposed using a polynomial fitting of the drop profile. This technique has similar accuracy to ADSA-P but is applicable to non-axisymmetric systems also [108].

Direct Force Measurement by AFM

Drelich et al. [109] have reviewed the use of AFM in determining the surface tension of a solid. Although this technique is very sensitive to experimental conditions and requires extensive setup and calibration, it is applicable to microscopic surfaces that are too small for regular sessile drop techniques [104]. Corrections must also be made for the elastic deformation of the materials. The theory for this technique is based on the work of adhesion between two materials, being the solid surface of interest and the instrument probe. The pull-off (adhesion) force, F, is measured directly in this experiment as a function of W_A

$$F = 2\pi R W_A \tag{31}$$

where R is the diameter of the probing tip. The coefficient 2π assumes the particles in contact are perfectly rigid. Once W_A is known, the Young equation can be combined with Eq (12) to obtain the Young-Dupre equation [37]:

$$\cos\theta = W_A/\gamma_{lv} - 1 \tag{32}$$

Similarly the surface tension can be solved using a constant, c, generally 1.5 or 2 depending on the model chosen; more details can be found in Ref. [109].

$$\gamma_{sv} = F/2c\pi R \tag{33}$$

Rate of Penetration into Powder

The rate of penetration relation is utilized when it is desirable to know the amount of time it will take for a liquid to wet a porous medium; examples include enhanced oil recovery operations, the movement of water through geological systems, or absorption in the clean-up of spilled liquids [110]. In this dynamic contact angle measurement, the liquid enters the powder at a given velocity, v, and subsequently wets the surfaces by capillary forces as a function of γ_{lv} and θ as shown in the Washburn equation [111]:

$$\cos\theta = 4v\eta l/\gamma_{lv} r \tag{34}$$

Here, η is the viscosity of the penetrating liquid, l is the length of the capillary path in the powder, and r is the average pore size; the equation assumes inertial and gravitational effects to be negligible. Often the technique is used to find the γ_{lv} of the wetting liquid that minimizes the rate of penetration. Refer to Lavi and Marmur [110] or Subrahman-yam et al. [112] for more information on this method.

SOME SPECIFIC APPLICATIONS OF SURFACE ENERGETICS TO ORGANIC COATINGS

Coatings Application and Defects

Flow phenomena, and their control, at surfaces are very important to coatings film application technology [12,113]. It is such an important consideration that there have been several books written on this topic since the first version of this chapter [12,114,115]. The creation of uniform thin films at high speeds involves many problems that are determined by a combination of the application geometry, the velocity of the substrate relative to the liquid coating, the physical properties of the liquid coating, especially the energetics of the surface of the liquid coating, the surface of the substrate, and the new liquid/solid and gas/liquid interfaces created in the application processes. Analysis of several application techniques is given below to illustrate the importance of the use of concepts discussed in the prior portion of this chapter.

Dip Coating

Dip coating is a coating method in which a sheet of material is constantly withdrawn vertically from a coating liquid bath at constant velocity, producing a constant film thickness coating adhering to the sheet, which is usually then dried or cured to produce the final coating on the sheet (see Fig. 18). This problem was originally analyzed by Landau and Levich [116], and its solution has been given in the most commonly used form by Probstein [117]. Only the solution of the problem will be given here, but it is representative of the problems identified by chemical engineers as coating flows. In these cases, the geometry of the coating device, the relative velocity, v, of the object to be coated, and

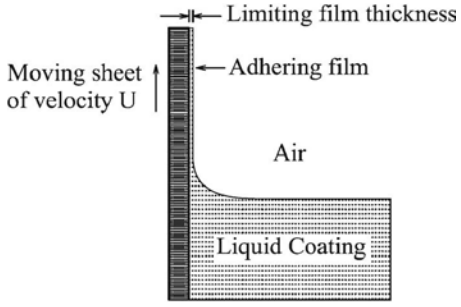

Fig. 18—Schematic of dip coating process.

the physical properties of the coating fluid (surface tension, γ; viscosity, η; density, ρ; and acceleration of gravity, g) fix the solution to the coating flow problem. In this case, the limiting film thickness, δ_f, at large distances from the coating bath surface, is given by

$$\delta_f = 0.946 \frac{(\eta\nu)^{2/3}}{\gamma^{1/6}\sqrt{\rho g}} \tag{35}$$

This solution is derived from the physical effects of surface tension, as described above, plus the Navier-Stokes equation fluid mechanics. These authors assume Newtonian viscosity behavior of the liquid, i.e., the viscosity, η, is independent of shear rate, time-independent surface tension, and an absence of surface tension gradient-driven flows (Marangoni flows), with the appropriate boundary conditions determined by the coating process. This solution can be used by the coating designer and user to establish a first order estimate of the film thickness of the liquid film by the properties of the coating and the velocity of sheet withdrawal. Further analyses of the dip coating processes are given in more recent monographs [3,12,118].

Curtain Coating

As described above in the section on measurement of dynamic surface tension, analysis of the curtain coating process has yielded a measurement method for dynamic surface tension. In the analyses of this problem, Brown [89] and Ha-venburgh and Joos [96] both modeled curtain coating by a falling liquid film held in place by two vertical wires (see Fig. 19). The flux Q of falling liquid is

$$Q = v_0 h_0 \tag{36}$$

where v_0 is the velocity of the falling film and h_0 is the width of the falling film at time zero at the slot through which the liquid exits. The velocity of the falling film at a position x from the slot is given by

$$v^2 = v_0^2 + 2gx \tag{37}$$

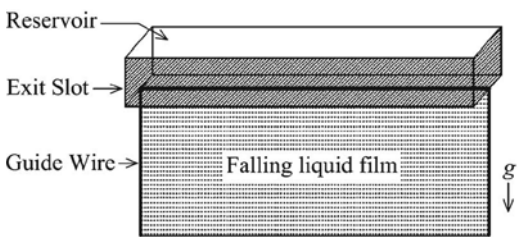

Fig. 19—Schematic of curtain coater.

where g is the acceleration of gravity. Since the flux of material is constant through the slot, we know that

$$Q = v_0 h_0 = hv \tag{38}$$

and therefore

$$h(x) = \frac{Q}{\sqrt{v_0^2 + 2gx}} \tag{39}$$

This equation gives the user a description of the thickness of liquid film as a function of distance from the slot of the curtain coater. This can also be used to estimate the surface tension at a given position x by the following relation [96]:

$$\gamma(x) = \frac{\rho h(x) v_0^2}{2} \tag{40}$$

These equations give the application engineer a reasonably complete description of the curtain coating process. Stokes and Evans [3] and Guthoff [119] give more recent descriptions with a discussion of multilayered curtain coating processes. Fig. 20 illustrates the system discussed in these references. Miamoto and Katagari [120] give an extensive discussion of curtain coating stability with respect to the falling film and and give the following criteria for stability

$$\rho Q v > 2\gamma \tag{41}$$

Electrostatic Spray

The application of surface energetics to the problem of charged liquid droplets was first done by Rayleigh [121]. In this study, the electrical repulsion forces between charges on a drop are equated to the surface tension forces holding a drop together to give the following equation as an estimate of the upper limit on the charge that can be held on a drop

$$q = \sqrt{16\pi\varepsilon r^2 \gamma} \tag{42}$$

where ε is the dielectric constant of the drop and r is the drop radius. This can be used to gain an estimate of the drop size in electrostatic spray of liquid paints. Further stability analysis of this problem indicates that if a drop at this charge limit breaks up, the total energy of the system will be minimized if it does so into n droplets, where n is given by

$$n = \frac{q^2}{4\pi\varepsilon r_0^2} \tag{43}$$

where r_0 is the radius of the original drop [122]. This charge limit has been studied and verified experimentally by several workers [123,124] and also applied to problems of spray painting [125]. All of this work further illustrates the importance and extensive applications of surface energetics to coatings use. A computer simulation of electrostatic spray processes has been used to predict spray patterns on planar substrates [126].

Powder Coating

An environmentally friendly process that often yields high-performance coating films is the powder coating process. This process is one of the fastest growing in terms of market for recently introduced application methods for organic coatings [127]. The process can be described by many of the variables that describe liquid electrostatic painting for both

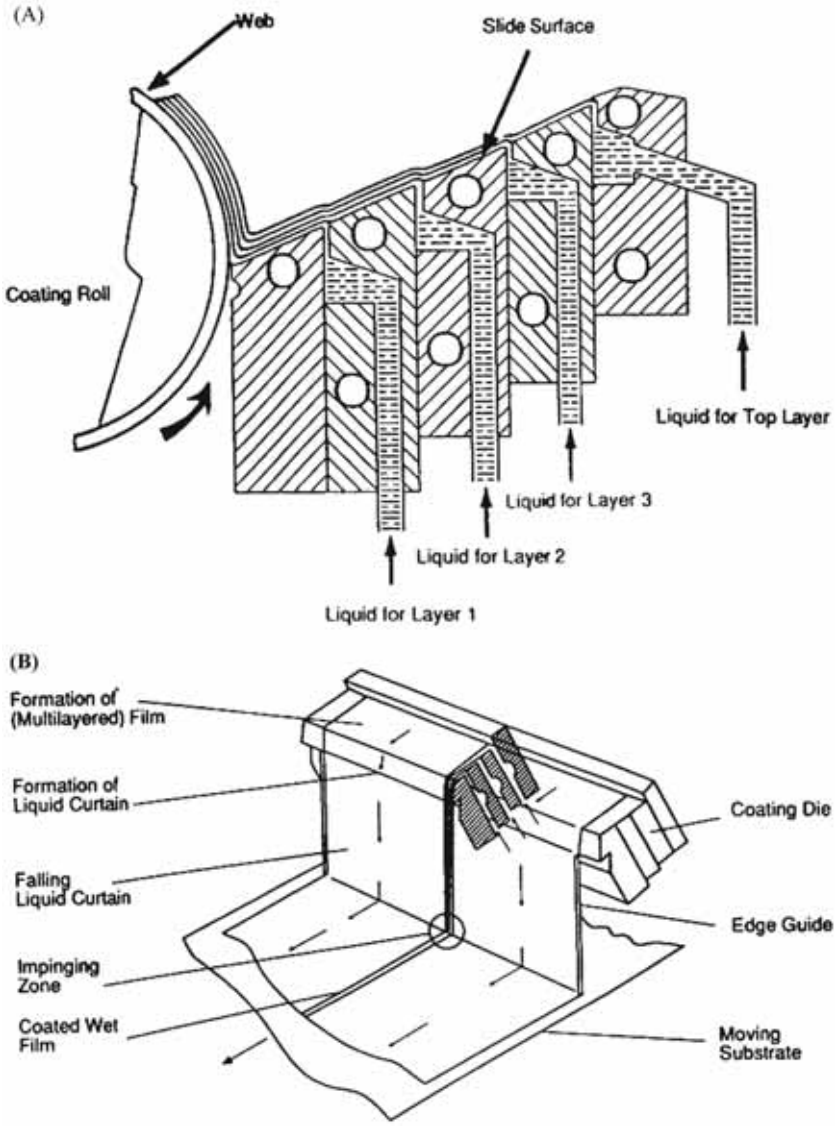

Fig. 20—Schematic of multiple layer (A) curtain coater and (B) slide coater. (*Image duplicated from Figs. 4.2 and 4.3 of Ref. 119*). Reprinted with permission of John Wiley & Sons, Inc.

electrostatic spray powder coating and electrostatic fluidized bed coating [128,129].

Coating Defects

There are many ways in which surface energetics are involved in coating defects, and these are discussed in many references (for example, see Ref. [12]). There is indeed, a whole book devoted to this topic [12]. Surface defects occur by either imperfect coating applications or distortions of the film during the film formation process [130]. The control and prevention of defects in organic coating films requires a knowledge of surface energetics and film formation processes. Cratering occurs, for example, when a suface active impurity with a lower surface tension than the bulk coating spreads over the surface of a wet film displacing or thinning the coating film. The leveling process occurs because of the Laplace pressure at sites of curvature, such as brushmarks, in coatings. Bubbles stabilized by surfactant adsorption can be carried into films during application and cause subsequent imperfections. Any thinning or non-uniformity in film is a potential site for corrosion attack on the underlying substrate, especially in purely barrier coatings [131].

Cleaning and Pretreatment of Substrates for Coating

A very important step in the total process of creating a high-performance organic coating/substrate system is the cleaning and pretreatment of the substrate prior to the coating application step. The processing time and costs of the cleaning step often exceed that of the coating and curing steps, indicating the importance often assigned to this part of the coating process by many users. The specific purpose of cleaning and pretreating substrate surfaces is to control and/or modify the surface energy of the substrate so that a coating may be successfully applied to the substrate and that the coating will subsequently adhere properly to the substrate and provide the performance desired. Cleaning, as a general rule, involves the removal of substances foreign to the substrate by a surfactant/detergent

solution, followed with rinsing by a solvent that leaves the substrate surface clean of contaminants. This may have to be preceded by a mechanical sandblasting, grinding, sanding, scrubbing, etc., to remove thick layers of mil scale, rust, scum, and other built-up material on what is the real substrate. Vapor or organic solvent degreasing/cleaning is also often used to yield a clean surface for coating. These mechanical cleaning steps, along with the cleaning and rinsing of the surface with low surface tension solutions that leave no residue, are best done just before the coating step lest recontamination occur while waiting for the coating step. The goal of all these cleaning procedures is to insure a uniform surface that has a uniform contact angle, usually and desirably zero, for wetting by the coating, and to insure the interface created is the coating liquid/substrate interface only. The mechanical sanding, polishing, etc., will also contribute to a lower contact angle by the surface roughness effect discussed above. Oil, dirt, rust, or other contaminants will give poor and incomplete wetting and poor adhesion of the coating at the contaminated sites. Complete wetting is further assisted by insuring the surface tension of the coating liquid is low so that all air is displaced by the coating and the contact angle between the liquid coating and the substrate is zero, or near to it. The surface tension of the liquid coating is best lowered by the polymer of the system or by surfactant additives to the liquid system. Attempts to control the surface tension by the solvent can cause problems in having the surface tension increase as the solvent evaporates. As mentioned above, control of surface defects in coating processes is often achieved by proper cleaning and handling of the objects/substrates coated in the process [12].

Substrate pretreatment is usually performed just after the cleaning discussed above and is done to further insure complete wetting and adhesion of the coating, as well as, in the case of metallic substrates, to deposit a corrosion inhibitive layer [132]. In the case of plastic substrates, the pretreatment may be corona or flame modification to oxidize the surface layer and lower the contact angle to near zero. Metal pretreatments often involve the deposition or creation of a rough-surfaced crystalline layer of metallic phosphates, which give an easily wetted surface.

Standard Surface Phenomena Testing Methods

ASTM International is a source of testing methods and procedure documents (www.ASTM.org). Table 1 contains a listing of several ASTM documents that are related to surface technology and may be useful to those investigating in this area of science. In addition to this listing, other ASTM methods exist that may be pertinent and can be found at the above indicated web site.

TABLE 1—ASTM standards used in testing surface phenomena (partial listing)

Designation	ASTM Title
C813	Hydrophobic Contamination on Glass by Contact Angle Measurements
D971	Interfacial Tension of Oil Against Water by the Ring Method
D2578	Wetting Tension of Polyethylene and Polypropylene Films
D3825	Dynamic Surface Tension by the Fast-Bubble Technique
D5725	Surface Wettability and Absorbency of Sheeted Materials Using an Automated Contact Angle Tester
D5946	Corona-Treated Polymer Films Using Water Contact Angle Measurement
D7334	Surface Wettability of Coatings, Substrates and Pigments by Advancing Contact Angle Measurement
D7490	Measurement of the Surface Tension of Solid Coatings, Substrates and Pigments Using Contact Angle Measurements
D7541	Standard Practice for Estimating Critical Surface Tensions

SUMMARY

The concepts of surface energy, surface tension, and wetting and contact angle phenomena are of exceptional importance to the science and technology of organic coating; these are topics that are ongoing. Their understanding is vital for the proper formulation and application of coating. Many of the features of the final organic coating/substrate system are controlled by proper understanding of the surfaces of the liquid coating and the substrate, as well as creation of a proper coating/substrate interface. Both the static and dynamic aspects of liquid surface properties should be considered and the dynamic aspects properly accounted for in coating production and application. These concepts have been reviewed, and references to further reading in this important area of organic coatings science have been given.

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Solubility Parameters

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NOMENCLATURE

c	=	Dispersion cohesion energy from Figs. 2 and 3
D	=	Dispersion cohesion (solubility) parameter—in tables and computer printouts
DM	=	Dipole moment—Debyes
ΔE_d	=	Dispersion cohesion energy
ΔE_p	=	Polar cohesion energy
ΔE_h	=	Hydrogen bonding cohesion energy
ΔE_V	=	Energy of vaporization (=) cohesion energy
ΔG^M	=	Molar free energy of mixing
H	=	Hydrogen bonding cohesion (solubility) parameter—in tables and computer printouts
ΔH_v	=	Molar heat of vaporization
ΔH^M	=	Molar heat of mixing
P	=	Polar cohesion (solubility) parameter—in tables and computer printouts
R	=	Gas constant (1.987 cal/mole K)
R_s	=	Distance in Hansen space
R_O	=	Radius of interaction sphere in Hansen space
RED	=	Relative energy difference, R_S/R_0
ΔS^M	=	Molar entropy of mixing
T	=	Absolute temperature
T_b	=	(Normal) boiling point
T_c	=	Critical temperature
V_M	=	Molar volume
ΔT	=	Lydersen critical temperature group contribution
α	=	Thermal expansion coefficient
δ_d	=	Dispersion cohesion (solubility) parameter
δ_h	=	Hydrogen bonding cohesion (solubility) parameter
δ_p	=	Polar cohesion (solubility) parameter
δ_T	=	Total cohesion (solubility) parameter
φ_i	=	Volume fraction of component "i"
X	=	Polymer-liquid interaction parameter (Flory-Huggins)

INTRODUCTION

SOLUBILITY PARAMETERS ARE USED IN THE COAT-ings industry to select solvents. Liquids with similar solubility parameters will be miscible, and polymers will dissolve in solvents whose solubility parameters are not too different from their own. The basic principle is "like dissolves like." Solubility parameters help put numbers into this simple qualitative idea.

The solubility parameter approach has been used for many years to select solvents for coating materials. The lack of total success has stimulated research. The skill with which solvents can be optimally selected with respect to cost, solvency, workplace environment, external environment, evaporation rate, flash point, etc., has improved over the years as a result of a series of improvements in the solubility parameter concept and widespread use of computer techniques. Most, if not all, commercial suppliers of solvents have computer programs to help with solvent selection. One can now easily predict how to dissolve a given polymer in a mixture of two solvents, neither of which can dissolve the polymer by itself.

This contribution to the paint testing manual unfortunately cannot include discussion of all of the significant efforts leading to our present state of knowledge of the solubility parameter. An attempt is made to outline developments, provide some background for a basic understanding, and give examples of uses in practice. The key is to determine which affinities the important components in a system have for each other. For coatings, this means affinities of solvents, polymers, pigment surfaces, additives, and substrates.

It is noteworthy that the concepts presented here have developed toward not just predicting solubility, which requires high affinity between solvent and solute, but to predict affinities between different polymers leading to compatibility, and affinities to surfaces to improve pigment dispersion and adhesion. Attempts are also being made to extend these developments, largely attributable to the coatings industry, to understand affinities and phenomena for a large number of other materials not specifically related to coatings. In these applications, the solubility parameter has become a tool, using well-defined liquids as energy probes, to measure the similarity, or lack of same, of key components. Materials with widely different chemical structures may be very close in affinities. Only those materials that interact differently with different solvents can be characterized in this manner. Many inorganic materials, such as fillers, do not interact differently with these energy probes since their energies are (presumed to be) very much higher. Changing their surface energies by various treatments can lead to a surface that can be characterized. It is also known that the surfaces of such materials are covered with water. The extent to which this is bound will influence practical performance, i.e., how easily can it be replaced?

Solubility parameters are cohesion energy parameters since they derive from the energy required to convert a liquid to a gas. The energy of vaporization is a direct measure of the total (cohesive) energy holding the liquid's molecules

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together. All types of bonds holding the liquid together are broken by evaporation, which has led to the concepts described in more detail below. The term cohesion energy parameter is more appropriately used when referring to surface phenomena.

HILDEBRAND PARAMETERS

The term solubility parameter was first used by Hildebrand and Scott [1,2]. The solubility parameter is the square root of the cohesive energy density

$$\delta = (c \cdot e \cdot d)^{1/2} = \left(\frac{\Delta E_v}{V_M} \right)^{1/2} (\text{cal/cm}^3)^{1/2} \text{or MPA}^{1/2} \qquad (1)$$

where V_M is the molar volume and ΔE_V is the (measurable) energy of vaporization [see Eq (14)]. The solubility parameter is an important quantity in predicting solubility relations, as can be seen from the following brief introduction.

Thermodynamics requires that the free energy of mixing must be zero or negative for the solution process to occur spontaneously. The free energy change for the solution process is given by the relation

$$\Delta G^M = \Delta H^M - T\Delta S^M \qquad (2)$$

where ΔG^M is the free energy of mixing, ΔH^M is the heat of mixing, T is the absolute temperature, and ΔS^M is the entropy change in the mixing process.

The heat of mixing, ΔH^M, is given by Hildebrand and Scott as

$$\Delta H^M \approx \Delta E^M = \phi_1 \phi_2 V_M (\delta_1 - \delta_2)^2 \qquad (3)$$

where the ϕ's are volume fractions and V_M is the average molar volume of the solvent. It is important to note that the solubility parameter, or rather the difference in solubility parameters for the solvent-solute combination, is important in determining the solubility. It is clear that a match in solubility parameters leads to a zero heat of mixing, and the entropy change should ensure solution. The maximum difference in solubility parameters that can be tolerated where solution still occurs is found by setting the free energy change equal to zero in Eq (2). It is, in fact, the entropy change that dictates how closely the solubility parameters must match each other. It can also be seen that solvents with smaller molecular volumes promote lower heats of mixing, which, in turn, means that smaller solvent molecules will be thermodynamically better than larger ones when their solubility parameters are equal. A practical aspect of this effect is that solvents with relatively low molecular volumes, such as methanol and acetone, can dissolve a polymer at larger solubility parameter differences than expected from comparisons with other solvents with larger molecular volumes. The converse is also true. Larger molecular species may not dissolve even though solubility parameter considerations might predict this. This can be a difficulty with plasticizers.

A first impression ADD of the Hildebrand approach is that negative heats of mixing are not possible. Likewise, the approach is limited to regular solutions as defined by Hildebrand and Scott [2] and does not account for association between molecules, such as polar and hydrogen bonding interactions would require. The latter problem seems to have been largely solved with the use of multicomponent solubility parameters. Patterson and co-workers have cleared up many questions in polymer solution thermodynamics [3-8]. One of the more important matters was to clearly show that negative heats of mixing are allowed by the solubility parameter theory, thus eliminating one of the major mental stumbling blocks for further use of this concept.

A more detailed description of the theory presented by Hildebrand and the succession of research reports which have attempted to improve on it can be found in Barton's extensive handbook [9]. The slightly older excellent contribution of Gardon and Teas [10] is also a good source, particularly for coatings and adhesion phenomena. The approach of Burrell [11], who divided solvents into hydrogen bonding classes, has found numerous practical applications, and the approach of Blanks and Prausnitz [12], who divided the solubility parameter into two components, nonpolar and "polar," are worthy of mention, however, in that these have found wide use and greatly influenced the author's earlier activities, respectively.

It can be seen from Eq (2) that the entropy change can be considered beneficial to mixing. When multiplied by the temperature, this will work in the direction of promoting a more negative free energy of mixing. Higher temperatures will also promote this more negative free energy change. The entropy changes associated with polymer solutions will be smaller than those associated with liquid-liquid miscibility, for example, since the "monomers" are already bound into the configuration dictated by the polymer they make up. They are no longer free in the sense of a liquid solvent and cannot mix freely to contribute to a larger entropy change. This is one reason polymer-polymer miscibility is difficult to achieve. The free energy criterion dictates that the polymer solubility parameters match extremely well since there is little help from the entropy contribution when progressively larger molecules are involved. However, polymer-polymer miscibility can be promoted by introduction of suitable co-polymers or co-monomers that interact specifically within the system.

HANSEN SOLUBILITY PARAMETERS

A widely used solubility parameter approach to predicting polymer solubility is that proposed by the author. The basis of these so-called Hansen solubility parameters is that the total energy of vaporization of a liquid consists of several individual parts [13–17]. Needless to say, without the work of Hildebrand and Scott [1,2] and others not specifically referenced here such as Scatchard, this postulate could never have been made. The total cohesive energy, ΔE_t, can be measured by evaporating the liquid, i.e., breaking all the cohesive bonds. It should also be noted that these cohesive energies arise from interactions of a given solvent molecule with another of its own kind. The basis of the approach is, therefore, very simple, and it is surprising that so many different applications have been possible over the past 40 years. A number of applications are discussed below. A lucid discussion by Barton [18] enumerates typical situations where problems occur when using solubility parameters. These are most often where the environment causes the solvent molecules to interact with or within themselves differently than when they make up their own environment, i.e., as pure liquids.

Materials having similar (Hansen) solubility parameters have high affinity for each other. The extent of the similarity in a given situation determines the extent of the interaction. The same cannot be said of the total or Hildebrand solubility parameter [1,2]. Ethanol and nitromethane, for example, have similar total solubility parameters (26.1 versus 25.1 $MPa^{1/2}$, respectively), but their affinities are quite different. Ethanol is water soluble, while nitromethane is not. Indeed, mixtures of nitroparaffins and alcohols were demonstrated in many cases to provide synergistic mixtures of two nonsolvents that dissolved polymers [13].

There are three major types of interaction in common organic materials. The most general are the "nonpolar" interactions, which derive from atomic forces. These have also been called dispersion interactions in the literature. Since molecules are built up from atoms, all molecules will contain this type of attractive force. For the saturated aliphatic hydrocarbons, for example, these are essentially the only cohesive interactions, and the energy of vaporization is assumed to be the same as the dispersion cohesive energy, ΔE_d. Finding the dispersion cohesive energy as the cohesion energy of the homomorph, or hydrocarbon counterpart, is the starting point for the calculation of the three Hansen parameters for a given liquid.

The permanent dipole-permanent dipole interactions cause a second type of cohesion energy, the polar cohesive energy, ΔE_p. These are inherently molecular interactions and are found in most molecules to one extent or another. The dipole moment is the primary parameter in calculating these interactions. A molecule can be primarily polar in character without being water soluble, so there is misuse of the term "polar" in the general literature. The polar solubility parameters referred to here are well-defined, experimentally verified, and can be estimated from molecular parameters as described below. As noted above, the polar solvents include those with relatively high total solubility parameters, which are not particularly water soluble such as nitroparaffins, propylene carbonate, tri-*n*-butyl phosphate, and the like. Induced dipoles have not specifically been treated by Hansen, but are recognized as a potentially important factor, particularly for solvents with zero dipole moments.

The third major cohesive energy source is hydrogen bonding, ΔE_h. Hydrogen bonding is a molecular interaction and resembles the polar interactions in this respect. The basis of this type of cohesive energy is attraction among molecules because of the hydrogen bonds. In this perhaps oversimplified approach, the hydrogen bonding parameter has been used to more or less collect the energies from interactions not included in the other two parameters. Alcohols, glycols, carboxylic acids, and other hydrophilic materials have high hydrogen bonding parameters. Other researchers have divided this parameter into separate parts, for example, acid and base cohesion parameters, to allow both positive and negative heats of mixing. These approaches will not be dealt with here, but can be found described in Barton's Handbook [9] and elsewhere [19–21]. The most extensive division of the cohesive energy has been done by Karger et al. [22], who developed a system with five parameters: dispersion, orientation, induction, proton donor, and proton acceptor. The Hansen hydrogen-bonding parameter may be termed an electron interchange parameter as well. As a single parameter, it has remarkably accounted well for the experience of the author and keeps the number of parameters to a level, which allows ready practical usage.

It is clear that there are other sources of cohesion energy in various types of molecules arising, for example, from induced dipoles, metallic bonds, electrostatic interactions, or whatever type of separate energy can be defined. Hansen stopped with the three major types found in organic molecules. It was and is recognized that additional parameters could be assigned to separate energy types. The description of organometallic compounds could be an intriguing study, for example. This would presumably parallel similar characterizations of surface-active materials, where each separate part of the molecule requires separate characterization for completeness. The Hansen parameters have mainly been used in connection with solubility relations, mostly, but not exclusively, in the coatings industry, but their use is now spreading to other industries.

Solubility and swelling have been used to confirm the solubility parameter assignments of many of the liquids. These have then been used to derive group contribution methods and suitable equations based on molecular properties to arrive at estimates of the three parameters for additional liquids. The goal of a prediction is to determine similarity or not of the cohesion energy density parameters. The strength of a particular type of hydrogen bond or other bond, for example, is important only to the extent that it influences the cohesive energy density.

Hansen parameters do have direct application in other scientific disciplines of interest to the coatings industry, such as surface science, where they have been used to characterize the wettability of various surfaces and adsorption properties of pigment surfaces [10,14,16,23–25]. Many other applications of widely different character have been discussed by Barton [9] and Gardon [26]. Surface characterizations have not been given the attention deserved in terms of a unified similarity-of-energy approach. The author can certify that thinking in terms of similarity of energy, whether surface energy or cohesive energy, can lead to rapid decisions and plans of action in critical situations where data are lacking. In other words, the everyday industrial crisis situation can often be reduced in scope by appropriate systematic approaches based on similarity of energy.

The basic equation that governs the assignment of Hansen parameters is that the total cohesion energy, ΔE_t, must be the sum of the individual energies that make it up

$$\Delta E_t = \Delta E_d + \Delta E_p + \Delta E_h \tag{4}$$

Dividing this by the molar volume gives the square of the total (or Hildebrand) solubility parameter as sum of the squares of the Hansen *D, P,* and *H* components.

$$\frac{\Delta E_t}{V_M} = \frac{\Delta E_d}{V_M} + \frac{\Delta E_p}{V_M} + \frac{\Delta E_h}{V_M} \tag{5}$$

$$\delta_t = \delta_d^2 + \delta_p^2 + \delta_h^2 = D^2 + P^2 + H^2 \text{ (computer printouts)} \tag{6}$$

METHODS AND PROBLEMS IN THE DETERMINATION OF PARTIAL SOLUBILITY PARAMETERS

The best method to calculate Hansen solubility parameters depends to a great extent on what data are available.

Hansen originally adopted an essentially experimental procedure and established numbers for 90 liquids based on solubility data for 32 polymers [13]. This procedure involved calculation of the nonpolar parameter according to the procedure outlined by Blanks and Prausnitz [12]. This calculational procedure is still in use and is considered to be the most reliable and consistent for this parameter. It is outlined below. The division of the remaining cohesive energy between the polar and hydrogen bonding interactions was done by trial and error to fit experimental polymer solubility data. A key to parameter assignments in this initial trial and error approach was that mixtures of two nonsolvents could be systematically found to synergistically (but predictably) dissolve given polymers. This meant that these had parameters placing them on opposite sides of the solubility region, a spheroid, from each other. Having a large number of such predictably synergistic systems as a basis, reasonably accurate divisions into the three energy types were possible.

Using the experimentally established, approximate, δ_p and δ_h parameters, Skaarup [15] found that the Böttcher equation could be used to calculate the polar parameter quite well, and this led to a revision of the earlier values to those now in wide use for these same liquids. These values were also consistent with the experimental solubility data for 32 polymers available at that time and Eq (6). Furthermore, Skaarup developed the equation for the solubility parameter "distance," R_s, between two materials based on their respective partial solubility parameter components

$$R_s = 4(\delta_{d1} - \delta_{d2})^2 + (\delta_{p1} - \delta_{p2})^2 + (\delta_{h1} - \delta_{h2})^2 \qquad (7)$$

This equation was developed from plots of experimental data where the constant 4 was found convenient and correctly represented the solubility data as a sphere encompassing the good solvents. When the scale for the dispersion parameter is doubled compared with the other two parameters, essentially spherical rather than spheroidal regions of solubility are found. This greatly aids two-dimensional plotting and visualization. There are, of course, boundary regions where deviations can occur. These are most frequently found to involve the larger molecular species being less-effective solvents compared with the smaller counterparts that define the solubility sphere. Likewise, smaller molecular species, such as acetone and methanol, often appear as outliers in that they dissolve a polymer even though they have solubility parameters placing them at a distance greater than the solubility sphere radius, R_0. This dependence on molar volume is inherent in the theory developed by Hildebrand and Scatchard as discussed above. Smaller molar volume favors lower heats of mixing, which in turn promotes solubility. Such smaller molecular volume species, which dissolve "better" than predicted by comparisons based on solubility parameters alone, should not necessarily be considered outliers. This statement is justified by Eq (3), where it can be seen that the molar volume and the square of the solubility parameter difference are weighted equally in estimating the heat of mixing in the Hildebrand theory.

The molar volume is frequently used as a fourth parameter to describe molecular size effects. These are especially important in correlating diffusion phenomena with the solubility parameter, for example. The author has preferred to retain the three well-defined, partial solubility parameters with a separate, fourth, molar volume parameter, rather than to multiply the solubility parameters by the molar volume raised to some power to redefine them. In response to a reviewer request stating that molar volumes calculated by software that is generally available do not agree with those found by the author, it can be said that the approach of dividing the molecular weight by the density was the way the molar volume was found when the ideas for this chapter emerged over 40 years ago. The author has seen no reason to diverge from this practice. When densities are not known or cannot be found in standard reference works, recourse can be taken to comparison with related compounds or other suitable procedure for determining the density. There are various types of free volume, which can be a cause of some difference in estimations depending on the assumptions made, but a deeper discussion at this point appears to be beyond the scope of this chapter.

The exact reason for the constant 4 in Eq (7) is discussed below. It is currently considered both as an experimental result related to the entropy changes in the systems described and as a theoretically well-defined constant. The author has also found in unpublished studies that values close to 5 could represent solubility data equally well for a few cases studied. The differences in solubility parameters between the solvent and solute in the polar and hydrogen bonding parameters are larger by a factor of two than is tolerated when nonpolar solvents dissolve the same polymer. This factor of 2 is squared to give 4 in Eq (7). The term "specific interactions" is often applied to the molecular polar and molecular hydrogen bonding (electron interchange) interactions implying that these are especially beneficial to achieving a solution since larger differences in the characteristic parameters are allowed with a successful result.

Another way to view this is as follows. It is assumed that the (center-of-the-sphere) partial solubility parameters assigned by computer optimization techniques to polymers using Eq (7) are the theoretically correct ones. A solvent with parameters corresponding to the center is to be changed in quality. If the nonpolar parameter difference only is changed by one unit, the effect on R_s is four units. If the polar or hydrogen bonding parameter difference is changed by one unit, the effect on R_s is also one unit. The entropy changes associated with the polar and hydrogen interactions have reduced the total (free energy change) effect by a factor of 4 and are thus four times larger than those associated with the nonpolar interactions.

The discussion above follows from the fact that the boundaries of the regions of solubility are characterized by a free energy change of zero for the solution process. The Flory-Huggins limiting chi parameter, χ, of about 0.5 is also characteristic for the boundary of the solubility region. Patterson [6,27], in particular, has been instrumental in showing the relations between the chi parameter and solubility parameters. Patterson's work led to the developments reported in the next section. This is strictly valid only for the interactions described by this theory. So-called theta solvents will also be located in boundary regions on solubility parameter plots with these same restrictions. Much polymer research has focused on these boundary

regions only, for the above reasons and because relatively small changes in temperature, molecular weight, solvent quality, etc., give large easily measurable changes in other quantities.

The approach of computer optimizing solubility data to spheres, which is currently in use, still seems most favorable, at least until an improvement is offered by an improved theory. Plotting experimental solubility data defines boundaries of solubility, which in fact are fixed by the free energy of mixing being experimentally equal to zero.

Equation (7) is readily used on a computer (or on a hand calculator), and supplementary relations allow easier scanning of large sets of data. It is obvious that solubility, or high affinity, requires that R_s be less than R_0. The ratio R_s/R_0 has been called the RED number, reflecting the relative energy difference. A RED number of 0 is found for no energy difference. RED numbers less than 1.0 indicate high affinity, RED equal to or close to 1.0 is a boundary condition, and progressively higher RED numbers indicate progressively lower affinities. Scanning a sizeable computer output for RED numbers less than 1.0, for example, rapidly allows location of the most interesting liquids for a given application.

The revised set of parameters for the 90 solvents was the basis for group contribution procedures developed by (most notably) Van Krevelen [28] and Beerbower [17,29], who also used Fedors, work [30]. These various developments have been summarized by Barton [9], although Beerbower's latest values have only appeared in the NASA document [29]. Table 1 is an expanded table of Beerbower group contributions, which was distributed among those who were in contact with Beerbower in the late 1970s. Beerbower also developed a simple equation for the polar parameter [17], which involved only the dipole moment and the square root of the molar volume. This is also given below and has been found quite reliable by Koehnen and Smolders [31]. This equation has also been found reliable by the author as well, giving results generally consistent with Eq (6), which, again, is the basis of the whole approach. Koehnen and Smolders also give correlation coefficients for other calculation procedures to arrive at the individual Hansen parameters.

A sizeable number of liquids have now been assigned Hansen parameters using the procedures described here. Many of these have not been published. Exxon Chemical Corporation [32,33] has indicated a computer program with data for over 500 solvents and plasticizers, 450 resins and polymers, and 500 pesticides. The author's files contain the three parameters for about 1200 liquids, although several of them appear with two or three sets of possible values awaiting experimental confirmation. In some cases, this is due to questionable physical data, for example, for latent heats of vaporization or wide variations in reported dipole moments. Another reason for this is that some liquids are chameleonic [34] as defined by Hoy in that they adopt configurations depending on their environment. Hoy [34] cites the formation of cyclic structures for glycol ethers with (nominally) linear structure. The formation of hydrogen bonded tetramers of alcohols in a fluoropolymer has also been cited [35]. The term "compound formation" can be found in the older literature, particularly where mixtures with water were involved, and structured species were postulated to explain phenomena based on specific interactions among the components of the mixtures. Barton has recently discussed some of these situations and points out that Hildebrand or Hansen parameters must be used with particular caution where the extent of donor-acceptor interactions, and in particular hydrogen bonding within a compound, is very different from that between compounds [18]. Amines and water, for example, are known to associate. Pure component data cannot be expected to predict the behavior in such cases.

Still another reason for difficulties is the large variation of dipole moments reported for the same liquid. The dipole moment for some liquids depends on their environment, as discussed below. A given solvent can be listed with different values in files to keep these phenomena in mind.

Large data sources greatly enhance searching for similar materials and locating new solvents for a polymer based on limited data, for example. Unfortunately, different authors have used different group contribution techniques, and there is a proliferation of different "Hansen" parameters for the same chemicals in the literature. This would seem to be an unfortunate situation, but may ultimately provide benefits. In particular, partial solubility parameter values found in Hoy's extensive tables [9,36] are not compatible with the customary Hansen parameters reported here. Hoy has provided an excellent source of total solubility parameters. He independently arrived at the same type division of cohesion energies as Hansen, although the methods of calculation are quite different.

Many solvent suppliers have also presented tables of solvent properties and/or use computer techniques to get these in their technical service. Partial solubility parameters not taken directly from earlier well-documented sources should be used with caution. In particular it can be noted that the Hoy dispersion parameter is consistently lower than that found by Hansen. Hoy subtracts estimated values of the polar and hydrogen bonding energies from the total energy to find the dispersion energy. This allows for more calculation error and underestimates the dispersion energy since the Hoy procedure does not appear to fully separate the polar and hydrogen bonding energies. The Van Krevelen dispersion parameters appear too low. The author has not attempted these calculations, being completely dedicated to the full procedure described here, but values estimated independently based on the Van Krevelen dispersion parameters are clearly low. A comparison with related compounds, or similarity principle, gives better results than those found from the Van Krevelen dispersion group contributions.

In the following, calculation procedures and experience are presented according to the procedures found most reliable for the experimental and/or physical data available for a given liquid.

RECENT DEVELOPMENTS—THEORY

A new understanding of the Hansen solubility parameter approach has developed since the publishing of the 14th edition of the Gardner-Sward Handbook [37,38]. Chapter 2 in Ref. [38] and also Chapter 2 in Ref. [39] include a comparison of the HSP approach with different theories of polymer solution behavior. These include those developed or modified by Huggins, Flory, Hildebrand, Prigogine, and Patterson [6,27,38–42].

TABLE 1—Group contributions to partial solubility parameters

Functional Group	Molar Volume, ΔV (cm³/mol)		London parameter, $\Delta V\delta_D^2$ (cal/mol)			Polar parameter, $\Delta V\delta_P^2$			Electron transfer parameter, $\Delta V\delta_H^2$ (cal/mol)		Total parameter, $\Delta V\delta^2$ (cal/mol)	
	Aliphatic	Aromatic[e]	Alkane	Cyclo	Aromatic	Alkane	Cyclo	Aromatic	Aliphatic	Aromatic	Aliphatic	Aromatic
CH_3^-	33.5	Same	1125	Same	Same	0	0	0	0	0	1,125	Same
$CH_2<$	16.1	Same	1180	Same	Same	0	0	0	0	0	1,180	Same
—CH<	–1.0	Same	820	Same	Same	0	0	0	0	0	820	Same
>C<	–19.2	Same	350	Same	Same	0	0	0	0	0	350	Same
CH_2 = olefin	28.5	Same	850±100	?	?	25±10	?	?	180±75	?	1,030	Same
—CH = olefin	13.5	Same	875±100	?	*?*	18±5	*?*	?	180±75	?	1,030	Same
>C = olefin	–5.5	Same	800±100	?	?	60±10	?	?	180±75	?	1,030	Same
Phenyl-	. . .	71.4	. . .	. . .	7530	. . .	. . .	50±25		50±50[a]	. . .	7,630
C-5 ring (saturated)	16	. . .	. . .	250	. . .	0	0	. . .	0	. . .	250	. . .
C-6 ring	16	Same	. . .	250	250	0	0	0	0	0	250	250
—F	18.0	22.0	0	0	0	1,000±150	?	700±100	0	0	1,000	800[e]
=F_2 twid[d]	40.0	48.0	0	0	0	700±250[a]	?	500±250[a]	0	0	1,700	1,360[e]
=F_3 triplet[d]	66.0	78.0	0	0	0	?	?	?	0	0	1,650	1,315[e]
—Cl	24.0	28.0	400±100	?	1,300±100	1,250±100	1,450±100	800 ±100	100±20[a]	Same	2,760	2,200[e]
=Cl_2 twin[d]	52.0	60.0	3,650±160	?	3,100±175[a]	800±150	?	400±150[a]	165±10[a]	180±10[a]	4,600	3,670[e]
=CL_3 triple[d]	81.9	73.9	4,750±300[a]	?	?	300±100	?	?	350±250[a]	?	5,400	4,300[e]
—Br	30.0	34.0	1,050±300[a]	1,500±175	1,650±140	1,250±100	1700±150	800 ±100	500±100	500 ±100	3,700	2,960[e]
=Br_2 twin[d]	62.0	70.0	4,300±300[a]	?	3,500±300[a]	800±250[a]	?	400±150[a]	825±200[a]	800±250[a]	5,900	4,700[e]
=Br_3 triplet[d]	97.2	109.2	5,800±400[a]	?	?	350±150[a]	?	?	1,500±300[a]	?	7,650	6,100[e]
—I	31.5	35.5	2,350±250[a]	2 200±250[a]	2,000±250[a]	1,250±100	1,350±100	575+100	1,000±200[a]	1,000±200[a]	4,550	3,600[e]
=I_2 twin[d]	66.6	74.6	5,500±300[a]	?	4,200±300[a]	800±250[a]	?	400±150[a]	1,650±250[a]	1,800±200[a]	8,000	6,400[e]
≡I_3 triplet[d]	111.0	123.0	?	?	?	?	?	?	?	?	11,700	9,3 50[e]
—O— ether	3.8	Same	0	0	0	500±150	600±150	450±150	450±25	1,200±100	800	(1,650±150)
>CO ketone	10.8	Same	. . .[c]	2,350±400	2,800±1352	25,000±7%)/*V*	1,000±300	950±300	800±250[b]	400±125[a]	4,150	Same
—CHO	(23.2)	(31.4)	950±300	?	350±275	2,100±200	3,000±500	2,750±200	1,000±200	750±150	(4,050)	Same
—COO–ester	18.0	Same	. . .[c]	?	. . .	(56,000±12%)/*V*	?	(338,000±12%)/*V*	1,250±150	475±100[a]	4,300	Same
—COOH	28.5	Same	3,350±300	3,550±250	3,600±400	500±150	300±50	750±350	2,750±250	2,850±250[a]	6,600	Same
—OH	10.0	Same	1,770±450	1,370±500	1,870±600	700±200	1,100±300	800±150	4,650±400	4,650±500	7,120	Same
=$(OH)_2$ twin or adjacent	26.0	Same	0	?	?	1,500±100	?	?	9,000 ±600	9,300±600	10,440	Same
—CN	24.0	Same	1,600±850[a]	?	0	4,000±800[a]	?	3,750±300[a]	500±200[b]	400±12[a]	4,450	Same
—NO_2	24.0	32.0	3,000±600	?	2,550±125	3,600±600	?	1750±100	400±50[b]	350±50[a]	7,000	(4,400)
—NH_2 amine	19.2	Same	1,050±300	1,050±450[a]	150±150[a]	600 ±200	600±350[a]	800 ±200	1,350±200	2250±200[b]	3,000	Same
>NH_2 amine	4.5	Same	1,150±225	?	?	100±50	?	?	750±200	?	2,000	Same
—NH_2 amide	(6.7)	Same	?	?	?	?	?	?	2,700±550[a]	?	(5,850)	Same
≡PO_4	28.0	Same	. . .[c]	?	?	(8100±10%)/*V*	?	?	3,000±500	?	(7,000)	Same

[a]Based on very limited data. Limits shown are roughly 95 % confidence; in many cases, values are for information only and not to be used for computation.
[b]Includes unpublished infrared data.
[c]Use formula in $\Delta V\delta_p^2$ column in calculation, with *V* for total compound.
[d]Twin and triplet values apply to halogens on the same C atom, except that $\Delta V\delta_p^2$ also includes those on adjacent C atoms.
[e]These values apply to halogens attached directly to the ring and also to halogen attached to aliphatic double-bonded C atoms.
[f]From R. F. Fedors[25].

For those familiar with the widely used Flory interaction coefficient, χ_{12} it can be shown [38,39] that there is a relation between this and the RED number given by Eq (8).

$$\chi_{12} \text{ corresponds to } \chi_c\,(\text{RED})^2 \qquad (8)$$

χ_c is usually taken as being near 1/2 for the interaction of typical solvents with polymers of very large molecular weight. Unfortunately, χ_{12} does not explicitly take account of hydrogen bonding. Equation (8) is therefore only indicative of a relation had the Flory approach included polar and hydrogen bonding interactions explicitly.

It is instructive to arrange Eq (8) in the form given in Eq (9):

$$(\text{RED})^2 = (R_s/R_o)^2 \text{ corresponds to } \chi_{12}/\chi_c \qquad (9)$$

$(R_s)^2$ corresponds to χ_{12}, both being interaction parameters. These are respectively divided by the corresponding limiting or critical values that allow solubility to find $(\text{RED})^2$. These limiting values are $(R_o)^2$ in the Hansen system and χ_c in the Huggins-Flory approach. Thus R_s greater than R_o indicates nonsolubility just as values of χ_{12} greater than χc have the same function. Values of R_s and χ_{12} that are less than zero are not allowed (even though one finds many measured values of the latter in the literature which are negative).

The coefficient 4 in Eq (7) has been found correct for all practical purposes in over 1,000 correlations using Hansen solubility parameters. The coefficient 4 in front of the difference in the nonpolar interactions shows that the specific interactions described by the differences in the polar and hydrogen bonding parameters are only 0.25 times as significant as the differences in the nonpolar term. This factor (0.25) is predicted theoretically by the Prigogine corresponding states theory of polymer solutions for the importance of specific interactions relative to the atomic/nonpolar interactions [38–42]. This same factor can also be traced back to still earlier approaches (Lorentz-Berthelot mixtures) studying affinities among gases, for example [42]. The Hansen approach and the (first term in the) Prigogine approach are in agreement with each other. The so-called geometric mean to estimate the interaction between two unlike species is used in both of these, and the coefficient 4 experimentally confirms that this type of mean is also valid for hydrogen bonding interactions. The coefficient 4 must be used to differentiate the behavior of the atomic (nonpolar, dispersion, or London) type forces from that of the molecular dipolar and molecular hydrogen bonding forces. The Hansen approach cannot be considered empirical. The Huggins-Flory and subsequent "new Flory" approaches seem inadequate for other than strictly nonpolar systems since hydrogen bonding is not included. The pioneering Hildebrand solubility parameter approach did not treat specific interactions either, although it led the author to develop the Hansen approach that does. The Prigogine approach is too difficult to use and lacks specific consideration of hydrogen bonding as well. This leaves the Hansen approach as the only proven, reliable, and generally useful means to systematically study the common types of interactions involved in systems with hydrogen bonding and with permanent dipoles. It is not in conflict with the other theories. It extends them in a general way to applications with polar and hydrogen bonding.

Panayiotou has recently used a statistical thermodynamica approach to calculate the HSP that is reported in Chapter 3 in Ref. [39]. Expanding on earlier work, he first calculates the hydrogen bonding solubility parameter. After this the other HSP and the total solubility parameter are calculated. There is also a new large set of group contributions to help those not fully competent in statistical thermodynamics. The values for all the parameters for about 50 liquids calculated by Panayiotou are in amazingly good agreement with those reported by Hansen over 40 years ago [13–16]. There is also exceptionally good agreement for a number of the common polymers. These results, coupled with the agreement, or perhaps better, lack of disagreement, with the other theories of polymer solutions, appear to confirm that the three-parameter approach based on a division of the cohesion energy is fundamentally sound.

CALCULATION OF THE DISPERSION SOLUBILITY PARAMETER, δ_d

The δ_d parameter is calculated according to the procedures outlined by Blanks and Prausnitz [12]. Figs. 1 and 2, or 3, can be used to find this parameter depending on whether the molecule of interest is aliphatic, cycloaliphatic, or aromatic. These figures have been inspired by Barton [9], who converted earlier data to SI units. All three of these figures have been straight line extrapolated into a higher range of molar volumes than that reported by Barton. Energies found with these extrapolations have also provided consistent results. The solubility parameters in SI units, $\text{MPa}^{1/2}$, are 2.0455 times larger than those in the older centimeter, gram, second system, $(\text{cal/cc})^{1/2}$, which still finds extensive use in the United States, for example.

The figure for the aliphatic liquids gives the dispersion cohesive energy, ΔE_d, whereas the other two figures directly report the dispersion cohesive energy density, c. The latter is much simpler to use since one needs only take the square root of the value found from the figure to find the respective partial solubility parameter. Barton also presented a similar figure for the aliphatic solvents, but it is inconsistent with the energy figure and in error. Its use is not recommended. When substituted cycloaliphatics or substituted aromatics are considered, simultaneous consideration of the two separate parts of the molecules is required. The dispersion energies are evaluated for each of the types of molecules involved, and a weighted average for the molecule of interest based on numbers of significant atoms is taken. For example, hexyl benzene would be the arithmetic average of the dispersion energies for an aliphatic and an aromatic liquid, each with the given molar volume of hexyl benzene. Liquids such as chlorobenzene, toluene, and ring compounds with alkyl substitutions with only two or three carbon atoms have been considered as cyclic compounds only. Such weighting has been found necessary to satisfy Eq (6).

The author has directly used these figures to find the cohesion energy for nonpolar molecules. This introduces a small but unaccountable error since, for example, ΔE_D, for an aromatic compound such as toluene, is not equal to the total cohesion energy ΔE_t. In practice (so far) this has not led to any apparent problems. The error becomes less significant as the polar and hydrogen bonding effects increase.

The critical temperature, T_c, is required to use the dispersion energy figures. If the critical temperature cannot be found, it must be estimated. A table of the Lydersen group contributions, ΔT, [43] as given by Hoy [36] for calculation of the critical temperature, is included here as Table 2. In some cases, the desired groups may not be in the table, which means some educated guessing is required. The end result does not appear too sensitive to these situations. The normal boiling temperature, T_b, is also required in this calculation. This is not always available, either, and must be estimated by similarity, group contribution, or

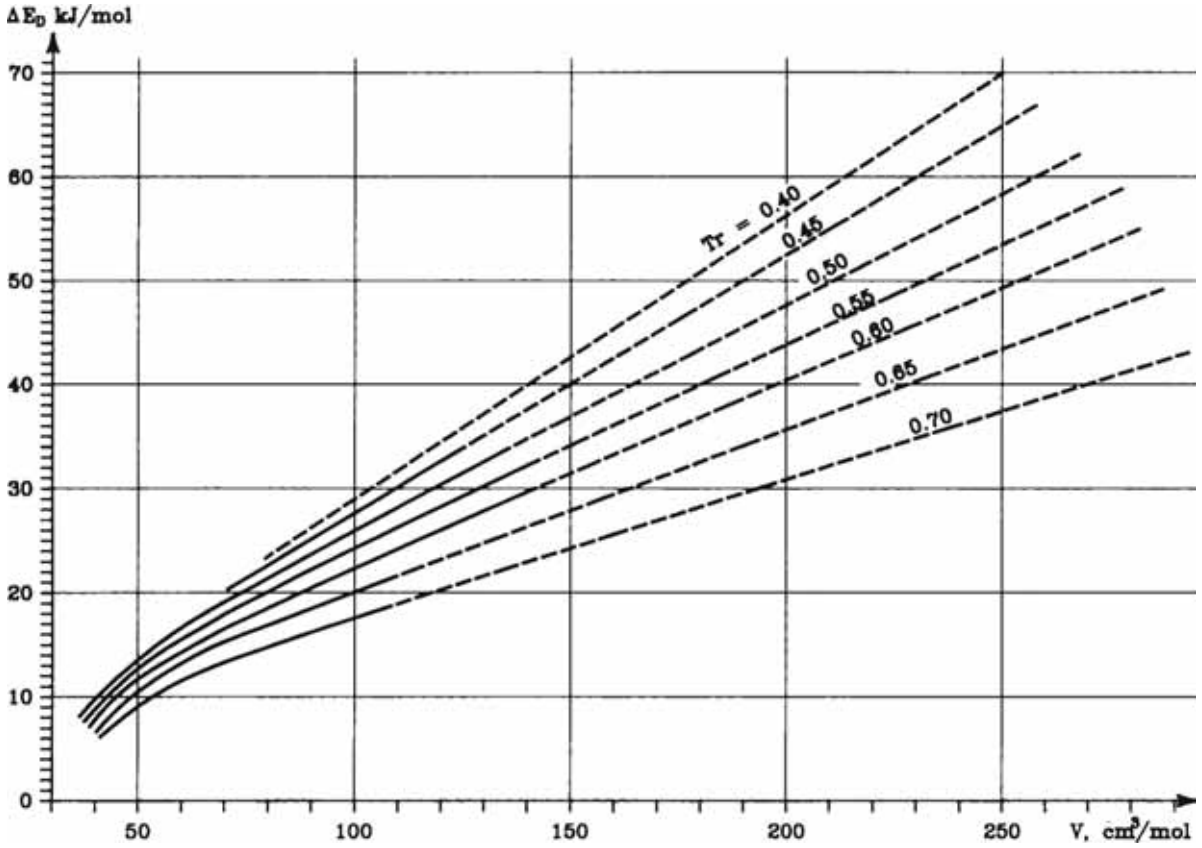

Fig. 1—Energy of vaporization for straight chain hydrocarbons as a function of molar volume and reduced temperature.

other technique. The Lydersen group contribution method involves the use of Eqs (10) and (11),

$$T_b / T_c = 0.567 + \sum \Delta_T - \left(\sum \Delta_T\right)^2 \quad (10)$$

$$T_r = T / T_c \quad (11)$$

where T has been taken as 298.15 K.

The dispersion parameter is an atomic force parameter. The size of the atom is important. It has been found that corrections are required for atoms significantly larger than carbon, such as chlorine, sulfur, bromine, etc., but not for oxygen or nitrogen, which have a similar size. The carbon atom in hydrocarbons is the basis of the dispersion parameter in its present form. These corrections are applied by first finding the dispersion cohesive energy from the appropriate figure. This requires multiplication by the molar volume for the cyclic compounds using data from the figures here since these figures give the cohesive energy densities. The dispersion cohesive energy is then increased by adding on the correction factor. This correction factor for chlorine, bromine, and sulfur has been taken as 1,650 J/mol for each of these atoms in the molecule. Dividing by the molar volume and then taking the square root gives the (large atom corrected) dispersion solubility parameter.

The need for these corrections has been confirmed many times, both for interpretation of experimental data

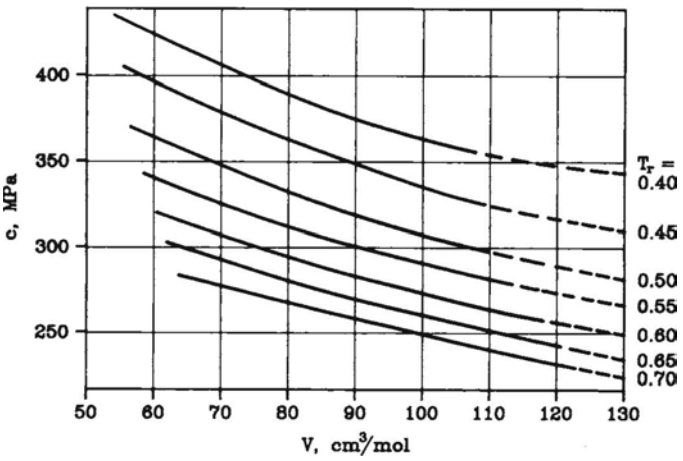

Fig. 2—Cohesive energy density for cycloalkanes as a function of molar volume and reduced temperature.

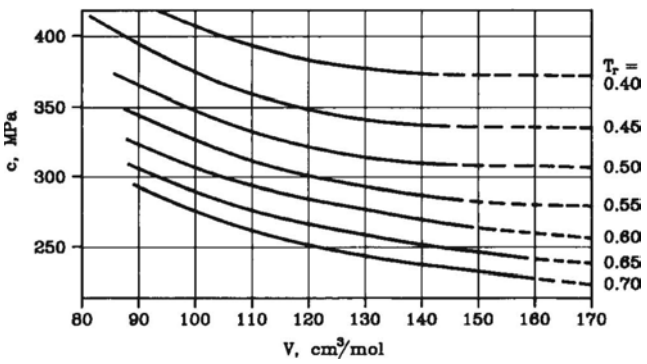

Fig. 3—Cohesive energy density for aromatic hydrocarbons as a function of molar volume and reduced temperature.

TABLE 2—Lydersen group constants

Group	Aliphatic, ΔT	Cyclic, ΔT	ΔP_T^P	Aliphatic, ΔP	Cyclic, ΔP
CH_3	0.020	. . .	0.0226	0.227	. . .
CH_2	0.020	0.013	0.0200	0.227	0.184
>CH—	0.012	0.012	0.0131	0.210	0.192
>C<	0.000	–0.007	0.210	0.210	0.154
═CH_2	0.018	. . .	0.0192	0.198	. . .
═CH—	0.018	0.011	0.0184	0.198	0.154
═C<	0.000	0.011	0.0129	0.198	0.154
═CH aromatic	. . .	. . .	0.0178	. . .	. . .
═CH aromatic	. . .	. . .	0.0149	. . .	. . .
—O—	0.021	0.014	0.0175	0.16	0.12
>O epoxide	. . .	. . .	0.0267	. . .	. . .
—COO—	0.047	. . .	0.0497	0.47	. . .
>C═O	0.040	0.033	0.0400	0.29	0.02
—CHO	0.048	. . .	0.0445	0.33	. . .
—CO_2O	. . .	. . .	0.0863	. . .	. . .
—OH→	. . .	. . .	0.0343	0.06	. . .
—H→	. . .	. . .	–0.0077	. . .	. . .
—OH primary	0.082	. . .	0.0493	. . .	. . .
—OH sec.	. . .	. . .	0.0440	. . .	. . .
—OH tert.	. . .	. . .	0.0593	. . .	. . .
—OH phenolic	0.035	. . .	0.0060	–0.02	
—NH_2	0.031	. . .	0.0345	0.095	. . .
—NH—	0.031	0.024	0.0274	0.135	0.09
>N—	0.014	0.007	0.0093	0.17	0.13
—C≡N	0.060	. . .	0.0539	0.36	. . .
—NCO	. . .	. . .	0.0539	. . .	. . .
HCON<	. . .	. . .	0.0546	. . .	. . .
—CONH—	. . .	. . .	0.0843	. . .	. . .
—CON<	. . .	. . .	0.0729	. . .	. . .
—$CONH_2$	. . .	. . .	0.0897	. . .	. . .
—OCONH—	. . .	. . .	0.0938	. . .	. . .
—S—	0.015	0.008	0.0318	0.27	0.24
—SH	0.015	. . .	. . .	. . .	. . .
—Cl 1°	0.017	. . .	0.0311	0.320	. . .
—Cl 2°	. . .	. . .	0.0317	. . .	. . .
Cl_2 twin	. . .	. . .	0.0521	. . .	. . .
Cl aromatic	. . .	. . .	0.0245	. . .	. . .
—Br	0.010	. . .	0.0392	0.50	. . .
—Br aromatic	. . .	. . .	0.0313	. . .	. . .
—F	0.018	. . .	0.006	0.224	. . .
—I	0.012	. . .	. . .	0.83	. . .
Conjugation	. . .	. . .	0.0035	. . .	. . .
c is double bond	. . .	. . .	–0.0010	. . .	. . .
trans double bond	. . .	. . .	–0.0020	. . .	. . .
4 Member ring	. . .	. . .	0.0118	. . .	. . .
5 Member ring	. . .	. . .	0.003	. . .	. . .
6 Member ring	. . .	. . .	–0.0035	. . .	. . .
7 Member ring	. . .	. . .	0.0069	. . .	. . .
Ortho	. . .	. . .	0.0015	. . .	. . .
Meta	. . .	. . .	0.0010	. . .	. . .
Para	. . .	. . .	0.0060	. . .	. . .
Bicycloheptyl	. . .	. . .	0.0034	. . .	. . .
Tricyclodecane	. . .	. . .	0.0095	. . .	. . .

and to allow Eq (6) to balance. Research is definitely needed in this area. The impact of these corrections is, of course, larger for the smaller molecular species. The taking of square roots of the larger numbers involved with the larger molecular species reduces the errors involved in these cases since the corrections themselves are relatively small.

It can be seen from the dispersion parameters of the cyclic compounds that the ring also has an effect similar to increasing the effective size of the interacting species. The dispersion energies are larger for cycloaliphatic compounds than for their aliphatic counterparts, and they are higher for aromatic compounds than for the corresponding cycloaliphatics. Similar effects also appear with the ester group. This group appears to act as if it were, in effect, an entity that is larger than the corresponding compound containing only carbon (i.e., its homomorph), and it has a higher dispersion solubility parameter without any special need for corrections.

The careful evaluation of the dispersion cohesive energy may not have major impact on the value of the dispersion solubility parameter itself because of the taking of square roots. Larger problems arise because of Eq (4). Energy assigned to the dispersion portion cannot be reused when finding the other partial parameters using Eq (4) [or Eq (6)]. This is one reason why group contributions are recommended for the polar and hydrogen bonding components in some cases below. The author has not used older tables of group contributions for the dispersion parameter. These were found to be not as reliable as the longer procedure discussed above when data are available. Frequent use has been made of simple comparisons of similarity to molecules whose dispersion parameters have already been established. The group contributions for the dispersion solubility parameter presented by Panayiotou in Chapter 3 in Ref. [39] appear to be a good third alternative, however.

CALCULATION OF THE POLAR SOLUBILITY PARAMETER, δ_p

The earliest assignments of a polar solubility parameter were given by Blanks and Prausnitz [12]. These parameters were in fact the combined polar and hydrogen bonding parameters as used by Hansen and cannot be considered polar in the current context. The first Hansen polar parameters [13] were reassigned new values by Skaarup according to the Böttcher equation [15]. This equation requires the molar volume, the dipole moment (DM), the refractive index, and the dielectric constant. These are not available for many compounds, and the calculation is somewhat more difficult than using the much simpler equation developed by Beerbower [17]

$$\delta_p = \frac{37.4}{(V_M)^{1/2}}(\mathrm{DM}) \qquad (12)$$

The constant 37.4 gives this parameter in SI units.

Equation (12) has been consistently used by the author over the past few years, particularly in view of its reported reliability [31]. This reported reliability appears to be correct. The molar volume must be known or estimated in one way or another. This leaves only the dipole moment to be found or estimated. Standard reference works have tables of dipole moments, with the most extensive listing still being McClellan [44]. Other data sources also have this parameter as well as other relevant parameters and data such as latent heats and critical temperatures. The so-called DIPPR database has been found useful for many compounds of reasonably common usage, but many interesting compounds are not included in DIPPR. This abbreviation is for Design Institute for Physical Property Research,[2] Project 801 of the American Institute of Chemical Engineers at the Pennsylvania State University [45]. When no dipole moment is available, similarity with other compounds, group contributions, or experimental data can be used to estimate the polar solubility parameter.

It must be noted that the fact of zero dipole moment in symmetrical molecules is not basis enough to assign a zero polar solubility parameter. An outstanding example of variations of this kind can be found with carbon disulfide. The reported dipole moments are mostly 0 for gas phase measurements, supplemented by 0.08 in hexane, 0.4 in carbon tetrachloride, 0.49 in chlorobenzene, and 1.21 in nitrobenzene.

There is a clear increase with increasing solubility parameter of the media. The latter and highest value has been found experimentally most fitting for correlating permeation through a fluoropolymer film used for chemical protective clothing [46]. Many fluoropolymers have considerable polarity. The lower dipole moments seem to fit in other instances. Diethylether has also presented problems as an outlier in terms of dissolving or not, or rapid permeation or not. Here the reported dipole moments [44] vary from 0.74 to 2.0 with a preferred value of 1.17, and with 1.79 in chloroform. Choosing a given value seems rather arbitrary. The chameleonic cyclic forms of the linear glycol ethers would also seem to provide for a basis of altered dipole moments in various media [34].

When Eq (12) cannot be used, the polar solubility parameter has been found using the Beerbower table of group contributions, by similarity to related compounds, and/or by subtraction of the dispersion and hydrogen bonding cohesive energies from the total cohesive energy. The question in each case is: "Which data are available and judged most reliable?" New group contributions have also been developed from related compounds where their dipole moments are available. These new polar group contributions then become supplementary to the Beerbower table.

For large molecules, especially those with long hydrocarbon chains, the accurate calculation of the relatively small polar (and hydrogen bonding) contributions present special difficulties. The latent heats are not generally available with sufficient accuracy to allow subtraction of two large numbers from each other to find a very small one. In such cases the similarity and group contribution methods are thought best. Unfortunately, latent heats found in a widely used handbook [47] are not clearly reported as to the reference temperature. There is an indication that these are 25°C data, but checking indicated many of the data were identical with boiling point data reported elsewhere in the literature. A more recent edition of this handbook has a completely different and less voluminous section for the latent heat of evaporation [48]. Again, even moderate variations in reported heats of vaporization can cause severe

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problems in calculating the polar (or hydrogen bonding) parameter when Eqs (4) or (6) are strictly adhered to.

CALCULATION OF THE HYDROGEN BONDING SOLUBILITY PARAMETER, δ_h

In the earliest work, the hydrogen bonding parameter was almost always found from the subtraction of the polar and dispersion energies of vaporization from the total energy of vaporization. This is still widely used where the required data are available and reliable. At this stage, however, the group contribution techniques are considered reasonably reliable for most of the required calculations and, in fact, more reliable than estimating several of the other parameters to ultimately arrive at the subtraction step just mentioned. Therefore, in the absence of reliable latent heat and dipole moment data, group contributions are judged to be the best alternative. Similarity to related compounds can also be used, of course, and the result of such a procedure should be essentially the same as for using group contributions. The work of Panayiotou in Chapter 3 of Ref. [39], discussed above, also provides an alternative method to arrive at the hydrogen bonding parameter.

SUPPLEMENTARY CALCULATIONS AND PROCEDURES

The procedures listed above are those most frequently used by the author in calculating the three partial solubility parameters for liquids where some data are available. There are a number of other calculations and procedures that are also helpful. Latent heat data at 25°C have consistently been found from latent heats at another temperature using the relation given by Fishtine [49].

$$\frac{\Delta H_v(T_1)}{\Delta H_v(T_2)} = \left[\frac{T_c - T_1}{T_c - T_2}\right]^{0.38} = \left[\frac{1 - T_{r1}}{1 - T_{r2}}\right]^{0.38} = \left[\frac{1 - T_{r1}}{1 - T_{r2}}\right]^{0.38} \quad (13)$$

This is done even if the melting point of the compounding being considered is higher than 25°C. The result is consistent with all the other parameters, and to date no problems with particularly faulty predictions have been noted in this respect, i.e., it appears as if the predictions are not significantly in error. When the latent heat is given in cal/mole, the above equation is used to estimate the latent heat at 25°C. RT equal to 592 cal/mole is then subtracted from this according to Eq (14) to find the total cohesion energy, ΔE_V, in cgs units at this temperature:

$$\Delta E_v = \Delta E_t = \Delta H_v - RT \quad (14)$$

Only limited attempts have been made to calculate solubility parameters at a higher temperature. Solubility parameter correlations of phenomena at higher temperatures have generally been found satisfactory when the established 25°C parameters have been used. Recalculation to higher temperatures is possible, but has not been found necessary. In this direct but approximate approach, it is assumed that the parameters all demonstrate the same temperature dependence, which, of course, is not the case. It might be noted in this connection that the hydrogen bonding parameter, in particular, is the most sensitive to temperature. As the temperature is increased, more and more hydrogen bonds are progressively broken, and this parameter will decrease more rapidly than the others.

The gas phase dipole moment is not temperature dependent, although the volume of the fluid does change with temperature, which will change its cohesive energy density. Beerbower has suggested relations to predict the changes of the partial solubility parameters with temperature [17]. The coefficient of thermal expansion, α, appears in all of these relations. These are

$$\frac{d(\delta_d)}{dT} = -1.25\alpha\delta_d \quad (15)$$

$$\frac{d(\delta p)}{dT} = -0.5\alpha\delta_p \quad (16)$$

$$\frac{d(\delta p)}{dT} = -\delta_H(1.22\times10^{-3} + 0.5\alpha) \quad (17)$$

A computer program has been developed by the author to assign the three Hansen parameters for solvents based on experimental data alone. This has been used in several cases where the parameters for the given liquids were desired with a high degree of accuracy. The procedure is to enter solvent quality, good or bad, into the program for a reasonably large number of polymers where the solubility parameters and appropriate radius of interaction for the polymers are known. The program then locates that set of δ_d, δ_p, and δ_h parameters for the solvent that best satisfies the requirements of a location within the spheres of the appropriate polymers where solvent quality is good and outside of the appropriate spheres where it is bad.

An additional aid in estimating the Hansen parameters for many compounds is that these parameters can be found by interpolation or extrapolation, especially for homologous series. The first member may not necessarily be a straight line extrapolation, but comparisons with related compounds should always be made where possible to confirm assignments. Plotting the parameters reported in Table 3 for homologous series among the esters, nitroparaffins, ketones, alcohols, and glycol ethers will aid in finding the parameters for related compounds.

Table 3 contains Hansen solubility parameters for a large number of liquids and plasticizers. These are given in SI units. Over 800 HSP values can be found in Refs. [38,39].

SOLUBILITY PARAMETERS FOR POLYMERS

The solubility parameters for numerous polymers and film formers are given in Table 4. Suppliers and trademarks are given in Table 5. These data are based on solubility determinations unless otherwise noted. There are four parameters, the three describing the nonpolar, polar, and hydrogen bonding interactions as for the liquids, and the fourth, R_0, a radius of interaction for the type of interaction described. Most of these are taken from a report [50] from the Scandinavian Paint and Printing Ink Research Institute. (This institute unfortunately no longer exists.) Additional values have been contributed according to the notes in the table to indicate the types of data, which have been correlated with these techniques. Barton [51] has also provided solubility parameters for many polymers in a handbook. Additional values are also found in Refs. [38,39].

Experimental determination of polymer solubility parameters involves trying to dissolve the polymer at a

TABLE 3—Hansen solubility parameters for selected liquids (solvents in alphabetical order)

No.	Solvent	Dispersion	Polar	Hydrogen Bonding	Molar Volume
1	Acetaldehyde	14.7	12.5	7.9	56.6
2	Acetic acid	14.5	8.0	13.5	57.1
3	Acetic anhydride	16.0	11.7	10.2	94.5
4	Acetone[a]	15.5	10.4	7.0	74.0
5	Acetonitrile	15.3	18.0	6.1	52.6
6	Acetophenone[a]	19.6	8.6	3.7	117.4
7	Acrylonitrile	16.0	12.8	6.8	67.1
8	Allyl alcohol	16.2	10.8	16.8	68.4
9	Amyl acetate	15.8	3.3	6.1	148.0
10	Aniline	19.4	5.1	10.2	91.5
11	Anisole	17.8	4.1	6.7	119.1
12	Benzaldehyde	19.4	7.4	5.3	101.5
13	Benzene[a]	18.4	0.0	2.0	89.4
14	1.3-Benzenediol	18.0	8.4	21.0	87.5
15	Benzoic acid	18.2	6.9	9.8	113.1
16	Benzonitrile	17.4	9.0	3.3	102.6
17	Benzyl alcohol	18.4	6.3	13.7	103.6
18	Benzyl butyl phthalate	19.0	11.2	3.1	306.0
19	Benzyl chloride	18.8	7.1	2.6	115.0
20	Biphenyl	19.7	1.0	2.0	155.1
21	Bromobenzene	20.5	5.5	4.1	105.3
22	Bromochloromethane	17.3	5.7	3.5	65.0
23	Bromoform	21.4	4.1	6.1	87.5
24	1-Bromonaphtalene	20.3	3.1	4.1	140.0
25	Bromotrifluoromethane	9.6	2.4	0.0	97.0
26	Butane	14.1	0.0	0.0	101.4
27	1.3-Butanediol	16.6	10.0	21.5	89.9
28	l-Butanol[a]	16.0	5.7	15.8	91.5
29	2-Butanol	15.8	5.7	14.5	92.0
30	Butyl acetate[a]	15.8	3.7	6.3	132.5
31	Sec-butyl acetate	15.0	3.7	7.6	133.6
32	Butyl acrylate	15.6	6.2	4.9	143.8
33	Butylamine	16.2	4.5	8.0	99.0
34	Butyl lactate	15.8	6.5	10.2	149.0
35	Butyraldehyde	15.6	10.1	6.2	90.5
36	Butyric acid	14.9	4.1	10.6	110.0
37	Gamma butyrolactone[a]	19.0	16.6	7.4	76.8
38	Butyronitrile	15.3	12.4	5.1	87.3
39	Carbon disulfide	20.5	0.0	0.6	60.0
40	Carbon tetrachloride[a]	17.8	0.0	0.6	97.1
41	Chlorobenzene[a]	19.0	4.3	2.0	102.1
42	1-Chlorobutane	16.2	5.5	2.0	104.5
43	Chlorodifluoromethane	12.3	6.3	5.7	72.9
44	Chloroform[a]	17.8	3.1	5.7	80.7
45	3-Chloro-l-propanol	17.5	5.7	14.7	84.2
46	m-cresol	18.0	5.1	12.9	104.7
47	Cyclohexane	16.8	0.0	0.2	108.7
48	Cyclohexanol[a]	17.4	4.1	13.5	106.0
49	Cyclohexanone	17.8	8.4	5.1	104.0
50	Cyclohexylamine	17.2	3.1	6.5	113.8
51	Cyclohexylchloride	17.3	5.5	2.0	118.6

TABLE 3—(Continued)

No.	Solvent	Dispersion	Polar	Hydrogen Bonding	Molar Volume
52	Cis-decahydronaphthalene	18.8	0.0	0.0	156.9
53	Trans-decahydronaphthalene	18.0	0.0	0.0	156.9
54	Decane	15.7	0.0	0.0	195.9
55	1-Decanol	16.0	4.7	10.0	191.8
56	Diacetone alcohol[a]	15.8	8.2	10.8	124.2
57	Dibenzyl ether	19.6	3.4	5.2	197.4
58	Dibutyl phthalate	17.8	8.6	4.1	266.0
59	Dibutyl sebacate	13.9	4.5	4.1	339.0
60	o-dichlorobenzene[a]	19.2	6.3	3.3	112.8
61	2.2-Dichlorodiethyl ether	18.8	9.0	5.7	117.2
62	Dichlorodifluoromethane	12.3	2.0	0.0	92.3
63	1.1-Dichloroethane	16.5	7.8	3.0	84.2
64	1.1-Dichloroethylene	16.4	52	24	79.9
65	Di-(2-chloro-isopropyl) ether	19.0	8.2	5.1	146.0
66	Dichloromonofluoromethane	15.8	3.1	5.7	75.4
67	1.2-Dichlorotetrafluoroethane	12.6	1.8	0.0	117.6
68	Di-iso-butyl carbinol	14.9	3.1	10.8	177.8
69	Diethanolamine	17.2	10.8	21.2	95.9
70	Diethylamine	14.9	2.3	6.1	103.2
71	2-(Diethylamino) ethanol	14.9	5.8	12.0	133.2
72	Para-diethy l benzene	18.0	0.0	0.6	156.9
73	Diethyl carbonate	15.1	6.3	3.5	121.0
74	Diethylene glycol[a]	16.6	12.0	20.7	94.9
75	Diethylene glycol butyl ether acetate	16.0	4.1	8.2	208.2
76	Diethylene glycol hexyl ether	16.0	6.0	10.0	204.3
77	Diethylene glycol monobutyl ether	16.0	7.0	10.6	170.6
78	Diethylene glycol monoethyl ether	16.1	9.2	12.2	130.9
79	Diethylene glycol monomethyl ether	16.2	7.8	12.6	118.0
80	Diethylenetriamine	16.7	13.3	14.3	108.0
81	Diethyl ether[a]	14.5	2.9	5.1	104.8
82	Diethyl ketone	15.8	7.6	4.7	106,4
83	Diethyl phthalate	17.6	9.6	4.5	198.0
84	Diethyl sulfate	15.7	14.7	7.1	131.5
85	Diethyl sulfide	16.8	3.1	2.0	107.4
86	Di(isobutyl) ketone	16.0	3.7	4.1	177.1
87	Di(2-methoxyethyl) ether	15.7	6.1	6.5	142.0
88	N,N-dimethylacetamide	16.8	11.5	10.2	92.5
89	Dimethylformamide[a]	17.4	13.7	11.3	77.0
90	1,1-Di methyl hydrazine	15.3	5.9	11.0	76.0
91	Dimethyl phthalate	18.6	10.8	4.9	163.0
92	Dimethyl sulfone	19.0	19.4	12.3	75.0
93	Dimethyl sulfoxide[a]	18.4	16.4	10.2	71.3
94	Dioctyl phthalate	16.6	7.0	3.1	377.0
95	1,4-Dioxane[a]	19.0	1.8	7.4	85.7
96	Dipropylamine	15.3	1.4	4.1	136.9
97	Dipropylene glycol[a]	16.5	10.6	17.7	130.9
98	Dipropyiene glycol methyl ether	15.5	5.7	11.2	157.4,
99	Dodecane	16.0	0.0	0.0	228.6
100	Eicosane	16.5	0.0	0.0	359.8
101	Epichlorohydrin	18.9	7.6	6.6	78.4
102	Ethanethiol	15.7	6.5	7.1	74.3

TABLE 3—(Continued)

No.	Solvent	Dispersion	Polar	Hydrogen Bonding	Molar Volume
103	Ethanol[a]	15.8	8.8	19.4	58.5
104	Ethanolamine[a]	17.0	15.5	21.2	59.8
105	Ethyl acetate[a]	15.8	5.3	7.2	98.5
106	Ethyl acrylate	15.5	7.1	5.5	108.8
107	Ediyl amyl ketone	16.2	4.5	4.1	156.0
108	Ethylbenzene	17.8	0.6	1.4	123.1
109	Ethyl bromide	16.5	8.4	2.3	74.6
110	2-Ethyl-l-butanol	15.8	4.3	13.5	123.2
111	Ethyl butyl ketone	16.2	5.0	4.1	139.0
112	Ethyl chloride	15.7	6.1	2.9	70.0
113	Ethyl chloroformate	15.5	10.0	6.7	95.6
114	Ethyl cinnamate	18.4	8.2	4.1	166.8
115	Ethylene carbonate	19.4	21.7	5.1	66.0
116	Ethylene cyanohydrin	17.2	18.8	17.6	68.3
117	Ethylenediamine	16.6	8.8	17.0	67.3
118	Ethylene dibromide	19.2	3.5	8.6	87.0
119	Ethylene dichloride[a]	19.0	7.4	4.1	79.4
120	Ethylene glycol[a]	17.0	11.0	26.0	55.8
121	Ethylene glycol butyl ether acetate	15.3	4.5	8.8	171.2
122	Ethylene glycol monobutyl ether[a]	16.0	5.1	12.3	131.6
123	Ethylene glycol monoethyl ether[a]	16.2	9.2	14.3	97.8
124	Ethylene glycol monoethyl ether acetate	15.9	4.7	10.6	136.1
125	Ethylene glycol monomethyl ether[a]	16.2	9.2	16.4	79.1
126	Ethylene glycol monomethyl ether acetate	15.9	5.5	11.6	121.6
127	Ethyl formate	15.5	8.4	8.4	80.2
128	2-Ethyl hexanol	15.9	3.3	11.8	156.6
129	Ethyl lactate	16.0	7.6	12.5	115.0
130	Formamide[a]	17.2	26.2	19.0	39.8
131	Formic acid	14.3	11.9	16.6	37.8
132	Furan	17.8	1.8	5.3	72.5
133	Furfural	18.6	14.9	5.1	83.2
134	Furfuryl alcohol	17.4	7.6	15.1	86.5
135	Glycerol	17.4	12.1	29.3	73.3
136	Heptane	15.3	0.0	0.0	147.4
137	Hexadecane	16.3	0.0	0.0	294.1
138	Hexamethylphosphoramide	18.5	8.6	11.3	175.7
139	Hexane[a]	14.9	0.0	0.0	131.6
140	Hexylene glycol	15.7	8.4	17.8	123.0
141	Isoamyl acetate	15.3	3.1	7.0	148.8
142	Isobutyl acetate	15.1	3.7	6.3	133.5
143	Isobutyl alcohol	15.1	5.7	15.9	92.8
144	Isobutyl isobutyrate	15.1	2.9	5.9	163.0
145	Isooctyl alcohol	14.4	7.3	12.9	156.6
146	Isopentane	13.7	0.0	0.0	117.4
147	Isophorone[a]	16.6	8.2	7.4	150.5
148	Isopropyl palmitate	14.3	3.9	3.7	330.0
149	Mesitylene	18.0	0.0	0.6	139.8
150	Mesityl oxide	16.4	6.1	6.1	115.6
151	Methacrylonitrile	15.8	15.1	5.4	83.9
152	Methanol[a]	15.1	12.3	22.3	40.7
153	o-Methoxyphenol	18.0	8.2	13.3	109.5

Continued

TABLE 3—(Continued)

No.	Solvent	Dispersion	Polar	Hydrogen Bonding	Molar Volume
154	Methyl acetate	15.5	7.2	7.6	79.7
155	Methyl acrylate	15.3	6.7	9.4	90.3
156	Methylal	15.0	1.8	8.6	169.4
157	Methyl amyl acetate	15.2	3.1	6.8	167.4
158	Methyl butyl ketone	15.3	6.1	4.1	123.6
159	Methyl chloride	15.3	6.1	3.9	55.4
160	Methylcyclohexane	16.0	0.0	1.0	128.3
161	Methylene dichloride[a]	18.2	6.3	6.1	63.9
162	Methylene diiodide	17.8	3.9	5.5	80.5
163	Methyl ethyl ketone	16.0	9.0	5.1	90.1
164	Methyl isoamyl ketone	16.0	5.7	4.1	142.8
165	Methyl isobutyl carbinol	15.4	3.3	12.3	127.2
166	Methyl isobutyl ketone[a]	15.3	6.1	4.1	125.8
167	Methyl methacrylate	15.8	6.5	54	106.1
168	1-Methylnaphthalene	20.6	0.8	4.7	138.8
169	Methyl oleate	14.5	3.9	3.7	340.0
170	2-Methyl-1-propanol	15.1	5.7	15.9	92.8
171	Methyl-2-pyrrolidone[a]	18.0	12.3	7.2	96.5
172	Methyl salicylate	18.1	8.0	13.9	129.6
173	Morpholine	18.8	4.9	9.2	87.1
174	Naphtha.high-flash	17.9	0.7	1.8	181.8
175	Naphthalene	19.2	2.0	5.9	111.5
176	Nitrobenzene[a]	20.0	8.6	4.1	102.7
177	Nitroethane[a]	16.0	15.5	4.5	71.5
178	Nitromethane[a]	15.8	18.8	5.1	54.3
179	1-Nitropropane	16.6	12.3	5.5	88.4
180	2-Nitropropane[a]	16.2	12.1	4.1	86.9
181	Nonane	15.7	0.0	0.0	179.7
182	Nonyl phenol	16.5	4.1	9.2	231.0
183	Nonyl phenoxy ethanol	16.7	10.2	8.4	275.0
184	Octane	15.5	0.0	0.0	163.5
185	Octanoic acid	15.1	3.3	8.2	159.0
186	1-Octanol	16.0	5.0	11.9	157.7
187	2-Octanol	16.1	4.9	11.0	159.1
188	Oleic acid	16.0	28	6.2	317.0
189	Oleyl alcohol	16.0	2.6	8.0	316.0
190	Pentane	14.5	0.0	0.0	116.2
191	2.4-Pentanedione	17.1	9.0	4.1	103.1
192	1-Pentanol	15.9	5.9	13.9	108.6
193	Perfluoro(dimethylcyclohexane)	12.4	0.0	0.0	217.4
194	Perfluoroheptane	12.0	0.0	0.0	227.3
195	Perfluoromethylcyclohexane	12.4	0.0	0.0	196.0
196	Phenol	18.0	5.9	14.9	87.5
197	Bis-(m-phenoxyphenyl) ether	19.6	3.1	5.1	373.0
198	1-Propanol	16.0	6.8	17.4	75.2
199	2-Propanol	15.8	6.1	16.4	76.8
200	Propionitrile	15.3	14.3	5.5	70.9
201	Propylamine	16.9	4.9	8.6	83.0
202	Propyl chloride	16.0	7.8	2.0	88.1
203	Propylene carbonate[a]	20.0	18.0	4.1	85.0
204	Propylene glycol[a]	16.8	9.4	23.3	73.6

TABLE 3—(Continued)

No.	Solvent	Dispersion	Polar	Hydrogen Bonding	Molar Volume
205	Propylene glycol monobutyl ether	15.3	4.5	9.2	132.0
206	Propylene glycol monoethyl ether	15.7	6.5	10.5	115,6
207	Propylene glycol monoisobutyl ether	15.1	4.7	9.8	132.2
208	Propylene glycol monomethyl ether	15.6	6.3	11.6	93.8
209	Propylene glycol monophenyl ether	17.4	5.3	11.5	143.2
210	Propylene glycol monopropyl ether	15.8	7.0	9.2	130.3
211	Pyridine	19.0	8.8	5.9	80.9
212	2-Pyrolidone	19.4	17.4	11.3	76.4
213	Quinoline	19.4	5.6	5.7	118.0
214	Stearic acid	16.3	3.3	5.5	326.0
215	Styrene	18.6	1.0	4.1	115.6
216	Succinic anhydride	18.6	19.2	16.6	66.8
217	1.1.2.2-Tetrabromoethane	22.6	5.1	8.2	116.8
218	1.1.2.2-Tetrachloroethane	18.8	5.1	9.4	105.2
219	Tetrachloroethylene	18.3	5.7	0.0	101.2
220	Tetraethylorthosilicate	13.9	4.3	0.6	224.0
221	Tetrahydrofuran[a]	16.8	5.7	8.0	81.7
222	Tetrahydronaphthalene	19.6	2.0	2.9	136.0
223	Tetramethylurea	16.7	8.2	11.0	120.4
224	Toluene[a]	18.0	1.4	2.0	106.8
225	Tributyl phosphate	16.3	6.3	4.3	345.0
226	Trichlorobiphenyl	19.2	5.3	4.1	187.0
227	1.1.1-Trichloroethane	16.8	4.3	2.0	99.3
228	Trichloroethylene[a]	18.0	3.1	5.3	90.2
229	Trichlorofluoromethane	15.3	2.0	0.0	92.8
230	1.1.2-Trichlorotrifluoroethane	14.7	1.6	0.0	119.2
231	Tricresyl phosphate	19.0	12.3	4.5	316.0
232	Tridecyl alcohol	16.2	3.1	9.0	242.0
233	Triethanolamine	17.3	22.4	23.3	133.2
234	Triethylamine	17.8	0.4	1.0	138.6
235	Triethyleneglycol	16.0	12.5	18.6	114.0
236	Triethylene glycol monooleyl ether	16.0	3.1	8.4	418.5
237	Triethylphosphate	16.7	11.4	9.2	171.0
238	Trifluoroacetic acid	15.6	9.9	11.6	74.2
239	Trimethylbenzene	18.0	1.0	1.0	137.3
240	2.2.2,4-Trimethylpentane	14.1	0.0	0.0	166.1
241	2.2.4-Trimethyl-1.3-pentanediol M.I. butyral	15.1	6.1	9.8	227.4
242	Trimethyl phosphate	16.7	15.9	10.2	115.8
243	Water	15.5	16.0	42.3	18.0
244	Xylene	17.6	1.0	3.1	123.3
245	o-xylene	17.8	1.0	3.1	121.2

[a] Indicates use in author's standard set of test solvents.

given concentration, usually 10 % by weight, in a selection of solvents intended to maximize information regarding all types of interaction. Whenever possible, the author uses a set of parameters indicated with an "[a]" in Table 3. The "yes" or "no" solubility data can be plotted by hand or processed by computer to yield a "spherical" characterization as described above. Teas [52] has developed a triangular plotting technique, which helps visualization of three parameters on a plain sheet of paper. Examples are found in Refs. [9,10] as well.

Swelling, weight gain, solvent resistance, and surface attack have also been used as a primary data to characterize polymers. The weighted-averaging of the respective Hansen solubility parameters for the test liquids should be done with caution. Many polymers have polar and hydrogen bonding parameters higher than any liquids, for which

TABLE 4—Solubility parameters for polymers

	D	P	H	R
Cellulose acetobutyrate				
Cell it BP-300[a]	16.6	12.0	6.7	10.2
Cellulose acetate				
Cellidora A[a]	18.2	12.4	10.8	7.4
Cethyl cellulose				
Ethocel HE 10 ind[b]	17.9	4.3	3.9	5.9
Ethocel Std 20 ind[b]	20.1	6.9	5.9	9.9
Epoxy				
Araldite DY 025	14.0	7.4	9.4	13.7
Epikote 828	21.3	14.2	6.1	17.7
Epikote 1001	18.1	11.4	9.0	9.1
Epikote 1004	17.4	10.5	9.0	7.9
Epikote 1007	21.0	11.1	13.4	11.7
Epikote 1009	18.9	9.6	10.7	7.8
Phenoxy PKHH	23.4	7.2	14.8	14.9
Epoxy curing agents				
Versamid 100	23.8	5.3	16.2	16.1
Versamid 115	20.3	6.6	14.1	9.6
Versamid 125	24.9	3.1	18.7	20.3
Versamid 140	26.9	2.4	18.5	24.0
Polyurethane				
Desmophen 651	17.7	10.6	11.6	9.5
Desmophen 800	19.1	12.2	9.9	8.0
Desmophen 850	21.1	14.6	12.0	16.2
Desmophen 1100	16.0	13.1	9.2	11.4
Desmophen 1150	20.6	7.8	11.6	13.1
Desmophen 1200	19.4	7.4	6.0	9.8
Desmophen 1700	17.9	9.6	5.9	8.2
Desmolac 4200	18.7	9.6	9.9	8.2
Macrynal SM 510N	19.9	8.1	6.0	9.8
Phenolic resins				
Super Beckacite 1001[a]	22.7	6.4	8.2	19.4
Phenodur 373 U[a]	19.3	11.4	14.3	12.4
Hydrocarbon resins				
Piccolyte S-100[a]	16.14	0.4	2.8	8.4
Piccopale 110[a]	17.2	1.2	3.5	6.4
Piccoumarone 450 L[a]	19.0	5.4	5.6	9.4
Styrene-butadiene elastomer (SBR)				
Polysar 5630[a]	17.2	3.3	2.6	6.4

TABLE 4—(Continued)

	D	P	H	R
Acrylonitrile-butadiene elastomer				
Hycar 1052[a]	18.2	8.6	4.1	9.4
Polybutadiene				
Buna Hüls B-10[a]	17.1	2.2	3.3	6.4
Polyisoprene				
Cariflex IR 305[a]	16.2	1.4	–0.8	9.4
Polyisobutylene				
Lutonal IC/1203[a]	14.2	2.5	4.6	12.4
Lutonal I60	16.9	2.5	4.0	7.2
Polyvinylbutyl ether	17.4	4.3	8.4	7.4
Lignin powder[a]	19.7	14.3	14.7	11.4
Modaflow Multiflow	16.1	3.7	7.9	8.9
Polyvinylchloride				
Vipla KR[a]	17.2	7.4	8.2	3.4
Chlorparaffin				
Cereclor 70	20.0	8.3	6.8	9.8
Chlorparaffin 40	17.0	7.6	7.9	11.9
Chlorinated rubber				
Pergut S 5	17.4	9.5	3.8	10.0
Allopren R 10	17.4	4.3	3.9	6.1
Chlorinated polypropylene				
Parlon P 10[a]	19.8	6.2	5.3	10.4
Chlorosulfonated polyethylene				
Hypalon 20[b]	18.1	3.4	4.9	3.6
Hypalon 30[b]	18.2	4.7	2.0	5.0
Cyclized rubber				
Alpex[b]	19.9	0.0	0.0	9.4
Nitrocellulose				
1/2-sec-Nitrocellulose H 23[a]	15.1	14.4	8.6	11.2
Rosin derivatives				
Cellolyn 102[a]	21.2	0.9	8.3	15.4
Pentalyn 255[a]	17.2	9.2	14.0	10.4
Pentalyn 830[a]	19.6	5.7	10.7	11.4
Ester Gum 8L[a]	19.2	4.6	7.6	10.4
Polyamide				
Versamid 930[a]	17.0	–1.9	14.9	7.4
Versamid 961	18.9	9.6	11.1	6.2
Versamid 965	20.4	0.4	14.0	12.9
Isocyanate				
Desmodur L	17.5	11.3	5.9	8.5
Demodur N[a]	17.6	10.0	3.7	9.3
Suprasec F-5100[a]	19.7	12.9	12.8	11.4

TABLE 4—(Continued)

	D	P	H	R
Polyvinylbutyral				
Mowithal B 30 H	18.6	12.9	10.3	8.3
Mowithal B 60 H	20.2	11.2	13.2	11.2
Butvar B 76[a]	18.2	4.3	12.7	10.4
Polyacrylate				
Lucite 2042[a]	17.2	9.4	3.9	10.4
Lucite 2044	16.2	6.8	5.7	9.1
Plexigum MB 319	18.6	10.8	4.1	11.5
Plexigum M 527	18.4	9.4	6.5	10.7
PMMA[a]	18.2	10.3	7.7	8.4
Polyvinylacetate				
Mowilith 50[a]	20.5	11.0	9.4	13.4
Polystyrene				
Polystyren LG[a]	20.8	5.6	4.2	12.4
Vinylchloride/copolymers				
Laroflex MP 45	18.4	8.4	5.8	9.0
Vilit MB 30	20.0	8.3	6.7	9.4
Vilit MC 31	20.0	8.3	6.7	9.4
Vilit MC 39	18.4	7.6	6.7	6.8
Vinylite VAGD	17.1	10.4	6.5	7.5
Vinylite VAGH	16.5	10.9	6.4	7.7
Vinylite VMCA	17.7	11.1	6.9	8.7
Vinylite VMCC	17.6	11.1	6.8	8.8
Vinylite VMCH	17.6	11.1	6.4	8.6
Vinylite VYHH	17.4	10.2	5.9	7.8
Vinylite VYLF	18.1	10.3	4.2	8.3
Alkyds and polyesters				
Alftalat AC 366	18.6	10.0	5.0	10.4
Alftalat AM 756	23.0	2.2	4.2	16.9
Alftalat AN 896	22.9	15.2	7.6	18.1
Alftalat AN 950	22.6	13.8	8.1	17.1
Alftalat AT 316	20.5	9.3	9.1	12.4
Alftalat AT 576	19.2	5.3	6.3	11.9
Alkydal F 261 HS	23.6	1.0	7.6	19.0
Alkydal F 41	20.6	4.6	5.5	12.6
Duroftal T 354	17.3	4.2	7.9	9.3
Dynapol L 812	22.6	13.1	5.8	16.8
Dynapol L 850	20.0	6.2	7.0	9.5
Plexal C-34[a]	18.1	9.0	4.8	10.4
Soalkyd 1935-EGAX	18.0	11.6	8.5	9.0
Vesturit BL 908	18.8	12.0	6.0	11.5
Vesturit BL 915	17.7	13.0	7.6	11.5

TABLE 4—(Continued)

	D	P	H	R
Amino resins				
BE 370	20.7	6.1	12.7	14.8
Beetle 681	22.2	–0.4	10.1	18.4
Cymel 300[a]	19.9	8.3	10.4	14.4
Cymel 325	25.5	15.2	9.5	22.2
Dynomin MM 9	18.8	14.0	12.3	10.5
Dynomin UM 15	19.9	15.8	13.4	11.7
Soamin M 60	15.9	8.1	6.5	10.6
Synresen A 560	22.1	5.0	11.3	15.5
Plastopal H[a]	20.3	8.1	14.6	12.4
Uformite MX-61	22.7	2.8	5.4	16.2
Acrylate resins				
Uracron 15	19.2	7.7	5.7	10.6
Paraloid P 400	19.2	9.6	9.3	12.2
Paraloid P 410	19.6	9.1	6.8	12.2
Paraloid experimental resin QR 954	18.4	9.8	10.0	12.4
Silicone resins				
Baysilon UD 125	19.4	9.9	10.1	6.9
Wacker 190 F	16.6	1.9	8.0	8.0
Additional Special Data				
DEN 438 (Dow epoxy novolak)	20.3	15.4	5.3	15.1
DEN 444 (Dow epoxy novolak)	19.5	11.6	9.3	10.0
Zink silicate (CR)-Chemical resistance	23.5	17.5	16.8	15.6
2-Comp epoxy (CR)—Chemical resistance	18.4	9.4	10.1	7.0
Polyvinylidine fluoride	17.0	12.1	10.2	4.1
Coal tar pitch	18.7	7.5	8.9	5.8
PA6 polyamide chemical resistance	17.0	3.4	10.6	5.1
PA66 polyamide solubility	17.4	9.8	14.6	5.1
PA11 polyamide chemical resistance	17.0	4.4	10.6	5.1
Cellophane swelling	16.1	18.5	14.5	9.3
EVOH—solubility (ethylenevinyl alcohol)	20.5	10.5	12.3	7.3

Note: D = dispersion; P = permanent dipoles; H = hydrogen bonding; R = interation radius.

[a] Taken from Hansen, C. M., "Solubility in the Coatings Industry," *Fårg och Lack,* Vol. 17, No. 4, 1971, pp. 69–77.

[b] Calculated from solubility data in *Polymer Handbook,* 2nd Ed., John Wiley & Sons Inc., New York, 1975.

TABLE 5—List of suppliers and trademarks for paint binders and polymers

Suppliers	Trademarks
Bayer (D)	Cellit, Desmophen, Desmolac, Pergut, Cellidora, Desmodur, Baysilon Alkydal
Hercules (USA)	Piccolyte, Cellolyn, Pentalyn, Ester Gum, Parlon
Ciba-Geigy	Araldite
Shell (D)	Epikote, Cariflex
Union Carbide (USA)	Vinylite, Phenoxy
Hoechst (D)	Macrynal, Phenodur, Alpex, Mowithal, Alftalat, Mowilith
Reichhold (CH)	Super Beckasite, Uformite
Polymer Corp. (CAN)	Polysar
Goodrich (USA)	Hycar
Huls (D)	Vilit, Vesturit, Buna Huls
BASF (D)	Lutonal, Laroflex, Plastopal, Polystyren
Monsanto (USA)	Modaflow, Multiflow, Butvar
Montecatini Edison (I)	Vipla
ICI (GB)	Cereclor, Allopren, Suprasec
Du Pont (USA)	Lucite
Hagedorn (D)	1/2-sec. nitrocellulose H 23
Röhm (D)	Plexigum
Rohm and Haas (USA)	Paraloid
Dynamit Nobel (D)	Dynapol
SOAB (S)	Soamin
BIP Chemicals (GB)	Beetle
Dyno Cyanamid (N)	Dynomin
DSM Resins (S)	Uracron
Reichhold Chemie (CH)	Super Beckasite, Uformite
Wacker (D)	Wacker
Dow Chemical (CH)	Ethocel
Cray Valley Prod. (GB)	Versamid
W. Biesterfeld (D)	Chlorparaffin
Synres (NL)	Synresen
American Cyanamide (USA)	Cymel
Polyplex (DK)	Plexal
Pennsylvania Industrial Chemical Corp. (USA)	Piccopal, Piccoumarone

reason any average will be too low. This is discussed in more detail in Refs. [38,39].

APPLICATIONS

There are many applications documented in the literature where solubility parameters have aided in selection of solvents, understanding and controlling processes, and, in general, offered guidance where affinities among materials are of prime importance. In all of the examples below the technical aspects only are discussed. It is clear that worker safety and environmental impact must also be considered in any solvent usage. Discussion of these aspects is beyond the scope of this report.

To find the optimum solvent for a polymer using solubility parameters, it is most desirable to have the solubility parameters for the polymer. Matching the parameters of an already existing solvent or combination of solvents can be done, but does not necessarily optimize the new situation. The optimum depends on what is desired of the system. A solvent with highest possible affinity for the polymer is both expensive and probably not necessary.

Most coatings applications involve solvents safely within the solubility limit with a maximum of cheaper hydrocarbon solvent. Some safety is advised because temperature changes, potential variations in production, etc., can lead to a situation where solvent quality changes in an adverse manner. Balance of solvent quality on evaporation of mixed solvents is also necessary. Here again computer approaches are possible.

An oxygenated solvent frequently added to hydrocarbon solvent and that has been cost effective in increasing the very important hydrogen bonding solubility parameters has been *n*-butanol. The mixture of equal parts xylene and *n*-butanol can be used in conjunction with many polymers, but a third solvent, such as a ketone or ester, is often included in small amounts to increase the polar parameter/solvency of the mixture. Glycol ethers can also be added to hydrocarbon solvents with advantage, and the polar and hydrogen bonding parameters are higher than had *n*-butanol been added to the same concentration. There are many possibilities, and a solubility parameter approach is particularly valuable in quickly limiting the number of candidates.

Coalescing solvents in water-reducible coatings are often those with somewhat higher hydrogen bonding parameters than the polymer, which also means they are water soluble or have considerable water solubility. The distribution between the water phase and the dispersed polymer phase depends on the relative affinities for water and the polymer. Solvents that are not particularly water soluble will preferentially be found in the polymer phase. Such coalescing solvents may be preferred for applications to porous substrates, making certain they are where they are needed. Otherwise a water-soluble coalescing solvent would tend to follow the aqueous phase penetrating the substrate and not be available to do its job in the film itself.

When water evaporates, the solvent must dissolve to some extent in the polymer to promote coalescence. This can be determined and adjusted by either increasing or decreasing the affinity for the polymer.

Amines are frequently added in water-reducible coatings to neutralize acid groups in polymers, thus providing a water-solubilizing amine salt. Amine in excess of that required

for total neutralization acts like a solvent. Such amine salts have been characterized separately to demonstrate that they have higher solubility parameters than either (acetic) acid or organic bases [53]. These salts are hydrophilic and have very little affinity for coatings polymers, which means they are to be found in a stabilizing role in interfaces in the aqueous phase, still being attached to the polymer. Electrostatic repulsion contributes to stability as well.

Surface active agents, whether nonionic or ionic, are also to be found where the affinities of the respective parts of their molecules dictate their placement. The hydrophilic end with a high hydrogen bonding parameter will be in the aqueous phase, and the hydrophobic end will seek out an environment where energy differences are lowest.

Increases in temperature lead to lower hydrogen bonding parameters, especially. For this reason, solvents with high hydrogen bonding parameters, such as glycols, glycol ethers, and alcohols, become better solvents for most polymers at higher temperatures. This can markedly affect hot-room stability in water-reducible coatings, for example, since more of the solvent will partition to the polymer phase, which swells, becomes more fluid, and has altered affinities for stabilizing surface active agents, for example. They may dissolve too readily in the dispersed polymer. Carefully controlled, these temperature effects are an advantage in water-reducible, oven-cured coatings, leading to higher film integrity.

A simple approach to many practical problems is to make a two-dimensional plot of polar versus hydrogen bonding parameters with a circle (or estimated circle) for the polymer in question. One can plot the points for potential solvents and quickly arrive at a starting composition for an experiment. This can subsequently be adjusted if necessary. It should also be kept in mind that cyclic solvents generally have higher nonpolar parameters than aliphatic solvents.

A long list of applications, in coatings and elsewhere, was provided as early as 1975 in a review article by Barton [54]. Many applications are given in Table 6 and in the present discussion to give an idea of what can be studied systematically using this concept. More recent references and varied applications can be found in Refs. [9,10,38,39].

Beerbower [55] has given many of the more theoretical applications for solubility parameters including correlations of the Rehbinder effect of crushing strength of aluminum oxide under various liquids, the work of adhesion for liquids on mercury, the Joffe effect of the consequences of immersion in various liquids on the fracture strength of soda-lime glass, and correlations of friction on polyethylene treated with fuming sulfuric acid $H_2SO_4 + SO_3$ [55].

Direct and practical applications of solubility parameters in coatings have included their use as an aid in the selection of solvents and solvent blends for many years. Most solvent suppliers and frequent solvent users have computer programs for this purpose, although as noted above, such programs are not an absolute necessity. Reformulation to meet environmental requirements is especially important in this respect since one can quickly evaluate which of the alternatives is most likely to meet the given requirements. This includes reducing amounts of volatile organic solvent, worker safety, or other environmental concern. Optimum formulation in such cases often involves mixtures.

The main thing to remember in solvent selection using solubility parameters is that the resultant values for mixtures can be estimated from volume fraction averages for each solubility parameter component. Solvent quality can be adjusted by the RED number concept or graphically as described above.

A computer search for nearest neighbors for a given single solvent has been used many times to locate alternates. A similar application is to predict which other solvents will probably be aggressive to a chemically resistant coating where very limited data have indicated a single solvent or two are somewhat aggressive. A nearest neighbor search involves calculation of the quantity R_s for a whole

TABLE 6—Examples of the use of the solubility parameter

Activity coefficients
Aerosol formulation
Biological materials and compatibility
Chromatography
Coal solvent extraction
Compressed gases
Cosmetics
Cryogenic solvents
Dispersion
Dyes
Emulsions
Gas-Liquid solubility
Grease removal
Membrane permeability and swelling
Paint film appearance
Pharmaceutical
Pigments
Plasticizers, polymers, resins
Plasticization
Polymer and plasticizer compatibility
Printing ink
Reaction rate of radical polymerization
Resistance of plastics to solvents
Rubber blends
Solid surface characterization—organic and inorganic
Solid surface modification
Solvent extraction
Solvent formulation, environmental aspects
Surface tension
Urea-water solutions
Vaporization of plasticizers
Viscosity of polymer systems
Water-based polymer systems, coalescents

database, for example, and then arranging the printout in RED number order with the potentially most aggressive at the top of the list. Solvents with RED less than 1.0 are "good" and easily recognized.

In many cases a marginal solvent is desired, in which case RED numbers just under 1.0 will be sought. Marginal solvent quality will ensure that polymer adsorbed onto pigment surfaces has little reason to dissolve away from that surface where it is desired as a stabilizing factor in the product. The solvent in this case should have a RED number for the pigment surface greater than 1.0 to aid in the planned affinity approach to pigment dispersion stability. A sketch of the optimum relations is given in Fig. 4, where the marginal solvent is Number 1. Solvent 2 would probably be too expensive and, in addition, will probably dissolve the polymer too well. In special applications this extended polymer chain configuration is desirable, but a solid anchor to the pigment surface is required. A good anchor has high affinity for the pigment surface and marginal or no affinity for the solvent. Solvent 3 would adsorb onto the pigment surface preferentially, and pigment dispersion stability will be poor. Pigments have been characterized by long-time suspension studies where some solvents will suspend the fines for days, months, or years, while others of similar viscosity yield rapid settling. The suspending solvents are the good ones and can be used to define a sphere for surface wetting/adsorption. Details of such characterizations are given in Refs. [38,39].

In other cases, better matches between solvent and polymer solubility parameters are required. This is true when two polymers are mixed and one of them precipitates. This is most likely the polymer with larger molecular weight, and it must be dissolved better. Lower RED numbers with respect to this polymer are desired, while still maintaining affinity for the other polymer. Miscible blends of two polymers have been found using a solvent mixture composed exclusively of nonsolvents. This is demonstrated schematically in Fig. 5, where it can be seen that different percentage blends of solvents 1 and 2 will have different relative affinities for the polymers. No other alternative theory of polymer solution thermodynamics can duplicate this predictive ability. Polymer miscibility is enhanced by larger overlapping solubility regions for the polymers as sketched in Fig. 6. Polymers A and B should be compatible, while C will not be. Such a systematic analysis allows modification of a given polymer to provide more overlap and enhanced compatibility. The advantages of a copolymer containing

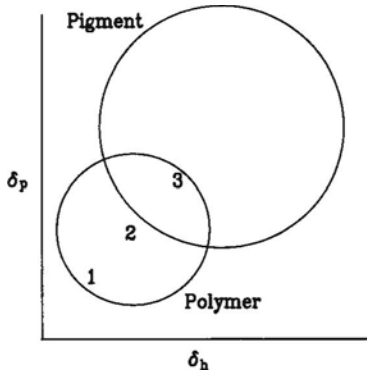

Fig. 4—Solubility parameter relations for optimum pigment dispersion stability.

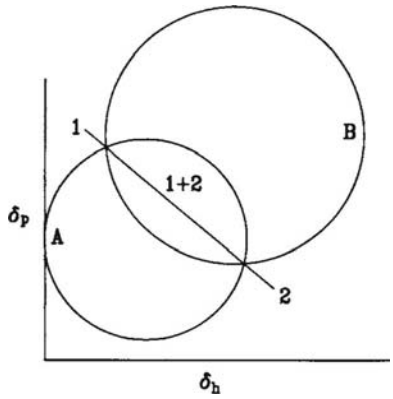

Fig. 5—Solubility relations for polymer mixtures can be quickly evaluated to ensure solution stability. Even mixtures of nonsolvents can be systematically used to regulate solution behavior.

the monomers of A or B and C should also be evident. Such a copolymer will essentially couple the system together.

Van Dyk et al. [56] have correlated the inherent viscosity of polymer solutions with the solubility parameter. This is interesting in that the solubility parameter is a thermodynamic consideration, while the viscosity is a kinetic phenomenon. Solvents with higher affinities give greater polymer chain extension in solution, and the inherent viscosity—the solution viscosity divided by the solvent viscosity at polymer concentrations approaching zero—is an expression reflecting polymer chain extension in solution. Higher intrinsic viscosities were found for solvents with solubility parameters nearest the polymer solubility parameters. As stated above, this approach may not always be advisable since many polymers have polar and hydrogen bonding parameters higher than the test liquids that have been used.

The use of supercritical gases as solvents has become more common in recent years. Space limitations prevent going into the details of these developments. It should be noted, however, that when a gas is compressed, its cohesive energy density increases. This means that nonpolar gases with their low nonpolar solubility parameters can begin to dissolve given organic materials, which otherwise have solubility parameters that are too high. Increasing

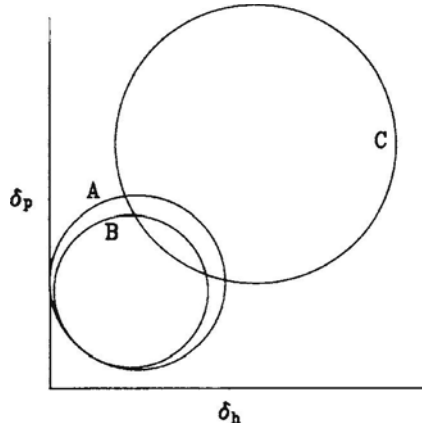

Fig. 6—Schematic representation showing expected miscibility of polymers A and B with each other but not with polymer C.

the nonpolar solubility parameter of the gas by increasing the pressure causes a closer match with the corresponding parameter for potential solutes. Similar behavior is found for polar gases such as carbon dioxide. The prevailing pressure and temperature conditions determine its cohesive energy density and changes in pressure or temperature change solubility relations for this reason. Whereas nonpolar gases are most suitably used for relatively nonpolar solutes, carbon dioxide—and in principle other polar gases—are most suitably used in connection with more polar solutes. The solubility parameters for carbon dioxide have been reported [57] based on the room temperature solubility of the gas in different liquids (δ_d, δ_p, δ_h equal to 15.3, 6.9, 4.1). These parameters resemble those of a higher ketone, but are subject to revision when larger data sets are processed. The δ_d, δ_p, δ_h parameters for carbon dioxide have been revised to 15.7, 6.3, and 5.7 based on a correlation with a perfect data fit and R_0 equal to only 3.3, using a much larger data set collected by Williams and reported in Chapter 10 of Ref. [39]. The HSP are also reported in this reference at higher temperatures and pressures. The δ_p parameter experimentally confirms the presence of sizeable values for compounds with zero dipole moments, and the δ_h parameter emphasizes the need to use terminology electron exchange for this parameter, traditionally called the hydrogen bonding parameter, since there is no hydrogen atom. Chapter 3 in Ref. [39] has a plot of the HSP for water at temperatures above the normal boiling point.

Pigment wetting/suspension characteristics have been presented earlier [10,14,16]. Mixtures of nonsuspending solvents could also be found which, when admixed, provided predictably higher affinity and suspension of pigment particles for prolonged periods of time. An exceptionally clear demonstration of pigment adsorption properties is given in Ref. [10] where a triangular plot of the three partial parameters shows the clearly different adsorption properties of untreated zinc oxide powder and organic phosphate surface-treated zinc oxide powder. This triangular approach to plotting was developed by Teas [52].

Other surface characterizations have also been given for surfaces such as coatings and metal substrates [23,24]. These characterizations have been of the type sketched in Fig. 7. Such cohesive energy plots can lead to systematic modifications of systems to improve adhesion. It might be added parenthetically that equal information can be obtained from plots of the cosine of the contact angle versus the solubility parameter as for plots of these same data versus liquid surface tension [23]. The energy information obtained in these types of studies, the critical surface tension, corresponds to the condition of RED equal to 1.0, with a solubility parameter approach, that is, marginal affinity.

The list of applications has recently been expanded to include correlations of the breakthrough times for common types of chemical protective clothing such as butyl rubber, nitrile rubber, plasticized polyvinyl chloride, neoprene, Viton rubber, polyvinyl alcohol, etc. [58]. Fig. 8 shows the importance of combined use of the RED number and molecular volume in correlating 3 h breakthrough times for a fluoropolymer chemical protective product [59]. Monomers with terminal double bonds diffuse more rapidly than comparisons with non-double-bonded molecules of similar size and solubility parameter would have predicted. The smaller cross section at the end of the molecule reminds

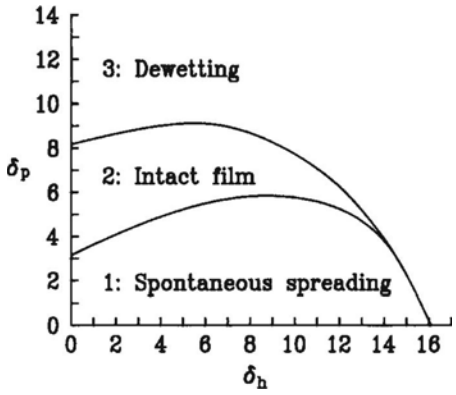

Fig. 7—Schematic diagrams showing surface energy/contact angle characterizations using the Hansen solubility parameters (cohesion energy parameters).

one of a nail, and the preferred direction and relative rapidity of transport become easily understandable.

In addition it should be noted that even biological materials, some of which have interest for coatings applications and use, have been assigned Hansen solubility parameters [60]. These include keratin (which relates to skin permeation), fat, sucrose, blood serum and zein (which are proteins), urea, lignin (wood penetration), and chlorophyll (which closely resembles lignin) [57,60]. The characterization of other biological materials is also possible, of course, with the assignment of HSP to DNA being one of the most recent results [39].

Even inorganic salts have been characterized by solubility parameters [61]. The practice of dissolving polymers in solutions of organic liquids and inorganic salts can thus be explained by the solubility parameter. A solubility parameter correlation of the chemical resistance of an inorganic zinc silicate coating is reported in Table 4. Finally, it might be noted that Hildebrand presented a chapter on the solubility parameters of metals [1]. Unfortunately, we do not often coat metal, but rather metal oxides, for which no solubility parameter work has been reported.

Examples in addition to the above are discussed in a larger context in Refs. [38,39]. The material in the following section has not been discussed in Ref. [38], but rather in Refs. [39,62]. Inclusion here is justified by the presence of solvents and additives in coatings, which may produce these catastrophic effects in rigid polymeric systems.

HANSEN SOLUBILITY PARAMETERS AND ENVIRONMENTAL STRESS CRACKING (ESC)

The Hansen solubility parameter approach allows systematic analysis of environmental stress cracking situations [62]. One can locate those liquids that are most likely to cause the problem based on limited experimental data for a reasonable number of different solvents. The state of the stress in a polymer is clearly important. Tensile stress is required for the phenomena to occur. Higher stress levels lead more easily to cracking. Test solvents to evaluate the stress level present in given polymers can be systematically located. However, it is clearly not just solubility relations that control the phenomena. The size and shape of the environmental challenge chemical are also important. These relate to the rate of uptake (diffusion coefficient). These factors collectively control how rapidly a challenge

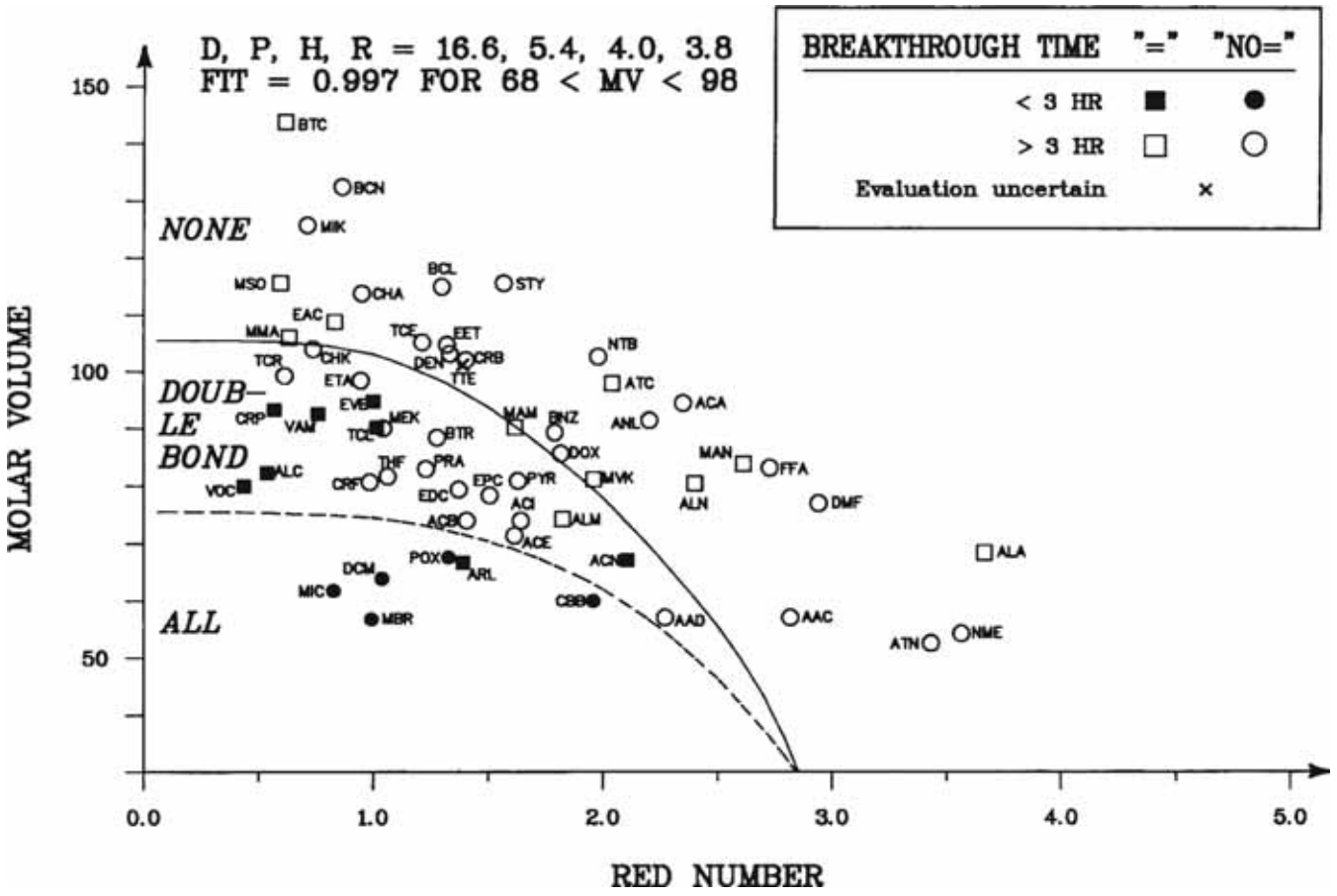

Fig. 8—Effects of molecular size (molar volume) and affinity (RED number) on the breakthrough time of Challenge 5100 [59].

chemical can absorb into the surface of a polymeric material, this being a requirement for the cracking to occur. The absorbed chemical changes the local stress-bearing properties, and cracking can occur in unfavorable situations. The times required may vary from seconds to years, depending on the situation. Stress relaxation caused by the plasticizing effect of absorbed liquid can reduce the risk of ESC, but can cause other problems, such as excessive softening of the polymer. ESC phenomena in polymers are not fully understood, but progress toward this goal is being made as discussed in the following.

In general, those solvents causing cracking of a given polymer will be taken up in lesser amounts at equilibrium absorption than those amounts which will fully dissolve the polymer. In terms of the Hansen approach, this means that there will be the usual spherical characterization for polymer solubility. Essentially concentric to this, but with a larger radius, is another spherical characterization encompassing both the true solvents at RED numbers less than about 0.8, and the cracking solvents at RED numbers typically between about 0.8 and 1.0. Fig. 9 shows these relations for a COC type (Cyclo-olefinic Copolymer) polymer. The basis for this correlation was to consider as aggressive (RED < 1) both those solvents that truly dissolve the polymer as well as those that cause cracking. This type of plot can be made for other polymers.

The above discussion is for exposure to a pure liquid. It is also known that aqueous solutions can leave smaller amounts of aggressive chemicals when the water has evaporated. In this case almost any solvent, either good or swelling only, will be a potential problem in this respect. The small amount acts like a concentrated solvent, but only at the surface. Solution can not occur, other than at the

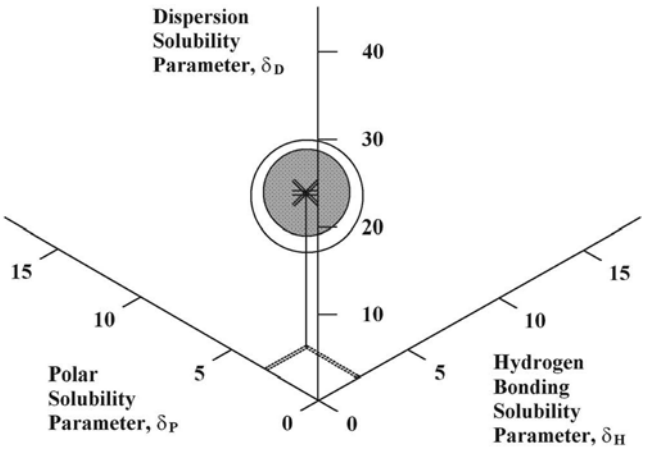

Fig. 9—Hansen solubility parameters correlate both solubility (inner sphere) and solubility plus environmental stress cracking (outer sphere). The liquids that crack the polymer without application of external stress have Hansen solubility parameters placing them in the clear shell in the figure. From Ref. [62]. Reprinted with permission from *Industrial and Engineering Chemistry Research,* Vol. 40, No. 1, 2001, pp. 21–25. Copyright 2001, American Chemical Society.

surface, because of the limited amount of solvent, but the stress situation at the surface is altered unfavorably, thus allowing cracks to form. There are also examples of ESC where there was no measurable weight gain of the liquids causing the failure. Crack initiation by the rotation of segments of polymers at the surface exposed to these liquids is thought to be the reason. The rotation is driven by the HSP of the liquid resembling the HSP of a buried or partially buried polymer segment, thus reducing the free energy of the system by rotation to surroundings of similar (cohesion) energy. Higher energy segments of polymers are most often buried just beneath the surface, if this is possible. The polymer segments in contact with air are most often those of lower energy, again, to keep the free energy at a minimum [39].

CONCLUSIONS

The background and many uses of the solubility parameter concept have been described in detail. Tables of solubility parameters for many liquids and polymers have been presented. Systematic use of solubility, swelling, or permeation data for polymers allows their characterization by these same cohesive energy parameters. Surfaces can also be characterized using these same parameters. This provides data for optimizing solvent selection, improving compatibility, and enhancing pigment dispersion and adhesion. When all of the materials involved in a given product and application can be characterized with the same energy parameters, the possibility exists to predict interactions among them, even in complicated situations. Methods for estimating the three Hansen solubility parameters have been given with as much detail as has been possible to ensure their more uniform use in the future. It has not been possible to deal with all the primarily theoretical problems with the solubility parameter concept. Some of these are dealt with in the literature cited, most notably in Refs. [6,9,10,18,26,38,39].

A simple approach is described to understand affinities in such varied materials as gases, liquids, polymers, biological materials, surfaces, organic and inorganic coatings, inorganic salts, and metals. An appeal made to the scientific community earlier [37] to expand research on this seemingly universal approach appears to have been responded to by Panayiotou in Chapter 3 of Ref. [39]. Statistical thermodynamics calculations of the δ_d, δ_p, and δ_h parameters, starting with the hydrogen bonding parameter, and extending to the other parameters, have shown amazing agreement with the values reported by the author 40 years ago [13–16]. Information related to the Hansen solubility parameters is continually being updated on the website www.hansen-solubility. com.

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Part 9: Films for Testing

39

Cure: The Process and Its Measurement

Thomas J. Miranda[1]

INTRODUCTION

AMONG THE MOST CRITICAL AND OFTEN MIS-understood properties of a coating are cure and the measurement of cure. If ASTM standard technology [1] is examined, one will find no listing for the word "cure." Cure is something that can have different meanings for different people. In the coating and paint field of study, cure is usually thought of as the chemical reaction between functional groups that results in cross-linking of a system by one or more of a variety of schemes including polymerization of monomers, rearrangement, condensation or elimination, reaction with adventitious moisture or oxygen, as well as others. However, the word can be taken to mean much more and should include the drying of a lacquer as when thermoplastic coatings are applied, the solidification and/or crystallization of polyolefins or other hot-melt applied coatings, the drying of latexes or emulsions that can form films through the high-pressure compacting forces of surface tension, as well as of other ways of forming a coherent, useful thin film with good mechanical, electrical, or other properties. This chapter will mainly be concerned with cross-linked systems and cure will be taken to mean reactions that result in a thermoset or network-formed coating [2], unless otherwise indicated.

The desired and often optimum chemical and physical properties of a coating are dependent on proper curing conditions—time, temperature, and humidity. For example, if a thermosetable, acrylic polymer-based lacquer is applied to a substrate and solvent is allowed to evaporate under ambient conditions, the resulting film might have cracks, low gloss, and be hard and brittle. Yet, the same system could result in a coherent, useful film if the solvent were evaporated under controlled temperatures for specific times. The film might still be brittle and have poor chemical resistance, but such factors may not be important in certain instances. However, strength properties will be markedly improved as a cross-linking agent is added, and the system is allowed to react under proper temperature conditions for an appropriate length of time. The resulting coating will be glossy, hard, tough, and chemical resistant. The time and temperature relationship and the interaction of these parameters has been reported by Neag and Prime [3] in the case of powder coating cure.

Concept of Cure

Polymer is a word meaning many (poly) units (mers) wherein the units are monomers or single-unit mers. Thus, polymers are high molecular weight molecules that are comprised of monomers that may be the same or different, though if the monomers comprising the polymer are different, the polymer is referred to as a "copolymer." Polymers are formed by a variety of polymerization mechanisms including addition (such as the polyacrylates, polyvinyls, etc.), cationic (as polyepoxides), condensation (as polyesters), coordination (as polyolefins), ring opening (as Nylon 6 and polylactones), and rearrangement (as polyurethanes).

These compounds known as polymers range from high to low molecular weight in nature. High molecular weight polymers can form coating films with high gloss and good mechanical properties; however, to achieve such useful properties, the applied solids must be low due to the high viscosities involved when such large-size molecules are used. In the coatings arena, usually low molecular weight polymers or oligomers comprising a relatively small number of chain units that either have one or more functional groups or a co-unit that has functional or polyfunctional groups on as many of the oligomer molecules as possible. If used alone, the oligomers would have poor mechanical and chemical properties and would either be sticky masses (glass transition temperature, Tg, below room temperature) or "rock hard" chunks (Tg above room temperature). To transform these oligomers into useful materials with good mechanical and other properties, it is necessary to build or increase molecular weight. This transformation is accomplished by the addition of a cross-linking agent to the coating formulation wherein said compound will react with the functional groups on the oligomers and then *cure* the liquid system into a film comprised of extremely high molecular weight molecules.[2]

It should be clear from the above that thermoplastic coatings are soluble in particular compounds we term "solvents" and, in addition, if heated will liquefy with the viscosity dependent on the molecular weight. In contrast, thermoset coatings are insoluble but will often swell in particular compounds and if heated may soften but will thermally degrade rather than liquefy.

Of course, additives [4] that will markedly improve the path to achieving a coating with designed gloss, good

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[2] The concept of molecular weight becomes lost when one discussed cross-linked systems. Dr. Herman Mark described the "rubber" in an automobile tire after vulcanizing or cross-linking as one gigantic molecule. Although the definition may be a bit ambitious, since defects and the laws of probability exist, it is a good model to keep in mind when thinking about cross-linked chemicals. Thus, a chemical coating can be thought of as a huge molecule with an extremely high molecular weight that is incapable of being dissolved.

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mechanical and chemical properties, as well as rapid cure are very important to the cure process. Accelerators, catalysts, or other additives insure that cure or cross-linking will be effected in an acceptable time. For example, in radiation cure [5], monomeric and/or oligomeric molecules are combined into a very fluid formulation and ultraviolet radiation-activated cationic or free-radical initiator additives known as photoinitiators cause the molecules to react in an extremely rapid manner at coating line speeds of even several hundred feet per minute. When an electron beam is used to effect cure of such systems, photoinitiators are not required, though flow-control additives would be used. With radiation activation, cure is achieved in the "snap of a finger."

When less-energetic reactions than those used in radiation curing are involved, the cure process will be relatively slow, say on the order of minutes at an elevated temperature. Examples of such a cure system might be the acid-catalyzed, aminoplast cross-linking of hydroxyl-functional oligomers to form thermoset films or the controlled evaporation of solvent or other diluent from lacquers or latexes to form thermoplastic films. In the case of powder coatings, the coating material is in a dry form and thermal energy is used to melt the powder particles and time at a temperature is required to allow the particles to flow into a continuous coating. If a cross-linking agent is present in the powder coating, the cure system must be orchestrated in such a manner that liquefaction and flow take place before significant network formation occurs. Very slow reactions occur in thermoset systems that cure by reaction of adventitious oxygen with unsaturation in the oligomeric molecules.

Many details regarding coating film formation [6] and the preparation of films for coating tests [7] can be found elsewhere.

CURING MECHANISMS

Lacquers

Lacquers consist of thermoplastic polymers that are dissolved in a solvent. When the coating is applied, the solvent evaporates under controlled conditions and a thermoplastic film is formed. This is the type coating used in certain high quality furniture finishes. A number of years ago, many automobiles were coated in this manner, but today such coatings are thermoset in nature.

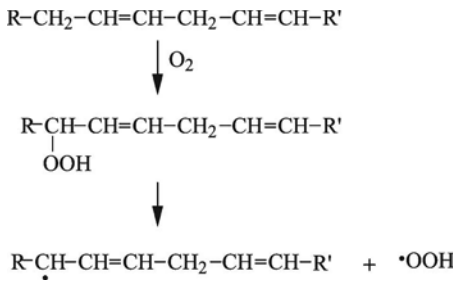
Emulsions and Latexes

Another means of forming a thermoplastic film is film formation from an aqueous-based emulsion or latex. In this instance, a polymer such as a vinyl acetate-acrylic copolymer latex is formulated with colorants and additives, cast, and the water carrier is evaporated with a coherent film resulting. In such systems, the water is not a solvent but a dispersing medium. Microscopically, the polymer appears as tiny ball bearings suspended in water with surface active agents present to keep the polymer particles dispersed and free from settling. As the water evaporates, hydrodynamic pressure causes the small spheres to crowd closer and closer until capillary action forces the particles to fuse and form a continuous film. If the polymer is too hard in nature, a poorly adherent, brittle film is formed. Often, this is the reason paint manufacturers recommend that water-based latex paints not be applied at low temperatures. To facilitate fusion and continuity, small amounts of a coalescing solvent such as diethylene glycol monobutyl ether are added to decrease the glass transition temperature. As described, the curing results in a thermoplastic coating. If desired, these systems can be made into thermoset films by incorporating a functional group into the latex molecules and employing a cross-linking agent.

Oxidative Cross-linking

Oxidative cross-linking takes place in systems that contain reactive, unsaturated double bonds as are found in unsaturated fatty acids, drying oils such as linseed, soy, tung, and tall oil (see Chapters 4 and 5 for a discussion of drying oils and driers), as well as certain alkyds and oleoresinous varnishes. This vehicle is formulated with a suitable solvent, a drier (often termed a "siccative") such as cobalt, manganese, or zirconium salts in the form of naphthenates, octanoates, or the like, and other ingredients. Curing takes place through adventitious oxygen interacting with the molecular unsaturation.

The coating film is applied by brushing, spraying, or other means and solvent is removed by evaporation. The resultant liquid or tacky film then undergoes an induction period in which natural antioxidants inherent in the starting materials are overcome as oxygen is absorbed from the atmosphere. This is followed by hydroperoxide formation on carbon atoms alpha to double bonds. This is followed by peroxide decomposition and formation of free radicals that initiate cross-link formation at the unsaturated sites with the result formation of a cross-linked thermoset film [8,9]. A simplified reaction scheme in which R and R′ are alkyl groups is shown below [10].



The starting materials are converted into polymer according to the following scheme:

$$\text{Initiation} \quad RH + O_2 \rightarrow R\cdot + \cdot OOH$$

$$\text{Propagation} \quad R\cdot + O_2 \rightarrow ROO\cdot$$

$$ROO\cdot + RH \rightarrow ROOH + R\cdot$$

$$\text{Termination} \quad ROO\cdot + R\cdot \rightarrow ROOR$$

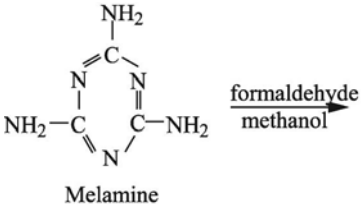
$$ROO\cdot + ROO\cdot \rightarrow ROOR + O_2$$

$$R\cdot + R\cdot \rightarrow R-R$$

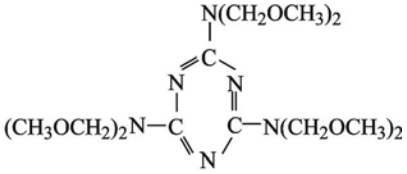
Termination by coupling increases the molecular size—say, doubling if the joined chains are the same in size—and eventually a network or cross-linked system is formed. If properly formulated, the final product has the desired chemical and physical characteristics.

Reactive Cross-linking

In this type of cure system, a reactive intermediate is added to a functionalized polymer or oligomer and a further chemical reaction is initiated by heating alone or in the presence of a catalyst or by some other means. The functionality on the polymer molecules often is hydroxy in nature. The reactive intermediate is often an amino compound such as hexa(methoxymethyl)melamine.



Melamine



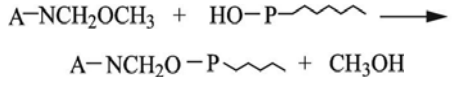
Hexa(methoxymethyl)melamine

MELAMINE

Melamine-formaldehyde condensates are often used to cure a reactive polymer. Melamine is 2,4,6-triamino-1,3,5-triazine, a compound prepared by condensing three molecules of dicyandiamide. Melamine, in turn, can be condensed with up to six molecules of formaldehyde and 6 molecules of methanol to form hexa(methoxymethyl) melamine (HMMA) (see Chapter 8) or an oligomeric phenolic compound (see Chapter 11).

Alcohols other than methanol can be used as the hydroxyl-capping groups. Examples of commonly used alcohols are isobutanol and butanol.

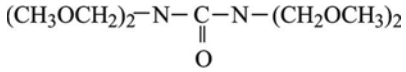
In practice, these compounds can be reacted with a functionalized polymer such as an acrylic or an alkyd that contain either acid or hydroxyl groups, which will react with the melamine compound to liberate an alcohol by-product with the multifunctional nature of the melamine compound leading to a cross-linked coating film. This cure system is briefly indicated by the following reaction scheme:



wherein A is the residue from HMMA and P represents the hydroxyl functionalized polymer that is being cross-linked. Note that after the above reaction, the residue A still has five functional groups that can react with other hydroxyl groups on the same polymer molecule or on other polymer molecules to set up the network. In addition to the by-product methanol, it is possible for formaldehyde to be a by-product. Narayan and coworkers [11] have addressed various aspects of the cure and properties of polyesters cured with HMMA. Numerous other articles can be found in the literature.

UREA COMPOUNDS

A scheme similar to that described above for HMMA and other melamine compounds is also applicable to ureaformaldehyde (UF) compounds. To form the UF compounds, urea is reacted with formaldehyde and the product is end capped with alkyl alcohols—usually methyl, isopropyl, or butyl alcohols. A full reacted urea intermediate in which methanol has been used as the capping agent has the following structure:



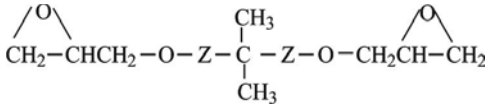
N,N'-bishydroxymethylurea

This multifunctional compound is capable of reacting with hydroxyl groups to produce cross-links with by-products such as alcohol, water, and formaldehyde.

Note that in the above examples, neither the melamines, ureas, or most polymers would form a good coating if used alone. The polymers act as flexibilizers and/or toughers for the hard, brittle cross-linking agents.

EPOXIDES

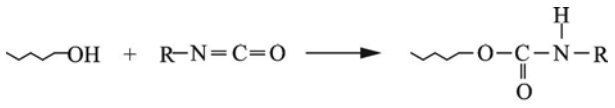
Epoxides represent a ring-opening-mechanism form of curing coatings. Aromatic epoxides are produced by the reaction of epichlorohydrin and bisphenol A, with the latter compound a condensation product of acetone and phenol. Aliphatic epoxides are prepared by the peroxidation of unsaturated linear or cyclic olefins. A typical epoxide used in coatings, is the diglycidylether of bisphenol A, which is described below and wherein Z is a phenylene group.



The epoxide groups can react with active hydrogen atoms such as those found on amine, hydroxyl, and carboxylic acid groups. Aromatic epoxides react very rapidly with amines and hydroxyl groups and cycloaliphatic epoxides react very rapidly with cations derived from acid functionality or hydroxyl groups. Opening an epoxide ring results in linkage to the donating compound an formation of a secondary hydroxyl group that may undergo further reaction. Thus, the above described epoxide may be considered as tetrafunctional when it is in the presence of active hydrogen atoms and as a result will rapidly lead to a highly cross-linked, cured coating. Under the proper conditions, the formed hydroxyl group can react with another epoxide group or with a melamine-formaldehyde compound to produce coatings with improved properties such as hardness, toughness, chemical resistance, and/or solvent resistance in the cured film.

URETHANES

Urethane linkages represent a rearrangement mechanism for the formation of cross-links and cure in polymeric systems. Urethanes are the reaction product of a hydroxyl group and an isocyanate group that undergo a rearrangement with the formation of a urethane linkage as described in the following.



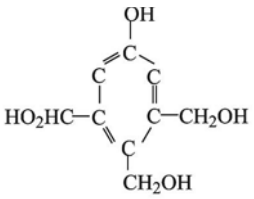
Isocyanate Urethane

This reaction is used in the manufacture of a broad range of products from insulation and seating foams, reaction injection moldings, in high-performance coatings, and other end uses. The isocyanate used in coatings and many other end uses is usually a di- or tri-functional compound that will lead to cross-linked systems. Monofunctional isocyanates are used to end-cap hydroxyl compound in the preparation of intermediates or to impart particular, desirable characteristics for certain end uses. Included are isocyanates such as iso-phorone diisocyanate, 4,4′-diphenylmethane diisocyanate, 4,4′-dicyclohexylmethane diisocyanate, trimers of hexam-ethylene diisocyanate, and others. The higher molecular weight isocyanates are preferred when practical, since they have a lower vapor pressure than their lower molecular weight counterparts and thus provide for improved working conditions. As would be expected, saturated epoxides have better weathering characteristics than aromatic epoxide coatings.

Isocyanates are used to cross-link a variety of polymers containing hydroxyl or amine functionality. In the case of amine functionality, the reactions are very rapid and result in the formation of urea cross-links. The reactions with hydroxyl functionality are usually catalyzed and proceed at easily controllable rates. Among the coating systems cured isocyanates or that contain urethane linkages are a variety of acrylic polymers and copolymers; polyesters; poly ether, polyester, and polylactone polyols; polyols capped with isocyanates and cured with adventitious moisture, urethane acrylates cured with ultraviolet or electron beam radiation, as well as others.

PHENOLICS

Phenolic compounds used in coatings are the condensation reaction products of phenol or substituted phenols and formaldehyde. Two main types of phenolics are made with the type depending on the catalyst used and the reaction conditions. When an acid is used as the catalyst, a thermoplastic, soluble novolac phenolic is obtained. Under basic conditions, the product obtained is a resole phenolic that is thermoset in character and is cross-linked in the final stages of the reaction. A phenol-formaldehyde condensate (P-F) may have the following structure:



Phenol-formaldehyde Condensate

Hydroxyl-containing oligomers such as the alkyds can be cross-linked through reaction of the hydroxy-methyl function of the P-F with an hydroxyl group on the alkyd with the elimination of water.

CURE MEASUREMENT

Complete or essentially complete cure development is a very important factor in meeting coating specifications and/or in determining the ultimate performance characteristics of any particular coating. Therefore, it is very important for the developer and the user of coatings to know how the curing process takes place and whether or not the final coating is adequately cured. As cross-links develop and molecular weight increases in a coating, performance characteristics such as adhesion, solvent resistance, toughness, hardness, gloss, and the like approach an optimum value, which is near a set, desired, or specification value. Coatings that are undercured will tend to be soft (lack hardness), have poor solvent resistance, and probably have poor adhesion. Overcured coatings may be hard and brittle, take on a dark, undesirable color, have low gloss, or not meet other criteria.

Cure measurement can be determined by simple, qualitative testing or through analytical techniques that require sophisticated instrumentation. Often simple testing can be used to give an investigator a quick benchmark and tell if they are on the correct developmental track. Then sophisticated techniques can be used to completely understand the coating system and the coating's ultimate properties. Finally, investigators attempt to correlate simple and sophisticated tests so performance features may be confidently determined during production, which is often taking place at high line speeds, with relatively simple testing. Also important is being aware that coating properties may change after leaving a thermal curing oven, a radiation source, or other curing device and properties after a length of aging time should be considered. Methods for measuring degree of cross-linking and the distance between cross-links can be found in Chapter 46.

Rapid test methods are desirable because of time constraints and cost, but sometimes they do not tell the true story. Yet, they do provide much useful information. It should be kept in mind that one is attempting to ascertain a molecular process, cross-linking (unless thermoplastics are involved), and its relationship to coating performance.

Most thermoplastic coatings cure or "dry" by simple evaporation of solvent. This is true for nitrocellulose, cellulose acetate, and solvent soluble acrylic lacquers wherein no cross-linking takes place. To measure cure of such systems, the time for either a print-free or tack-free condition is determined. As the evaporation process takes place, the nature of the coating goes from tacky to set-to-touch to tack free. On further drying, the coating becomes print free wherein a thumb print will not be visible on the coating surface. At times the effect of a twisted thumb print under moderate hand pressure will be observed. Another testing method involves dropping cotton linters or cotton balls onto the surface and noting the time after which they do not adhere to the coating. Thermoplastic or thermoset coatings on metal substrates can be quickly tested with a hand-held, fairly new nickel (U.S.A. five-cent piece) by applying a quick, rapid, gouging scratch with the edge of the coin to the coating and observing the results. One quickly finds out if the coating is tough and adherent, since

the hard, sharp coin edge will have a marked effect on the coating.

Solvent Rubs

A convenient, often-used method for determining cross-linking involves solvent rubs. A cloth soaked with a solvent such as methyl ethyl ketone (MEK) or acetone is rubbed vigorously back and forth on the film, and then the film is examined after a specific number of rubs. If the film is removed, softened, or loses gloss, it is considered inadequately cross-linked or it is considered nonresistant to solvent. Often, the number of back-and-forth double rubs that the film does pass is reported. Thermoplastic coating are not expected to pass the test. The tests involved include ASTM D5402, Practice for Assessing the Solvent Resistance of Organic Coatings Using Solvent Rubs, and ASTM D4752, Test Method for Measuring MEK Resistance of Ethyl Silicate (Inorganic) Zinc-Rich Primers by Solvent Rubs. Related tests include ASTM D5109, Test Methods for Copper-Clad Thermosetting Laminates for Printed Wiring Boards; ASTM D1676, Test Methods for Film-Insulated Magnet Wire; and ASTM D2671, Test Methods for Heat-Shrinkable Tubing for Electrical Use.

One difficulty associated with this test is that the individual testing the coating is not standardized. One person may exert more pressure than another and this can have a bearing on the final result. However, even with this deficiency, the test does provide useful information when the number of double rubs passed is reported.

Hardness

Hardness and scratch resistance provide another method for obtaining information about the degree of cross-linking and cure. There are a variety of tests that provide information about this characteristic. The topic is discussed in detail in another chapter in this manual.

PENCIL HARDNESS

A very simple, but complex, test for measuring the hardness of coatings is pencil hardness, which is carried out according to ASTM D3363, Test Method for Film Hardness by Pencil Hardness. The test originated with manufacturers of pencils who tried to develop a consistent means for checking the quality of pencils. Along the development way, someone suggested scratching a paint film, and it was noticed that the different hardness of pencils were able to penetrate the coating down to the substrate or to scratch the coating to different degrees.

The test was later used by coating technologists and currently is widely used in the industry to determine coating hardness. In this technique, a number of pencils of known hardness, usually from a specified manufacturer, are used. The pencil is trimmed so that 5 mm of "lead" is exposed. The lead diameter is 1.8 mm and is sharpened by rubbing it perpendicular to the surface of No. 400 carbide abrasive paper. The sharpened pencil is held at a 45° angle to the coating and pushed along the surface with hand pressure to attempt peeling away the coating. The pencil that fails to scratch or cut through the coating is considered the "Pencil Hardness Value." The method is simple, the equipment is low in cost, and results are quickly obtained. However, values obtained can be operator dependent as well as dependent on the method of sharpening the lead point, variances of lead hardness from different pencil lots, and different manufacturers. Yet, as mentioned above, the test is widely used and does provide useful information.

KNOOP AND PFUND HARDNESS

The Knoop hardness test, described in ASTM D1474 Test Methods for Indentation Hardness of Organic Coatings, is a useful test in which a spherical, pyramidal, or conical indentor is pressed into the film to cause indentation with the depth of penetration a measure of hardness. In the test, a 25 g load is applied for 18 s and the length of the indention line is measured with a microscope. The Knoop hardness number (KHN) is calculated from the expression [12]

$$KHN = L/A_p = L/l^2/C_p$$

where L is the applied load in kilograms, A_p is the projected indentation area in square millimeters, l is the length in millimeters of the long diagonal of the indentation mark, and C_p is an instrument constant. Because of the thinness of most coating films, this method is more useful for plastics, since it required almost a 75 % indentation into the film and can be influenced by substrate considerations. A more generalized formula than the above can be found in the referenced ASTM Test Method.

The Pfund Hardness Number (PFN) is obtained in an analogous manner by using a hemispherical quartz or sapphire indenter that is pressed into the film. PFN is calculated from the expression

$$PFN = L/A = 4L/\pi d^2 = 1.27L/d^2$$

where L is the applied load in kilograms, A is the area of the projected indentation in square millimeters, and d is the diameter of the projected indentation in millimeters.

SWARD HARDNESS

Sward hardness depends on the change in surface properties and the viscoelastic nature of a film. This method, which was discontinued in 1990, is used for automotive finishes and consists of a rocker containing two spirit-bubble indicators. The method is described in ASTM D2134, Test Method for Determining the Hardness of Organic Coatings with a Sward-Type Rocker and in ASTM D4366, Test Methods for Hardness of Organic Coatings by Pendulum Damping Tests. The pendulum is rocked and the number of swings are recorded and a reading is taken at the point where the swing distance is equal to half the original value. As cure increases, the Sward number increases. The value of a Sward test is that a number that can be compared to that of other coatings is obtained. This test must be conducted under very clean conditions as lint and surface imperfection can interfere with the results. Temperature control is another important factor. The difficulty with this test is that it only measures cross-link density or cure to a point. Then, it cannot detect further cure or over cure, since a plot of Sward numbers as a function of time or cure tends to reach a limiting value. A comparison [13] of hardness values obtained by different test methods is shown in Table 1.

TABLE 1—Hardness test comparisons [13]

Sample	KHN	Sward[a]	Pencil (Brands)				
			A	B	C	D	E
1	3.09	24	5B	6B	5B	6B	4B
2	4.33	28	4B	6B	6B	6B	4B
3	2.77	24	5B	6B	5B	4B	3B
4	2.61	22	3B	4B	5B	4B	3B
5	5.81	38	2B	2B	2B	2B	HB
10	25.7	54	H	H	H	H	2H
12	39.1	40	3H	2H	2H	4H	3H
14	—	40	8H	9H	7H	7H	9H

[a]Note how the values differ in this investigation—especially between the different brands of pencils and the limiting values of Sward Hardness.

IMPACT RESISTANCE

Tests that measure the impact resistance of a coating can be used to correlate with cure. An undercured coating may exhibit a low impact value, but as cross-link density increases, impact values improve. Of course, overcured coating may be brittle and have a low impact value. ASTM D2794, Test Method for Resistance of Organic Coatings to the Effects of Rapid Deformation (Impact), is a widely used test. It consists of placing a flat coated panel under a weighted spherical ball assembly and then dropping the weighted ball onto the panel from different heights. The cylinder in which the ball assembly is mounted is calibrated such that an operator can directly read the impact resistance in inch-pounds. The measurements are carried out by dropping the ball directly on the coated surface or on the reverse side with the results being reported as direct or reverse impact, respectively. The impact causes a dimple to form in the test panel, and it is examined visually or with a ten-power lens to determine the extent of cracking or other failure. This is a simple test that is widely recognized in the coatings industry, and it gives useful information about the performance characteristics of the coating.

Related tests include ASTM D5420, Test Method for Impact Resistance of Flat, Rigid Plastic Specimen by Means of a Striker Impacted by a Falling Weight (Gardner Impact); ASTM D950, Test Method for Impact Strength of Adhesive Bonds; and ASTM D2137, Test Methods for Brittleness Point of Flexible Polymers and Coated Fabrics. In addition to these methods, certain industries, such as the automotive industry, often develop their own in-house test methods and these will vary from manufacturer to manufacturer.

Thermal Analysis

Thermal analysis is an important analytical tool for determining the response of materials to changes in temperature and is useful in determining cure of coatings. The technique can be used to monitor the glass transition temperature, Tg, of a coating and this property can be related to cross-link density. For example, if a number of paint films that are cured at various times and/or temperatures are evaluated, thermal analysis can be used to determine the change in Tg as a function of a bake schedule or, for that matter, of formulation composition. From such studies, optimum cure cycles can be determined to ensure quality finishes are produced.

Thermal analysis devices have several modes for determining Tg and these include Differential Scanning Calorimetry (DSC), Thermomechanical Analysis (TMA), and Dynamic Mechanical Analysis (DMA). The glass transition temperature is a second-order transition, and it represents a temperature where segmental motion occurs in a polymer chain. This motion also causes a volume change in the polymer. Comparative changes of cross-linking measured by Sward hardness, evaporative rate analysis, and DSC indicated that the changes can be followed to high levels of cross-linking, but Sward measurements reached a limiting value while Tg continued to increase [14]. The importance of using the correct window of time and temperature when curing powder coatings has been described in the literature [15].

When DSC is used, a plot of endotherm/exotherm as a function of temperature is obtained at a set rate of temperature increase. As Tg is reached, there is an abrupt change in the endotherm that appears on the plot. Similarly, Tg can be measured using a plot of change in expansion as a function of temperature with the TMA method. In this method, a specimen is placed under a quartz probe and then heated. As the film expands, a plot is obtained in which a change in slope occurs. The intersection of the tangents of the expansion cure yields the Tg value. In the penetration mode, a depression occurs at Tg. Further details about thermal analysis can be found in the literature [16–19].

DYNAMIC MECHANICAL ANALYSIS

Another method for obtaining Tg is to use dynamic mechanical analysis in which a coating film is fixed to the ends of a tuning fork and the fork is driven over a frequency range and at different temperatures to provide a plot of damping as a function of temperature. Tg, being a second order transition, is a function of both temperature and of frequency. Information from both variables can be used to obtain information about the film [20].

TORSION PENDULUM

The torsion pendulum provides another way to obtain Tg as well as other dynamic properties such as the real and the imaginary shear modulus. A coating film is either imbibed into an inert substrate or used in a neat form (often difficult for this technique) and suspended between jaws and a counterbalanced disk that is used to apply a twisting torque to the specimen. The applied shear force then freely decays. A difficulty is that many coating films do not have the strength to support even the light stress of the counterbalanced disk, especially when the glass transition region is approached. This is why the coating is usually imbibed into an inert substrate such as fiberglass. If the sample is held at a constant temperature for a period of time, changes in cross-link density are reflected in modulus and damping changes. Details of the method and ways to construct a torsion pendulum can be found in the literature [21,22].

Impedance Measurements

Meyers [23] investigated the drying behavior of latex systems using ultrasonic impedance measurements. In his

studies, a latex coating was cast onto a quartz crystal and ultrasonic energy was beamed at an eleven degree angle at the underside of the coating, reflected to a detector that measured the attenuation of the initial beam as absorbed by the drying coatings. As water evaporated, there were changes in impedance that could be correlated to curing in the sense of drying.

EVAPORATIVE RATE ANALYSIS

A novel method for studying cure is Evaporative Rate Analysis (ERA), which was developed by Anderson and coworkers [24]. This methodology was applied to determine the cleanliness of the surface of spacecraft. It was reasoned that if a radioactive C^{14} liquid were placed on a clean surface, the evaporation would be retarded due to cleanliness. In fact, the opposite was true. Nevertheless, this technique was developed to measure the degree of cleanliness. If a small amount of diethyl succinate-C^{14} is deposited on a surface and a controlled sweep of nitrogen is applied over the surface, the rate of evaporation can be monitored using a Geiger counter. The principle is that on a clean surface, there is no interaction between the solvent and a clean substrate and as a result normal evaporation takes place. If, however, the surface contains a contaminant, then the radioactive liquid will interact with the surface contaminant and retard the rate of evaporation of the radioactive component. Plots that relate cleanliness to evaporation rate can be prepared.

The investigators applied this technique to the cure of organic coatings. They demonstrated that in an undercured surface, solvent retention increased and this led to longer residence times for the radioactive substance on the under-cured surface. By preparing coated panels having different cure times or temperatures, and then measuring the ERA of each panel, a plot of retention as a function of bake schedule was obtained. The method was applied to the cure of a variety of coatings by many coating technologists [14,24].

Other instruments are useful for determining the cross-linking of coatings including the Vibrating Needle Curometer that is used for liquid systems such as adhesive and sealants. The instrument drives a vibrating needle at a fixed frequency into the sealant or adhesive, and the damping amplitude is measured as a function of gel and cure time [25]. Products that can be monitored for cure with this technique include coatings, adhesive, foams, and sealants.

Recent Information

Readers are referred to other chapters in this manual for related cure-measuring techniques. The information provided in this chapter is also applicable to radiation-cured and powder coatings, since the performance of these coatings depends on proper extent of cross-linking consistent with the design of the polymers used [5,15].

In addition there have been recent advances in analytical techniques that provide coating chemists with better tools to understand the process of cross-linking [26]. Analytical techniques for measuring key polymer properties are reviewed in polymer chemistry texts [27–29]. A recent application of space technology in which a technique known as Near Infrared Thermal Processing is being used to cure a wide range of coatings, printing inks, and adhesives [30]. The technique involves high energy sources that radiate near the infrared spectrum (more than 90 % of the energy emitted is below 2 μm) and allow markedly higher rates of cure than infrared or hot air systems. The systems have high process efficiencies and reliability. The importance of cure and its characterization is apparent from the recent April 2006 two-part, virtual-learning course offered about this topic by the Federation of Societies for Coating Technology and presented by Dr. T. Provder.

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Film Preparation for Coating Tests

Robert D. Athey, Jr.[1]

THE PERFORMANCE OF A COATING FILM IN A TEST is likely to be dependent on the physical form of the film. For instance, film thickness is an important factor in physical and appearance measurements (until the coating gets too thick), so there must be some control of the film thickness. Appearance is also related to how smooth the film surface is, and care to make the film appropriately will ensure that the appearance measurements are germane to the end use. The substrate used as the carrier for the test film, even temporarily, may affect the property measurements, as well.

The primary concern in making films for tests is that the film prepared be homogeneous and consistent with previous or future films for the same test. The jargon of the trade calls the art of making films "casting," but many film formation methods are used to form the film, and each method has its own set of advantages and drawbacks.

TEST REQUIREMENTS OF FILMS

Test requirements come in two classes, appearance (aesthetics) and physical properties. Choice of application method for the film may affect the appearance in some cases. For instance, the "multicolor" paints must be applied by dip or spray techniques for laboratory testing or the appearance does not give the desired mottle of nearly circular spots. Roller, brush, or even drawdown bar will cause these spots to become streaks. Choice of application method for appearance includes drying technique, as some films require special drying conditions to attain their desired special appearance. Examples include leafing aluminum flake "metallic"-look paints, hammer tones, and wrinkle finishes.

Choice of application method driven by physical property testing is also necessary. Think carefully of the three kinds of stresses (tensile, compression, shear) and recognize that all are blended in a hardness or adhesion evaluation by indenter, pencil, mandrel bend, or dart impact test on a coating. Recognizing these stress combinations can make one aware of film preparation needs. In cases where adhesion is stronger than cohesion of the film, one should be able to distinguish between adhesive failure and cohesive failure. Film preparation should not conflict with these objectives.

The physical properties to be tested in specific ASTM methods have a "significance and use" section in the method to ascribe the relation of the test value to some "in use" performance criterion. The preparation of the test film should thus correspond to the standard field application of the material, as well.

Another portion of film influence on the test is film thickness. The presentation by the Technical Committee from Toronto in the 1990 National FSCT Meeting and Paint Show [1] dealt with hardness measurements in films of varying thickness. However, the control of film thickness was not as straightforward as might have been thought. Hardness values turned out to be dependent on film thickness along with other equally important variables [2].

Fluid rheology, concentration, and other factors govern the amount of coating left after the application process. Knowing the process variables associated with a film-casting technique are essential to getting what is needed for the ultimate test and results therefrom. Certain other properties of the film (opacity, permeability, erosion rate by some attacking mode, etc.) will depend on the thickness of the film. So, understanding thickness control in the casting process is crucial to obtaining meaningful results in terms of meeting specifications in reproducibility.

In instances where fluid or gas permeation resistance or corrosion barrier properties are to be tested, a "pinhole," "holiday," or "mud-crack" in the film is a fatal flaw. The film preparation technique must eliminate (as much as possible) any such fatal flaw, or the test method should prescribe what is to be done (for example, replications) in cases where an unseen fatal flaw is detected by the test.

FILM CASTING TECHNIQUES

Free Films

Free films, that is, films not applied permanently to a substrate, are used for a wide variety of tests and accordingly vary in thickness and size. The most common castings of free films are used for permeation or strength and elongation testing. They can also be used for cold flex tests or moisture/ solvent absorption studies related to permeation. Free film thickness can be measured as described in ASTM D1005, "Test Method for Measurement of Dry-Film Thickness of Organic Coatings Using Micrometers."

Probably the most common free film castings are laid down on a "nonstick" surface, such as the silicone-coated papers (available through Leneta and other suppliers), Teflon™, or polyethylene sheets. Release substrates are described in ASTM D823, Standard Practices for Producing Films of Uniform Thickness of Paint, Varnish, and Related Products on Test Panels. Lack of release-substrate wetting is the most common problem encountered when trying to obtain a continuous film. Water-borne coatings are especially difficult to formulate for good wetting of these substrates. One trick to use with such formulations

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Fig. 1—Vacuum plate pulling a vacuum through the side nozzle holds paper or paperboard substrates tight for drawdown film casting. (Courtesy of Paul N. Gardner Co.)

is to prepare the sample at higher than normal solids content, which results in increased viscosity and resistance to beading is improved. An alternative is to apply several coats until the dried "beaded-up" portions merge to form a continuous film.

A vacuum plate makes it easier to hold down the paper or polymer film for film casting and is an aid to good results. Fig. 1 is a diagram of the vacuum plate formed from aluminum. Older versions had eyes at the bottom surface through which screws could affix the plate to a tabletop. If this system is to be vacuum supplied from a sink faucet aspirator, a liquid trap (vacuum side-fitted Erlenmeyer flask) should be placed in line between the vacuum plate and the aspirator. This will ensure that any liquid coming from the aspirator will not get to the vacuum plate or coating substrate.

Grenko [3] suggested several coated paper techniques for obtaining free films, such as decal paper coated on the face side or outdated matte or semimatte photopaper. The decal paper could be floated on water and the paper peeled off. Grenkodid not describe the removal of photopapers from the film. He also cited Sager [4] for a technique using an embroidery hoop for holding nonmoisture proof cellophane. After the coating film had been applied, one simply poured water on the inverted cellophane and the coating film dropped off. These techniques are likely to be most appropriate for solvent-borne or 100 % reactive formulations. Water-borne coatings may be inappropriately leached or weakened by the water used to loosen and isolate the films.

Grenko [3] also mentioned the use of metal substrates for free film isolation. Brightwell [5] used glass onto which a thin silver film had been vacuum deposited. Bayor and Kempf [6] used thin aluminum foil that was later dissolved from most of the back by using hydrochloric acid doped with a minute amount of platinum chloride. The latter dissolved off only enough aluminum foil to leave a foil "frame" at the edges of the film to support it and to facilitate handling. This technique with aluminum foil dissolution in an acidic, aqueous medium presumes no sensitivity of the coating components to acid or water.

For thicker films (1 cm or more), a Pyrex™ TV or Teflon™ coated baking pan can be used with some success. For instance, about 300 mL of a latex formulation in a 9 by 12 in. (23 to 30 cm) Pyrex™ baking dish will yield a sufficient quantity of thick film for testing. Occasionally, there is a "mud cracking" problem, but it can be reduced periodically by releasing the edges of the film from the vertical sides of the dish with a spatula to allow uninhibited shrinkage. This way usually results in pieces of increased size, and 1 in.^{2} (6.25 cm^2) is all that is required for the moisture absorption or solvent-swell test. Using this technique, it is possible to obtain large enough pieces of test coating for moisture vapor transmission tests at an application thickness that is common for roof coatings.

The "mud cracking" problem is serious for any coating. The cause is the lack of "wet gel strength" to resist the tensile stresses within the shrinking membrane. Strictly speaking, unless the coating cross-links, it is not a gel, but simply a high-viscosity fluid or "pseudogel." Assuring that the upper surface does not "skin over" by controlling the humidity or solvent-vapor environment over the drying surface may alleviate the problem.

The literature describes mercury pool casting [7,8] or tin foil casting [9] with mercury amalgamation used to remove the tin without stressing the coating film. ASTM D4708, "Standard Practice for Preparation of Uniform Free Films of Organic Coatings," also describes the tin foil amalgamation technique. These techniques are no longer in common use, as the mercury vapor is deemed a health hazard and caution is advised if the technique is attempted.

Rarely, but occasionally, for instance, a free film of a polymer or binder material is needed for testing water vapor permeation or absorption. Some of these tend to be tacky, and powder applied to the surface will make them easier to handle. Although pearl cornstarch is preferred over the powdered talc for this purpose, baby powders and similar talcum powders are often used.

Rotational casting is a means of obtaining nonporous, non-mud cracked-free films. The standard jar-mill roller (see Fig. 2) may be used with a variety of open containers (quart or gallon jars, earless paint cans) with a 4-in. (10-cm) circle cut out of the bottom, to centrifugally cast the film with good thickness control. An alternative device, the Caframo REAX2 rotating mixer [10] may be used to hold the paint can with its main axis along the rotation axis of the clamp (see Fig. 3).

The Los Angeles Society for Coating Technology Technical Committee successfully used this rotational casting technique in a study to obtain tensile and moisture vapor permeation film samples from acrylic latex compounded with silane-modified talcs [11]. It is derived from an older

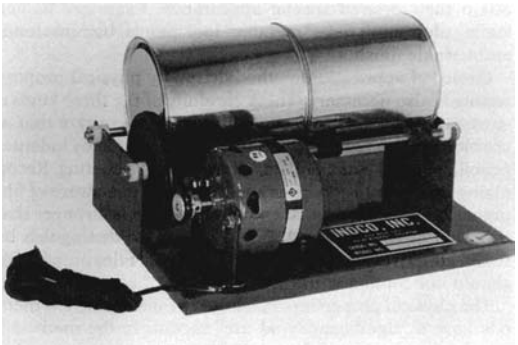

Fig. 2—Lab roller mill—Although this device is most often used for pebble milling, an empty "earless" paint can on the rollers may be used to cast films. (Courtesy of Indco Inc.)

Fig. 3—Heidolph "REAX 2"—This device was designed as a rotational mixer for fluids, but a gallon paint can will fit in it for rotational film casting, as well. (Courtesy of Heidolph USA.)

practice at the Thiokol Rubber Co. that was used to obtain films of castable elastomers in a rolling pipe [12].

Equipment for this technique is easy to set up and use. Introduce 100 mL of coating into a 1-gal can and let it roll overnight. This will result in a film approximately 6 by 18 in. (15 by 46 cm). That is a sufficient quantity for 6-in. (15-cm) tensile bars and 2-in. (5-cm) permeation circles. Close control of film thickness is achieved by knowing the area of the cylinder and concentration. From these, the weight of coating needed can be calculated. Films of tacky coatings or pressure-sensitive adhesive formulations can be made by this technique. After the film is formed, the can is placed in a refrigerator or freezer to facilitate film removal.

To obtain a centrifugally cast powder coating film, a sample of the powder is introduced into the can. Then, a hot air gun is held at the outside of the rolling can, and the powder coating will melt to coat the inside. Care is needed to eliminate scorching, and practice is needed to determine how close the flame should be to the can to get a good film. Other techniques to obtain a film include melting on a Teflon™ sheet on a hot plate or in between Teflon sheets in a heated press.

Spraying one to a silicone-coated paper is occasionally used to make free films. There is no problem with this technique when a skilled practitioner does it. However, films made with this technique may not give as good permeation test results as from one made by a film from a fluid-flow technique.

A note of caution should be added about handling free films made for physical testing. Any undue stresses may chip, stress, or crack the film. This is especially important for permeation or physical property tests. In the case of the latter, some materials are "notch sensitive," that is, the results of a tensile or other physical test may be markedly reduced by the presence of a notch, scratch, or crack in the film [13].

Dry Coatings on Substrates

Test coatings on a substrate are generally applied for a wide variety of appearance and physical property tests. Color and opacity are commonly evaluated on coated paper charts, though unsealed paper charts with a porous surface are available, as well. Coating on substrates to simulate actual use is common so the paint laboratory has many kinds of steel, aluminum, wood, or other substrates in stock as needed by the customer or the paint company.

Plastic panels are rarer, but they can be made available when needed. Several companies now offer such products. Plastic panels may need special surface preparation techniques to assure wetting and adhesion (solvent washes, chemical etches with alkali or acid, low-temperature plasma, or corona discharge or chemical oxidation, etc.). As painting plastics become more and more important for automotive, computer, sign, and other industries, the manufacturers are making panels available to potential paint suppliers.

Panels of metal are a special case for the preparation of test films for paint. It may be necessary to do a precoating surface preparation on the metal, and consultation with appropriate specifying agencies may be necessary. The Society for Protective Coatings (SSPC) has many grades of hot-rolled steel preparation techniques that vary from wire brushing through sand blasting to expose "white metal" [14]. Other preparations such as phosphatizing, galvanizing, anodizing, etc., are unique to specific industries or industry segments and will require lab preparation of panels or freshly treated panels from the customer or a commercial source. An annual handbook contains descriptions of some of these techniques for laboratory usage [15]. Preordered steel panels that are subsequently stored in special corrosion-inhibitor-treated packaging may skew exposure tests if they are not rigorously cleaned of corrosion inhibitor just prior to the coating steps. Cleaning procedures may require rinsing with hydrocarbon solvent or acetone and hot air drying just before paints are applied. Exposure panels made of metal must also have special edge protection to ensure that only the coated face has the exposure test applied.

The casting technique on a paper or paperboard substrate is a skill that is learned through apprenticeship. First, the panel needs to be clean and dust free. For horizontal castings, which is a way to obtain good flat films, it is necessary to ensure that the surface is level during casting and drying. Tape the chart or panel to the level surface so it does not curl as the film loses solvent or dispersing media and starts to shrink. Unsealed paper charts will curl in a convex manner since any water in the coating swells the paper fibers, and the substrate may try to curl the sheet in a concave manner when the film tries to shrink across the top surface from which evaporation is taking place. Vacuum plates are available, as noted earlier, to hold down the paper, foil, or cardboard chart during the film-casting process. The paperboard chart should be stored in the same humidity environment that will be used in drying/curing the coating as the wood-pulp fibers are hygroscopic.

Concrete, plaster, and asphalt/gravel test blocks or panels may be prepared in the laboratory or they may be purchased. However, whenever possible such blocks should be obtained from the customer since paint-laboratory results may not compare well with the customer's results if details such as porosity, surface salinity, surface pH, soluble calcium or sodium ion content, etc., are not equivalent. These materials may be hygroscopic and will need equilibration in the drying/curing environment prior to coating. In addition, some concrete castings, that is, tilt-up wall constructions, often have surface residues of form coatings that had been used to aid release from the forms. Surface

characterization for such release aids or rigorous cleaning may be needed. There is an ASTM standard practice for preparation of mortar panels for testing paints: ASTM D1734, "Standard Practice for Making Cementitious Panels for Testing Coatings."

Grenko [3] has described press coating of bitumens on aluminum or felts, with shims placed in the press to attain appropriate thickness. His work was based on earlier studies by Greenfield [16].

Wet Films for Testing

There are a variety of reasons one may want to have a close look at a wet coating film. Simply watching the drying process may make any problems with moisture condensation on the film, pigment float, etc., apparent. There are test films made to assess wet hiding or sag resistance (ASTM D4400, "Standard Test Method for Sag Resistance of Paints Using a Multinotch Applicator"). Good film casting practice, for example, a level surface for casting, consistent technique, etc., is a requirement for reproducibility of results. Equipment required for special tests will be included in the following section.

EQUIPMENT FOR FILM PREPARATION

Drawdown Bars

The drawdown bars are the simplest of the film casting devices to use. One simply makes a puddle of coating on the desired substrate and moves the drawdown bar over the puddle to make the desired wet film thickness. Application of the film with a drawdown bar nominally gives a good continuous film, but the spacing between the bar and the substrate may have little to do with the film thickness obtained. Speed of pulling the drawdown bar over the fluid will affect the film thickness since fluid rheology influences film thickness. High molecular-weight polymers may cause the edges of the film to draw in and increase the wet-film thickness. The formulation may not wet the drawdown bar, and, if this happens, it adds another factor to the control of film thickness. Wetz and coworkers [17] showed almost 100 % deposition of the wet film and found a relationship between wet-film and dry-film thickness.

$$T_{df} = 0.057 + 0.588GS(\rho_l/\rho_f)$$

or

$$T_{df} = 0.057 + 0.955T_{wf}(\rho_l/\rho_f)$$

where:

T_{df} = dry film thickness, mils,
T_{wf} = wet film thickness, mils,
ρ_l = density of liquid,
ρ_f = density of dry film,
G = clearance of drawdown barmils, and
S = weight fraction of solids in liquid.

Grenko [3] makes the point that these relationships are only true for drawdown blades having substantial flat surface between the leading edge of the bar and the trailing edge. The Byk-Gardner information [18] suggests the following expectations for cast films of varying thickness:

15 to 100 μm	50 %
100 to 300 μm	60 %
300 to 500 μm	80 %
over 500 μm	90 %

The hand-held drawdown bars are covered in an ASTM specification, Method E in ASTM D832, "Standard Practice for Rubber Conditioning for Low Temperature Testing."

A wide variety of drawdown bars are commercially available, and your local machine shop can make special orders of any design, if needed. Table 1 lists a few of the available types of drawdown bars, with commercial sources of some suppliers. Some rectangular design devices have differing gap depths on the sides so one may choose the film thickness needed for casting (see Figs. 4 and 5).

Stainless steel or aluminum are the preferred materials of construction, as corrosion can damage the region of the drawbar controlling thickness of applied film. Good laboratory practice dictates immediate cleaning of the paint contact surfaces after every usage to minimize the threat of corrosion or other damage. A caution on marking the draw down bars, as some manufacturers label them not with the gap spacing, but a number half the gap spacing since that is the expected wet film thickness to be obtained.

TABLE 1—Drawdown bars for film casting

Type	Design Details	Supplier[a]	Reference
"Bird" knife	Permanent fixed gap	Byk-Gardner	3
Two-path applicator	Bar has two cuts of different depth machined into top and bottom	P. N. Gardner	20
Eight-path applicator	Stainless-steel square tube with eight different depth cuts in each of top and bottom edges	P. N. Gardner	20
Gardner "Microm" applicator (also Hercules-Gardner adjustable [3])	Micrometers on each side lower or raise blade of "U" shaped device	P. N. Gardner	20
"Universal" blade applicator	Blade forms "U" shape with sides having slots and thumb screws to raise or lower	P. N. Gardner	20
Dow latex film applicator	"U"-shaped blade with wider cut for larger gap so second cast film	Byk-Gardner	3

[a] There may be many other suppliers, but only one is cited herein as a space-savings technique.

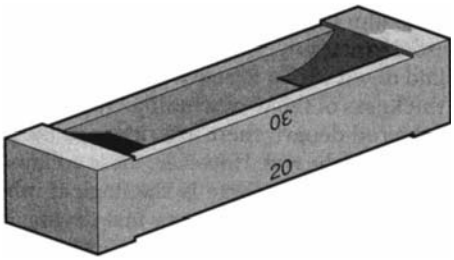

Fig. 4—Applicator frame/step gap applicator—Two film thickness choices are available with this device. (Courtesy of Byk-Gardner Inc.)

Some drawdown bars have film thickness adjustment choices by micrometers or other techniques (see Table 1 and Fig. 6). When these are used, the settings should be checked with feeler gages to make certain user wear has not made them inaccurate. These also require dismantling and cleaning after every use. If oil is used to inhibit corrosion and make the mechanics move smoothly, make sure they are rigorously cleaned of oil prior to usage.

Several drawdown bars have gradations of cuts into the wet-film thickness controlling surfaces. For instance, the Erichsen suppliers offer the Kruse Multi Clearance applicator, having six to ten adjacent film strips of 10 to 200 μm in thickness for assessment of color yield, opacity, etc. (see Fig. 7) [19]. A similar device, the Leneta TG19 Logicator, is intended for hiding power and spreading rate measurements. It is available from Gardner [20] and has eight "gates" ranging from 2.65 to 10.4 mil in depth.

There are motorized film application devices specified in Method C of ASTM D823, "Standard Practices for Producing Films of Uniform Thickness of Paint, Varnish, and Related Products on Test Panels." The Model 509/1 Film Applicator from Erichsen [19] may be fitted with any sort of drawdown bar or blade (see Fig. 8). Speed of the motion of the applicator may be preset, so the variation among several samples may be minimized.

Two devices Grenko [3] included with drawdown bars are more like bulk coating devices, as they do not require putting down a puddle of coating before applying the blade. Indeed, these devices contain the coating and apply it to a stack of sheets, one sheet at a time as the sheets are pulled out from underneath the device. One such device is the Parks Film-O-Graph cylinder. One puts the cylinder on a stack of Leneta charts or metal panels, fills the cylinder with the coating, and pulls each sheet from underneath the cylinder. A portion of the rim edge of the cylinder is milled

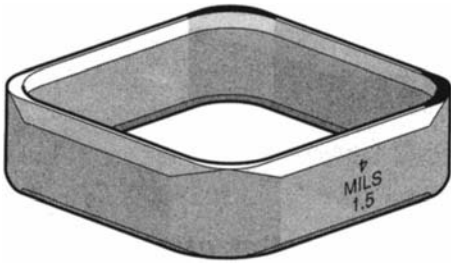

Fig. 5—Multiple clearance applicator—Eight film thickness choices are available on one device. (Courtesy of Byk-Gardner Inc.)

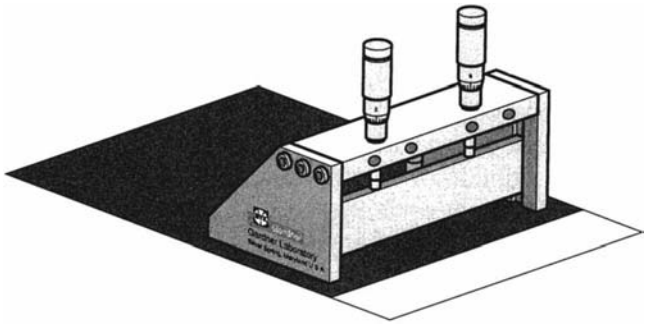

Fig. 6—Fllm casting knife—Micrometers adjust the blade clearance. (Courtesy of Byk-Gardner Inc.)

out to act as the gate to allow coating at a desired thickness. One may even use it for very viscous coatings (even putty) by forcing the fluid through the tube with a loose-fitting plug from the top and wiping the bottom of the tube over the substrate to be coated.

The second of the devices discussed was the Parks Rapid coater. Paper sheets were stacked in the bottom of a box with their ends out of a side slot at the bottom. The box was then filled with coating fluid, and each sheet was withdrawn individually. Grenko [3] noted that this was not a precision device, but it was adequate for some purposes.

Grenko [3] also described the flat Parks Film-O-Graph, which used a flat plate with spring clips to hold shims along the sides of the sheet of substrate. One poured the coating onto the substrate between the shims and used a bar such as a ruler or other straight edge to doctor off the excess and make the coating as thick as the shims. Bending of the scraper bar by the very slightest amount would make very thin films almost impossible, but for thick films (for example, roof coatings), this technique worked well.

Some applicators are meant only for the wet film tests. Two especially useful applicators for these are the sag test devices and the wet hiding test devices. The latter, most frequently the Pfund Cryptometers (available from Erichsen [19] and Byk-Gardner [20]), have black or white glass (ceramic) beds over which a transparent wedged cover levels the coating film (see Fig. 9). Although these devices are quite hard, care in cleaning will assure they do not get scratched. They must be stored carefully, wrapped, and covered.

The sag test film casters in effect drawdown several narrow films in gradations of film thickness. Many are simply slotted U-shaped drawdown bars with variations in slot depth from 1 to 6 mil, 3 to 12 mil, and 14 to 60 mil.

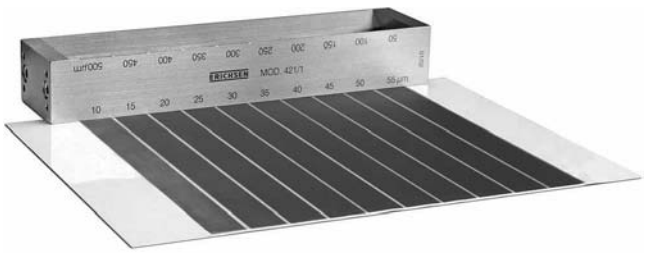

Fig. 7—Multiple gap drawdown bar—Six or eight gaps are machined along the same edge for casting side-by-side films for comparison. (Courtesy of Erichsen GMBH & Co.)

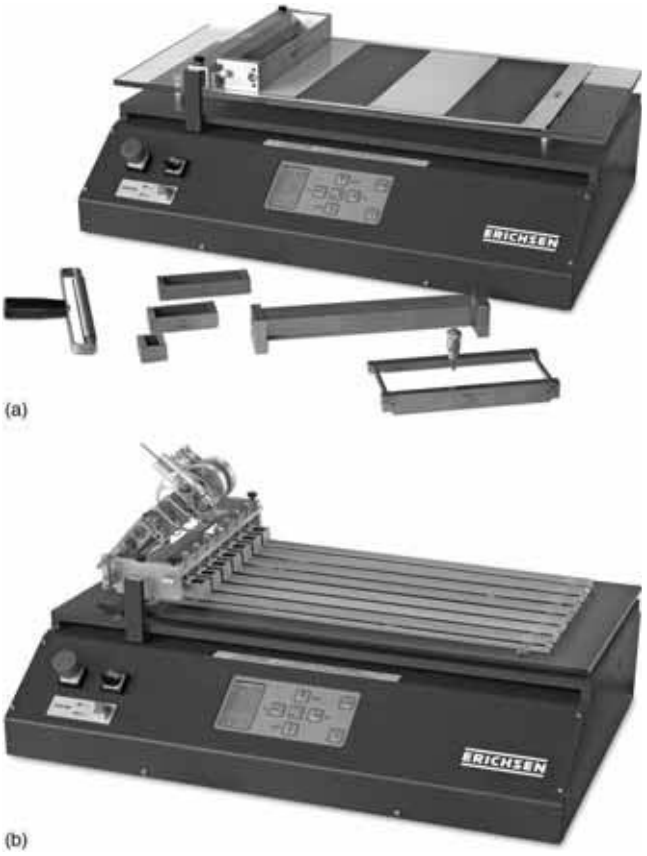

Fig. 8—Electrically driven drawdown device—Four speeds may be chosen to control drawdown rate. (Courtesy of Erichsen GMBH & Co.)

However, the New York Paint Club Technical Committee designed a special "leveling test blade" that had double slots for each depth with a wide space between each set of double slots [21]. Their slots are 1, 2, 4, 8 and 16 mil in depth (see Fig. 10).

How a paint film drips or sags depends on the rheological characteristics, and the thickness of the coating that first sags may be related to the gravity-applied shear stress by the outer elements furthest away from the substrate on that film. Other rheological factors (high shear viscosity, ca. 10 000 s^{-1}, for instance) are also important in sag and leveling. Sag test devices complying with ASTM D3730, "Standard Guide for Testing High-Performance Interior Architectural Wall Coatings," and several federal specifications as well as the New York leveling test blades are available from Gardner [20] and Byk-Gardner [18].

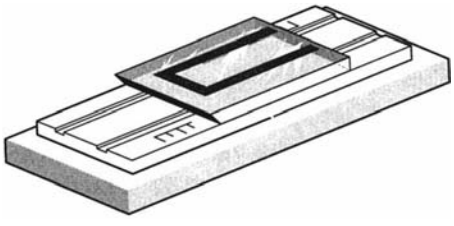

Fig. 9—Pfund crytometer—The white style shown is for black/dark paints, while a similar black style is used for white/light paints. (Courtesy of Byk-Gardner Inc.)

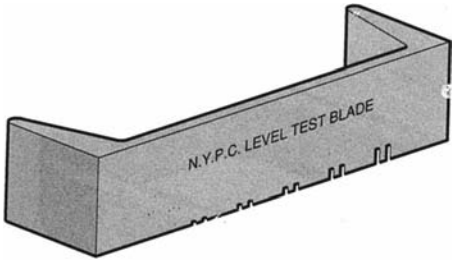

Fig. 10—New York paint club leveling test blade—The slotted blades are for assessment of sag and leveling. (Courtesy of Byk-Gardner Inc.)

Wire-Wound Rods

For very thin films, the wire-wound rods are quite useful for quickly and easily applying films. The wire-wound rods are simple rods of 12- or 16-in. (30- to 40-cm) length, of 1/4, 3/8, or 1/2 in. (0.63, 0.45, or 1.27 cm) diameter, with a spiral wind of wire tight about 75 % to 80 % of the rod. Table 2 shows a selection of the wet film thickness that is obtained from the rods with different wire diameter.

The film laid down with a wire-wound rod is almost exactly a tenth the thickness of the wire winding. Strictly speaking, as the film has the rod depart, there are ridges in the film in the direction of travel of the rod. However, these collapse to make a quite smooth film unless there is rheological inhibition in the formulation or the coating is very fast drying. This technique is quite effective to simulate paper or can coating end products. There are industrial production systems that employ wire-wound rods to meter coatings onto roll substrates, as well.

TABLE 2—Selected coating thickness obtained from various wire-wound rods

Wire		Wet Film Thickness	
Size	Diameter (in.)	Mils	Micrometers
2.5	0.0025	0.25	6.4
3	0.003	0.3	7.6
3.5	0.0035	0.35	8.9
4	0.004	0.4	10.2
4.5	0.0045	0.45	11.4
5	0.005	0.5	12.7
5.5	0.0055	0.55	14.0
6	0.006	0.6	15.2
10	0.01	1.0	25.4
20	0.02	2.0	50.8
30	0.03	3.0	76.2
40	0.04	4.0	101.6
50	0.05	5.0	127.0
60	0.06	6.0	152.4
70	0.07	7.0	177.8
80	0.08	8.0	203.2
90	0.09	9.0	228.6

Fig. 11—Spiral wire drawdown applicator—The handle shown grips the end of the wire-wound rod for application with one hand. (Courtesy of Erichsen GMBH & Co.)

A similar device called the "spiral-film applicator" is available from Erichsen [19]. It is a wire-wound rod with a perpendicular handle (see Fig. 11). It is available to apply a film thickness of from 10 to 200 μm in widths of 80, 150, or 220 mm. Byk-Gardner offers a handle that attaches to the ends of the wire-wound rod for lab film preparation as well [18]. The Accu-Lab™ Lab Drawdown Machine has a rod holder and substrate holder to assure precision in laboratory manual film preparation [22].

There are also two-wire rods in which a second, smaller wire is wound in the grooves made by the first winding wire. These yield higher application rates than do the single-wound wire rods. There is potentially an advantage to the two-wire rods since they leave a different pattern in the coating. The ridges left are larger and may level faster and more uniformly.

Spray Outs

Spray application, including by weight on a panel hanging on a balance in a spray booth, can be done with good precision. Good spray-out application on panels can be done by those skilled in the art. To control the weight applied in a spray booth, a triple beam balance may be attached to a beam 5 or 6 ft (1.5 or 1.8 m) above the floor, and a hanger-wire panel holder is hung from it as the spray target. A cardboard shield over the balance will keep off overspray off the positioned balance. Take off a few tenths of a gram to give a pointer indicator warning when the spray has almost reached the desired weight. Spray quickly to minimize evaporation.

There are automated spray devices. Grenko [3] related the automated spray device design from Bell Labs [23] to Method A of ASTM D823. The Bell Labs design has the gun travel over stationary panels, while an alternative design has the panels on a moving belt under a stationary spray gun, similar to a design reported from Battelle [24]. In either case, the amount of coating applied to the panel is controlled by the speed of the moving belt and by nonvolatile content of the sprayed fluid. Grenko [3] notes the sample panels on the moving belt may be held to the belt with magnets or suction cups. Erichsen [19], Gardner [20],

Fig. 12—Single setting lab spray applicator. (Courtesy of Erichsen GMBH & Co.)

and others offer automated spray applicators for laboratory sample preparation (see Figs. 12 and 13).

The spray technique is particularly important, but precautions are necessary to assure evenness of coating on the substrate. The spray pattern should extend beyond

Fig. 13—Programmable lab spray applicator. (Courtesy of Erichsen GMBH & Co.)

the edges of the substrate when the nozzle is aimed at the center of the target. The spray pattern—be it flat, fan, or circular—has less paint at the edges than at the center. Moving the spray nozzle across the target or the target under the center of the nozzle makes the deposition more likely to be consistent in thickness.

Dip Coating

Dip coating is particularly important in some special cases. For instance, the edge protection of corrodible panels in preparation for the application of a test coating is a common practice. Printed circuit board coatings, including conformal coatings and baseball bats, are other areas that employ this technology. A red lead vinyl 1/2-in. (1.27-cm) dip was successfully used for edge protection of exposure panels, since attack corroded only the desired exposure surfaces [25]. The point is that dipping assures film thickness without holidays and other techniques do not provide such assurance. This is particularly true for odd-shaped test specimens such as fragments of a pressurized gas cylinder and items as mentioned above.

Grenko [3] briefly reviewed two-dip coaters. Bruins [26] first designed a dip coater using a tire pump and needle valve to control the rate of panel withdrawal from the coating, while Payne designed an electric motor-driven device adopted for Method B of ASTM D823. A commercial laboratory device is available from Gardner [20], with variable withdrawal speeds of 2 to 20 in. (~5to ~50 cm) per minute. It can dip a panel of up to 2 lb (0.9 kg) and 1 ft^2 (0.3 m^2) in area—12 by 12 in. (30.5 by 30.5 cm).

Again, care must taken when dip coating. Film thickness control is a battle between wetting surface forces and the shear forces of drainage through the thickness of the film. Drip edges on the bottom edge may be avoided to some degree by having the panel holder inverted to hold the bottom edge upward for a portion (or intermittent portions) of the drying period.

Spin Coating

Grenko [3] described the work of Walker and Thompson [27] attaching a panel to a turntable and rotating for 1 min at 300 rpm to obtain a 25-μm varnish film thickness. He also described the Sward-Gardner [28] relation of film thickness (F) to viscosity (V in poise) and nonvolatiles, % N, as

$$F = 0.4N + V^4 + 3$$

where the spin rate was 290 rpm for 60 s. Their work had a precision of 5% to 10%, and corrections for time or rpm variations were offered. Parker and Siddle [29] suggested modifying the method by adjusting viscosity to equivalence for all fluids to be compared and using volume solids rather than weight percent nonvolatiles. Plots of film thickness versus volume percent nonvolatile were straight lines for nonhixotropic fluids, but curvature existed for thixotropic fluids.

A commercial lab spin coating device is currently available from Erichsen [19]. There are two versions, one with 600-rpm speed set, and another that is adjustable from 50 to 2000 rpm (see Fig. 14).

Fig. 14—Lab spin coating device. (Courtesy of Erichsen GMBH & Co.)

OTHER TIPS ON PRACTICE OF THE ART

Dust is always a problem, especially in formulation laboratories that have pigment dusting in the lab and plant. Cover cast films immediately to keep the dust off. The easiest cover is the top of a box or similar device. Simply cut out 1/2 in. (or ~1 cm) strip from two, three, or four sides for free flow of air. Of course, a similar cover can be made from thin plywood. Keep the cover on top of the lab refrigerator or bookshelf so it is always at hand.

Make sure the film is drying under appropriate temperature and humidity conditions. Something in the formulation may respond in an adverse manner to condensing moisture that can form droplets on the surface as evaporating solvent rapidly cools the system. In moisture-cure and reactive two-package urethanes, the condensing moisture may react with the isocyanates to modify degree of cure, which can reduce strength, solvent resistance, or other properties. In systems that do not react with the condensing water, one may still get pits, pinholes, or haziness from the condensing water droplets on the surface. Paint applicators are learning to pay attention to humidity variation and its effects on the end product surface.

CONCLUSION

How the film is prepared for testing can have a dramatic effect on the test results. The thought put into film preparation prior to preparation and the care used in film formation can be crucial factors in obtaining meaningful and reproducible results.

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Measurement of Film Thickness

John Fletcher[1] and Joseph Walker[2]

PREFACE

IN PREPARATION OF THIS CHAPTER, THE CONTENTS of the 14th edition were drawn upon. The current edition will review and update the topics, introduce new technology that has been developed, and include up-to-date references.

INTRODUCTION

One of the major requirements of paint and coating testing is the measurement and control of film thickness. Ensuring that a thickness specification is achieved is important in laboratory tests, manual paint application, automatic spraying, and other coating application methods, be they solvent based or powder coatings.

A number of test methods are available, and the choice is dependent on: (1) the location—laboratory or site; (2) the material coated—metal (ferrous or nonferrous), wood, plaster, brick, and plastic; (3) the condition of the coating—wet or dry, cured or uncured; and (4) the condition of the surface—rough or smooth, flat or shaped, thick or thin, etc.

WET FILM THICKNESS

The measurement of wet film thickness provides the first opportunity in the coating application process to check the coating thickness. It also offers an assessment of the spreading rate of paints. It is very important that wet film measurements are made as soon as the coating is applied to avoid error due to solvent loss during the curing process.

Reference to the technical data for volume solids in the coating is required to establish the wet and dry ratio so that wet film thickness values can be converted to dry film equivalents. Wet film gages are manufactured from a range of materials, aluminum, stainless steel, etc., and in most cases, wet film thickness gages can be cleaned with solvents and reused. The main exception to this are the notched gages (wet film combs) molded from plastic. Although the materials used, such as loaded ABS, are resistant to many solvents, it is recommended that plastic wet film combs be used only once.

Wet film measurement can be carried out on most substrate materials, both metal and nonmetal. However, the substrate must be rigid and not prone to distortion when the measurement device is applied.

ASTM D1212, Standard Test Methods for Measurement of Wet Film Thickness of Organic Coatings, describes the Inmont wet film gage (formally known as Interchemical gage and commonly known as the Wet Film Wheel) and the Pfund wet film gage. These two gages are detailed in the following sections, as Inmont Wet Film Gage (ASTM D1212 method A) and Pfund Wet Film Gage (ASTM D1212 method B).

ASTM D4414, Practice for Measurement of Wet Film Thickness by Notched Gages, describes a third wet film measurement method using notch gages, which are also known as wet film combs. This method is described in the section called Notch Gage.

Inmont Wet Film Gage (Wet Film Wheel)

The Inmont wet film gage consists of two concentric outer disks with an inner eccentric disk and a smaller diameter positioned between them as shown in Fig. 1. The outer disks are scaled, with the clearance between the inner disk and the outer disk from zero to a maximum value as shown.

The gage is used by placing the disks with the maximum clearance on the specimen of wet coating and rolled toward the minimum clearance on the gage in either direction. The paint will coat the inner disk until the clearance is greater than the wet film thickness. The point at which the coating stops on the inner wheel is referenced to the scale on the outer wheel and the value noted.

Starting from maximum value avoids the possibility of pushing paint ahead of the inner disk, creating an error condition when the gage indicates a value higher than the true wet film thickness. A number of range options are available for the wet film wheel and wheels with notched outer rims are particularly useful for measuring wet films in coil coating, as the notches help to ensure even rotation on the fast-moving substrate.

Pfund Wet Film Gage

As shown in Fig. 2, this gage consists of a convex lens, L, whose radius of curvature is 250 mm, at the lower end of tube T1 that slides in the outer tube T2. Compression springs, S, keep the lens out of contact with the paint film until pressure is applied on tube T1. In making a measurement, the gage is placed on the painted surface and the lens is pushed slowly through the film until stopped by the substrate. The pressure is released, and the diameter of the spot of paint transferred to the lens is measured. A 1-to-1 ratio for the thickness added by the paint displaced by the lens to the actual thickness has been assumed and is accounted for in the equation

$$t = D^2/16R \quad (1)$$

[1] *Technical Support Manager Elcometer Limited, UK.*
[2] *VP Sales & Marketing, Elcometer Inc., Rochester Hills, MI.*

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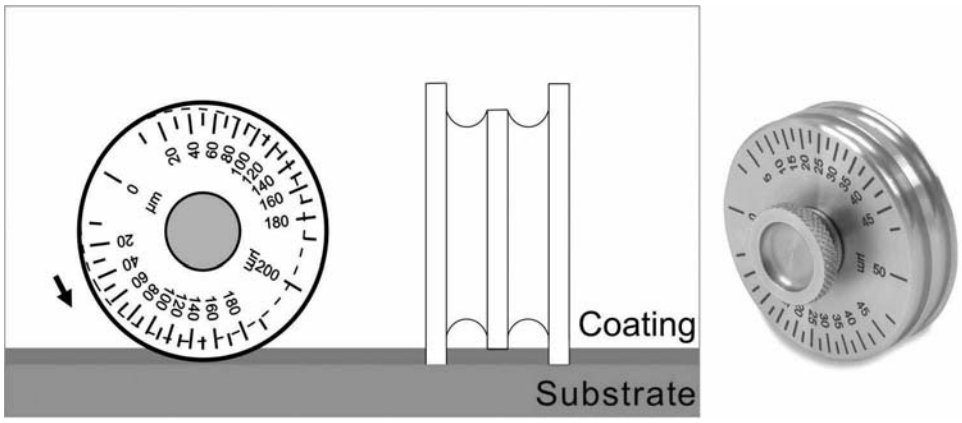

Fig. 1—Inmont gage (Interchemical) wet film wheel schematic diagram (left) and photograph (right).

where D = diameter, mm of spot and R = radius of curvature mm of the lens.

Table 1 gives film thickness and the corresponding spreading rate in square feet per gallon for spots from 3 to 38 mm in diameter.

It has been observed that a substantial proportion of paints do not obey the 1-to-1 relationship. The actual thickness, obtained by independent methods, may be several times, or only a fraction of, the thickness calculated by the equation. A small amount of thinner added to a paint may increase the diameter of the spot on the lens and give a corresponding increase in the calculated thickness. This phenomenon has been ascribed to the effects of surface tension. Hence, for best results, a correction factor should be established for each type of paint based on the known thickness of a freshly prepared film measured by the Inmont gage.

Reproducibility is within about 2 % for films 2 mils (50 μm) thick, decreasing to about 10 % for films 5 mils (125 μm) thick, and then becoming better as thickness increases.

Notch Gage (Wet Film Comb)

Notch gages (wet film combs) are formed on the edge of a strip of material so that each notch has a different clearance from the reference shoulders to that of its neighbors (Fig. 3). Many different materials are used to make these gages, such as stainless steel, aluminum, and plastic, in a variety of shapes: square, rectangle, triangle, hexagon, etc.

The Notch gage is a simple low-cost device, which is useful when approximate values of wet film thickness are satisfactory, as the notches have discrete values and are not continuous across the range of thickness. The gage is dipped vertically into the film until the reference shoulders are resting firmly on the substrate. The thickness of the film is between the highest coated notch or tooth face and the next highest, uncoated, value.

Several different methods of manufacture of these gages exist from spark-eroded stainless steel precision combs, through punched aluminum sheet, to plastic flow molded combs. The stainless steel combs can be certified with measurements of the tooth displacements, which are

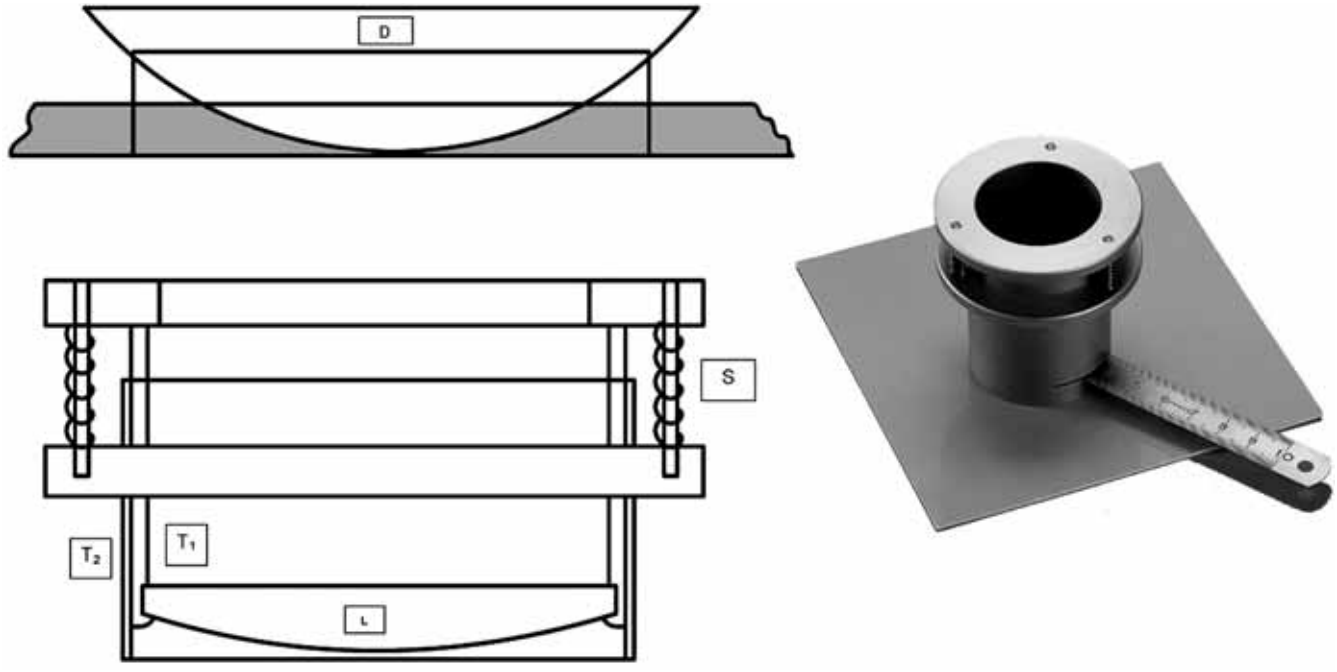

Fig. 2—Pfund gage schematic (left) and photograph (right).

TABLE 1—Spreading rate by Pfund film gage				
Diameter of the spot in mm	**Thickness of coat (mm)**	**Painted Coat (m^2/litre)**	**Painted Coat (sq.ft./US Gallon)**	**Painted Coat (sq.ft./imp. Gallon)**
3	0.00225	445	18.088	21.800
4	0.00400	250	10.175	12.250
5	0.00625	160	6.512	7.840
6	0.00900	111	4.522	5.440
7	0.01225	81.6	3.321	4.000
8	0.01600	62.5	2.543	3.340
9	0.02025	49.5	2.009	2.425
10	0.02500	40	1.628	1.960
11	0.03025	33	1.350	1.640
12	0.03600	28	1.130	1.372
13	0.04225	24	963	1.176
14	0.04900	20	830	980
15	0.05625	18	723	880
16	0.06400	15.6	636	765
17	0.07225	13.8	563	676
18	0.08100	12.3	502	603
19	0.09025	11	450	548
20	0.10000	10	407	490
21	0.11025	9.07	369	443
22	0.12100	8.26	336	405
23	0.13225	7.56	307	370
24	0.14400	6.95	282	340
25	0.15625	6.40	260	313
26	0.16900	5.92	241	290
27	0.18225	5.49	223	268
28	0.19600	5.10	207	250
29	0.21025	4.76	192	233
30	0.22500	4.44	180	218
31	0.24025	4.16	169	204
32	0.25600	3.90	158	192
33	0.27225	3.67	149	180
34	0.28900	3.46	141	169
35	0.30625	3.26	133	160
36	0.32400	3.08	125	152
37	0.34725	2.82	117	138
38	0.36100	2.77	113	129

traceable to national standards. As the stainless steel is hard wearing, this certificate can be valid over a period of up to one year. On the other hand, plastic combs, although manufactured from solvent-resistant ABS plastic, should only be used once as the solvent in the coating may soften the plastic. Plastic combs can be tagged and kept as a permanent record of wet film measurement.

Aluminum combs are prone to wear, and the condition of an aluminum wet film comb should be carefully checked before use.

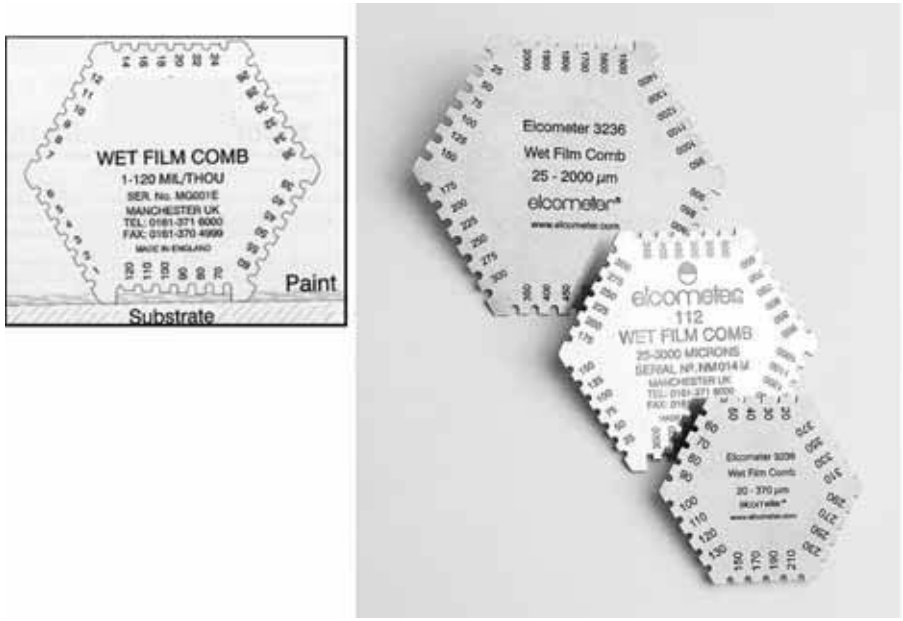

Fig. 3—Wet film comb schematic (left) and photograph (right).

Wet film gages are available covering many ranges, from 0.5 mil (2.5 μm) to 160 mils (4 mm/4000 μm). The teeth are normally square ended, but for thicker coatings pointed teeth are sometimes used.

Notch gages are supplied by various coating equipment suppliers, e.g., Elcometer Inc., Paul N Gardner, etc. and are fully described in ASTM D4414, Practice for Measurement of Wet Film Thickness of Organic Coatings by Notched Gages.

ASTM D4414 describes methods; Method A uses a square or rectangular notch gage made from a thin rigid material, and Method B uses a circular notch gage made from a thin rigid material.

Needle Micrometer

This method was used to study the relationship between the clearance of a doctor blade and the thickness of the wet film left by the blade [1]. A needle is attached vertically to the objective holder of a microscope. The barrel is lowered until the needle just touches the film that has been spread on a plain metal panel. The contact is observed through a horizontal microscope. When contact is made, the needle and its image reflected by the film just meet. The needle is then lowered into the film until it just touches the metal panel. This contact is noted by the deflection of a galvanometer in series with the panel, a dry cell, and the needle. The thickness of the film is calculated from the number of turns made by the focusing screw of the vertical microscope between the two points of contact.

It should be noted that this technique is only applicable to measurements made in a laboratory, as it is impractical for work on site. The equipment is no longer available but may still be in use in certain laboratories.

DRY FILM THICKNESS (DESTRUCTIVE METHODS)

As there are many circumstances under which coatings and paints are used with many different materials as the substrate, no single method of dry film thickness measurement is universal. Some methods are destructive, and these are most often used when nondestructive methods cannot be applied. The following sections describe the use of the Micrometers and Dial Gages, the Gardner Needle Thickness Gage, the Gardner Carboloy Drill Thickness Gage, and the Gardner Gage Stand and the Gardner Micro-Depth Gage.

Micrometers and Dial Gages

When a chip or flake of coating is freed from the surface of the coated object, its thickness can be measured directly using a micrometer. Alternatively, the total thickness of the substrate and coating can be measured; the substrate can then be re-measured after removing the coating with a scraper or solvent. The coating thickness is then the difference between the two measurements. This "before and after" coating measurement is also the basis of the method for manufacturing coated thickness standards.

ASTM D1005, Test Method for Measurement of Dry-Film Thickness of Organic Coatings using Micrometers, describes four methods as follows:

Procedure A—Stationary micrometer for measuring coatings applied to plane rigid surfaces.

Procedure B—Stationary micrometer for measuring free films.

Procedure C—Hand-held micrometer for measuring coatings applied to plane rigid surfaces.

Procedure D—Hand-held micrometer for measuring free films.

Procedures A and C require the thickness of the test panel and film to be measured and then the film is removed to allow just the thickness of the test panel to be measured. The difference between the two thickness values is then calculated and reported as the film thickness. It is also possible to measure the uncoated test panel in selected and identified locations before the coating is applied and the combined test panel and dry film measured together at the locations used for the initial measurements.

Procedures B and C require the preparation of free films as outlined in ASTM D2370 and detailed in ASTM D823.

Fig. 4—Dial micrometer.

Procedure D, using a hand-held micrometer mounted on a support with a clamp to hold the specimen (see Fig. 4), is recommended only for thicknesses over 0.5 mil and is accurate to ±0.1 mil.

A hand-held dial coating thickness gage (Fig. 5), may be used to measure coated samples. In this case the dial records the difference in position between the foot that sits on the surface of the coating and the stylus with its ball end, which passes through a hole prepared in the coating to the surface of the substrate. This is particularly useful for site work. However, for best accuracy and precision, the mounted dial gage specified in ASTM Method D1005 is preferred.

Gardner Needle Thickness Gage

This instrument is designed to measure the thickness of electrically nonconducting films on metal (conducting) substrates. It is small enough to be used in the field where the substrate can be made part of the electric circuit. The needle makes only a minute puncture in the film. In many instances, particularly in a go-no-go determination, the damage is so slight that the method may be considered nondestructive for many end users.

The aluminum housing case contains the needle screws for forcing the needle through the film and a lamp to signal when the needle contacts the substrate. For use in the field and for occasional use in the laboratory, the electric circuit comprises the needle, the substrate, a dry cell, the lamp, and a cord that connects with the substrate. In the laboratory, if many measurements are to be made, it is advisable to use a step-down transformer and to connect to a 110 V source.

The thickness is read on a dial attached to the screw. One turn of the dial raises or lowers the needle by 2 mils. The dial is graduated in steps of 0.05 mil. Range is 0 to 15 mils.

Fig. 5—Dial type coating thickness gage.

The zero setting of the needle is obtained by retracting the needle within the housing, placing the gage on a plane metal block, and lowering the needle until the lamp signals contact. The specimen replaces the block and the needle is lowered until the lamp again signals contact. The difference between the two readings is the thickness of the film.

Gardner Carboloy Drill Thickness Gage

In many instances films are so hard that they successfully resist penetration by the needle penetrometer described above. This difficulty has been overcome by substituting a Carboloy drill for the needle. The drill is a needle terminating in a pyramid having three faces. The drill is secured in a chuck that can be rotated and advanced independently. The rotation is controlled by finger action on a knob at the upper end of the chuck shaft. In all other respects, the operation is the same as that of the needle gage. This method is not now widely used.

Gardner Gage Stand

Although the Gardner needle gage and the Carboloy drill gage may be operated by manually holding the gage against the specimen, using the Gardner gage stand is less tiring and more accurate, especially when many measurements are to be made. The stand provides constant known pressure [up to 10 lb (5kg)] on the specimen and ensures that the needle or drill is always perpendicular to the specimen.

Gardner Micro-Depth Gage

Although in outward appearance this gage resembles the gages described in the last two subsections, only the

establishing of the zero setting is the same. Measurement is not restricted to nonmetallic films on metal—any type of film on any type of substrate may be measured, and the film is always damaged.

In this gage, a chisel replaces the needle of the gage. The zero setting having been established, the chisel is advanced by an amount estimated to be less than the thickness of the film. The gage is placed on the specimen and drawn toward the operator through a distance of a few millimeters. If the scratch made by the chisel does not penetrate the film, the chisel is advanced by a small increment, and another scratch is made. The procedure is repeated until the substrate is reached and exposed. Inspection is best made with the aid of a low-power magnifier. The range is 0 to 40 mils (1000 μm). Repeatability depends on the magnitudes of the increments and the compressibility of the film and substrate. For example, specimens with poor adhesion may be torn off, exposing the base, even if the chisel does not penetrate the film.

Microscope for Film Thickness

CLASSICAL METHOD

To use a microscope to assess film thickness, a section is prepared and the width of the coating is measured using a graticule in the eyepiece of the microscope. For an approximate assessment, a flake of the coating can be used, but for best results from this method the specimen should be prepared as follows.

The specimen is mounted in a block of wax. The face of the mount is cut or ground to a smooth surface. The prepared specimen is then inspected under the microscope.

BRIGHTWELL METHOD

This method does not require removal of a chip and elaborate mounting and preparation [2]. A tiny furrow is made in the film or a small chip is removed. A prism or ribbon of light is projected on the selected area at an angle of 45°. The distortion of the beam is examined with a microscope equipped with a micrometer eyepiece. Apparatus for this is available in the Schmaltz optical surface analyzer (Carl Zeiss).

The apparatus is calibrated by measuring known depths milled in a smooth metal block. The ribbon of light is focused on line A, and the filar micrometer reading is recorded. The procedure is repeated on line BC. The difference multiplied by the calibration factor equals the thickness of the film.

STOPPED METHOD

A cut is made in the film with a sharp knife. The microscope is focused, in turn, on the upper and lower edges of the cut. The thickness of the film is computed from the vertical adjustments of the microscope [3]. If the value is not known, it may be found as follows: Put a piece of plate glass on the stage. Lower the tube until it just touches the plate. Record the reading of the fine adjustment. Now raise the tube as far as possible and again record the fine adjustment. Now raise the tube as far as possible and again record the fine adjustment.

The distance of the tube from the plate divided by the number of turns of the adjusting screw gives the value for each turn.

TOOKE INSPECTION GAGE (PAINT INSPECTION GAGE)

ASTM D4138, Standard Test Methods for Measurement of Dry Film Thickness of Protective Coating Systems by Destructive Means, describes three methods as follows:

Test method A: Using grove cutting instruments
Test method B: Using grinding instruments
Test method C: Using drill bit instruments

The Tooke Inspection gage [4], also known as the Paint Inspection Gage (Fig. 6), provides for estimating the thickness of a film from the geometry of a V-groove cut in the film by a special tool. With the aid of a ×50 illuminated magnifier equipped with a reticle in the eyepiece, the operator measures the lateral distance from the top edge of the cut and the projection of the intersection of the cut and the substrate. To make a measurement, a "bench mark" of ink applied to the surface of the film serves to make the top edge of the cut readily visible. A short cut is then made at a right angle to the benchmark with the selected cutting tip. Film thickness is then obtained by counting the scale divisions as described previously.

SÄBERG DRILL

ASTM D4138 Test method C is similar to the method described in the previous subsection; however, a circular drill is used to penetrate the film. The hole can then be

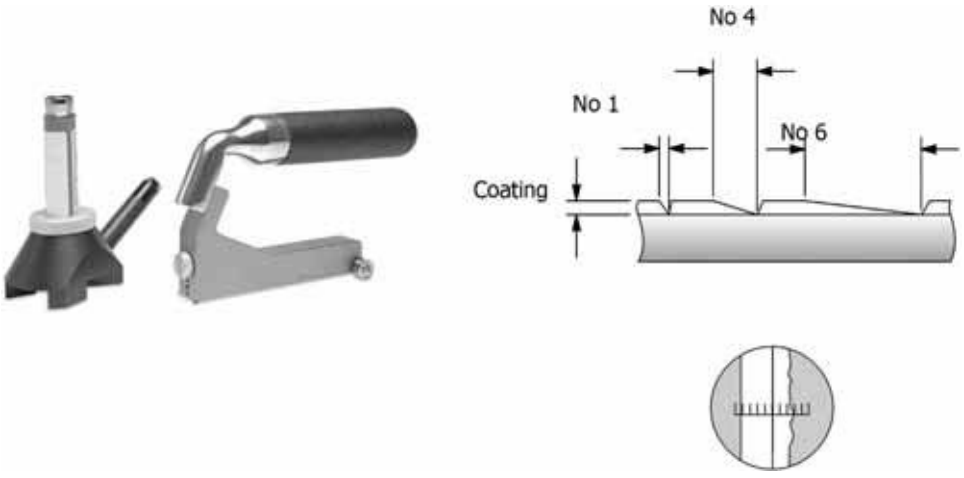

Fig. 6—Paint Inspection Gage (Tooke gage) with section through coating and view through the microscope.

Fig. 7—Säberg Drill.

inspected using the ×50 magnifier with graticule, and the width of the cut from the outer edge to the print where the drill penetrates to the substrate is a measure of the coating thickness. For the Säberg Drill illustrated in Fig. 7, the calculation of coating thickness is as follows:

1. For measurement in micrometers, multiply graduations by 20.0.
2. For measurement in mils, multiply graduations by 0.79.

DRY FILM THICKNESS (NONDESTRUCTIVE METHODS)

There are two main groups of gages for the nondestructive measurement of dry films on metal substrates and these are the permanent magnet gages, which can be used for coatings on magnetic metal substrates and electronic gages, which can be used for coatings on ferro-magnetic substrates, such as steel, nonferrous metals and where ultrasonic measurement methods are used on some nonmetal substrates. The following sections describe the Permanent Magnet Thickness Gages, the Electronic Thickness Gages with some of their features and limitations, and Ultrasonic Gages.

Permanent Magnet Thickness Gages

Permanent magnet coating thickness gages can be used to determine the thickness of films applied to magnetic substrates such as steel, iron, magnetic stainless steel, etc., providing that the coating is nonmagnetic. Materials such as nickel and cobalt, which are naturally magnetic, have to be treated with care, while paints containing magnetic particles, such as some ferrous micaceous iron oxide, can cause errors when using magnetic gages, both mechanical and electronic.

Simple magnetic coating thickness gages, also known as pull-off gages, use the principle that the attractive force between a permanent magnet and the magnetic metal substrate is inversely proportional to the distance between them.

The principal limitations are (1) the film must be sufficiently hard to prevent indentation, and (2) the film must not be tacky, causing the magnet to be held by the surface of the coating.

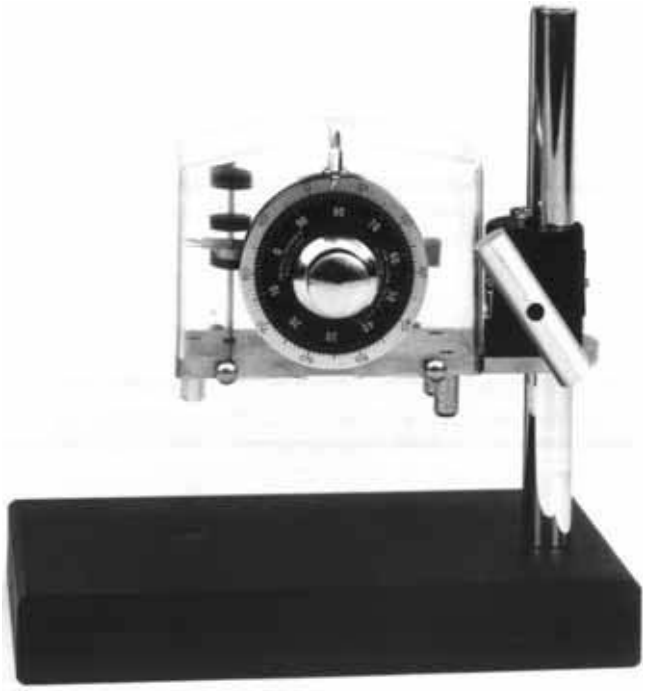

Fig. 8—Magne-Gage. (Courtesy of Magne-Gage Sales & Service Co., Inc.)

Electronic magnetic coating thickness gages are also available, but these will be described in a separate section entitled Electromagnetic Thickness Gages; this section includes the electronic gage based on the magneto-resistor (Hall-effect) probe.

MAGNE-GAGE

This instrument (Fig. 8) consists of a small permanent bar magnet, 2 mm in diameter, suspended from a horizontal lever arm [5]. The arm is actuated through a spiral spring by turning a dial. The tip of the magnet is brought into contact with the paint film (on iron or steel), and the dial is then turned until the magnet is detached. The attractive force between the magnet and the film support is indicated on the dial, and the thickness of the nonmagnetic paint film is obtained from a calibration curve relating thickness to dial reading.

The Magne-gage can be used to measure coatings on convex and concave surfaces as well as on flat ones provided the radius of the curvature is not too small. Unless special calibrations are made, cylinders should not be less than 1/2 in. (1.27 cm), in diameter spheres not less than 3/4 in. (1.9 cm), and flat pieces should be at least 3/4 in. (1.9 cm) square.

Magnets for thicknesses in the following ranges are available: 0.0 to 0.002, 0.002 to 0.007, and 0.007 to 0.025 in.

Within ASTM D7091 (Standard Practice for Nondestructive Measurement of Dry Film Thickness of Nonmagnetic Coatings Applied to Ferrous Metals and Nonmagnetic, Non-conductive Coatings Applied to Non-Ferrous Metals) the Magne-gage is described as a Type 1 or magnetic pull-off gage. It should be noted that the Magne-gage is not now in common use but the apparatus is still available in the USA.

Fig. 9—Magnetic coating pull-off thickness gage.

HAND-HELD MAGNETIC PULL-OFF GAGES

Electronic gages are superseding the mechanical gages, and some—such as the Tinsley gage and the chemigage—are no longer manufactured. However, many thousands of these Type 1 gages are still in use, so it is appropriate to describe them.

The simplest form of these gages contains a magnet suspended from a coil spring housed in a pen-style body manufactured from aluminum or plastic. A scale is drawn on the body and a marker is used to indicate the extension of the spring on the scale. The reading on the scale when the magnet lifts off the surface corresponds to the thickness of the coating.

The scale on these instruments is nonlinear, leading to low reading resolution at the maximum range, usually 20 mils (500 μm), and great care must be taken to ensure that they are used vertically to avoid the influence of gravity on the spring-magnet combination. Some of these types of gages have design features to overcome the gravity effect when the gage is used horizontally.

The accuracy of this type of gage is typically ±15 % of the readings and therefore these gages do not satisfy the accuracy requirement of ASTM D7091.

A common form of the hand-held magnetic pull-off gage is shown in Fig. 9. A balanced beam with a magnet fitted to one end and counterbalanced by a brass weight at the other is attached at the pivot to a helical spring. The other end of the spring is attached to a ring holding the scale. Rotation of the ring raises or lowers the magnet. This type of gage is described in ASTM D7091 as a Type 1 gage.

The gage is placed on the surface to be tested in any orientation as the balance weight ensures that gravity effects are neutralized. The ring or scale wheel is pushed forward (anticlockwise rotation) to bring the magnet in contact with the coating and to set the scale to a maximum reading. The ring or scale wheel is then rotated clockwise until the magnet breaks free, the thickness of the coating being indicated by a pointer.

This type of gage is calibrated against plated standards available from NIST, and accuracy against these standards of ±5 % of reading is achieved. It should be noted that the steel used to make NIST standards is not always representative of engineering steels, and therefore a practical operating accuracy of ±10 % is obtained in the field unless coated standards using steel that is typical of the substrate on which the coating is applied can be used to verify the accuracy of the gage for the specific application.

THE MAGNETIC RELUCTANCE GAGE

The coating thickness gage based on the magnetic permeability principle (Fig. 10) is one of the first magnetic thickness gages to be commercially available, having been patented in 1948. The magnetic flux from a permanent magnet acts on an armature suspended in between two magnetic arms of the unit, forming north and south poles. The turning moment of the magnetic flux is countered by a helical spring, and the magnitude of the magnetic flux changes with the distance between the tips of the magnetic arms (ball feet) and the substrate beneath the coating, i.e., the coating thickness. A pointer attached to the armature indicates the thickness of the coating. Gages covering thickness ranges from 0 to 3 mil (0 to 80 μm) to 0 to 0.75 in. (0 to 18 mm) are still available. The accuracy of this type of gage is typically ±10 % of the reading and these gages do not, therefore, meet the requirements of ASTM D7091. However, this type of gage is useful where electronic gages cannot be used, for example in places where flammable vapors are present or underwater.

Electronic Coating Thickness Gages

Electronic coating thickness gages use the electromagnetic induction principle or the Hall effect to measure nonmagnetic coatings on magnetic substrates or the eddy current principle to measure nonconductive coatings on non-ferrous metals. Gages can also make use of the Hall effect to measure coatings on magnetic substrates.

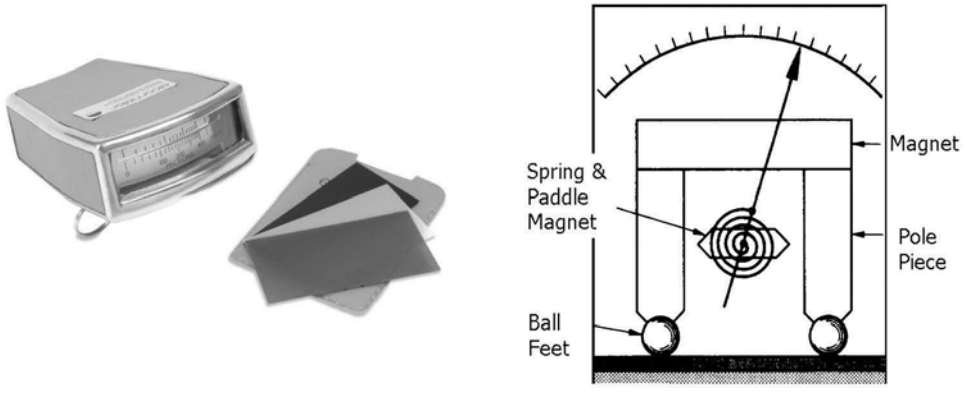

Fig. 10—Magnetic reluctance coating thickness gage.

ELECTROMAGNETIC INDUCTION PROBES

The electromagnetic induction method for measuring film thickness is based on the effect of a magnetic metal substrate on the balance of the alternating magnetic field in the probe tip, generated in the probe by a signal applied to the central coil that has two neighboring search coils.

When the probe is away from the influence of the substrate (free-air condition), the net voltage output from the two search coils tends to zero. As the substrate is brought toward the tip, the field is increasingly out of balance between the two search coils until, with the uncoated substrate in contact with the tip, the net voltage output from the coils tends toward V max.

The voltage output from the probe can be amplified and calibrated and then used to display a thickness value. Three types of electronic coating thickness gages have been developed on the basis of this probe technology using analogue, digital, and microprocessor electronics. ASTM D7091 describes these gages as Type 2 gages.

EDDY CURRENT PROBES

The eddy current method for measuring film thickness is used to measure coatings on nonferrous metals. It is based on the effect that a high-frequency alternating field (~3 000 000 Hz or 3 MHz) has an electrically conductive surface causing highly localized current (eddy currents) to flow. These currents generate their own magnetic fields, which influence the impedance of the coil, generating the high-frequency field. The magnitude of these changes is proportional to the distance from the probe coil to the substrate, that is, to the thickness of the coating.

This type of gage is also described as a Type 2 gage in ASTM D7091.

Calibration adjustment by adjustment to zero and to a known thickness on a piece of metal of the same type, shape, and thickness as the samples to be measured is vital to ensure accuracy. Modern eddy current instruments are available using microprocessor designs and some of these designs offer the facility for a dual-purpose ferrous (F) electromagnetic induction and nonferrous (N) eddy current principle combined in a single probe. Using the dual FNF probe, the gage can be made to measure automatically on either type of substrate, with the gage displaying the substrate type, F or N, when the measurement is complete and the reading displayed.

This type of gage can be used to measure paint galvanizing on a steel substrate. The F probe is used to measure the total thickness of the zinc and the paint on the steel and, if the zinc layer is 2 mil (50 μm) or greater, the N probe can be calibrated to measure the paint thickness only. By subtracting the paint thickness from the total thickness, the thickness of the zinc (galvanizing) can be estimated.

HALL EFFECT PROBES

This type of gage makes use of a probe that combines a permanent magnet with a Hall-effect semiconductor sensor a signal, which varies with the intensity of the magnetic field. The strength of the magnetic field is influenced by the distance of the magnetic substrate from the tip of the probe, i.e., the thickness of the coating.

The scale of these gages is nonlinear and they use either an analogue meter movement or digital electronics to indicate the thickness. In operation it is necessary to set zero on the uncoated metal and calibrate to a thickness of known value to obtain the best accuracy, as with other electronic gages.

These gages meet the requirements of ASTM D7091 and are also described as Type 2 gages.

ANALOGUE COATING THICKNESS GAGES

The simplest form of electronic coating thickness gage uses a nonlinear scale on a meter movement to display the voltage output from the probe against a thickness scale. These gages are now relatively expensive to manufacture and have almost completely been replaced by digital gages, although some of these gages may still be in use in the field.

In common with most electronic coating thickness gages, calibration adjustment to the substrate to be tested is required. Setting the needle to zero with the probe on the uncoated magnetic metal substrate and then setting the upper scale point, using the calibration control, with the probe on a known thickness of coating, will adjust the gage for use on surfaces typical of the uncoated metal substrate used.

Two forms of thickness standard are in common use: (1) the pre-coated type, which can be the plated type, as illustrated by the standards available from NIST, or the hard-wearing epoxy coating applied to metal substrates of known thickness type, and (2) the measured and unmeasured plastic shims available commercially from gage manufacturers. In many applications the plastic shims are preferred as the thickness standards for calibration adjustment because they can be used as a sample of the uncoated substrate to be measured, reducing the errors of calibration adjustment due to surface finish, curvature, substrate composition, and thickness of the substrate. More details of these sources of error are given later in this chapter under the heading "EFFECTS OF SURFACE FINISH, CURVATURE AND SUBSTRATE COMPOSITION ON ELECTROMAGNETIC AND EDDY CURRENT MEASUREMENTS."

DIGITAL COATING THICKNESS GAGES

Advances in electronic components and instrument design techniques over the last 30 to 40 years have made it possible to significantly reduce the size of coating thickness gages while retaining and enhancing the features users find necessary in their applications. The use of digital electronics means that the voltage output from the probe can be converted to a numerical value early in the processing of the signal, thus reducing the effects of temperature changes and component drift on the accuracy of the result. It is also possible to use a linear scaling, making it possible to have a fixed resolution over the full range of the instrument scale although resolutions are often enhanced in the 0 to 125 or 0 to 250 μm (0 to 5 mil or 0 to 10 mil) ranges.

It should be noted that this type of product has been superseded by microprocessor-based designs, although some digital gages are still being used. The same principles of calibration adjustment apply to digital electromagnetic coating thickness gages as they apply to the analogue types, and accuracy capabilities of ±5 % of readings are readily achieved using digital gages in the field.

MICROPROCESSOR ELECTROMAGNETIC THICKNESS GAGES

The application of microprocessor electronics to the design of portable coating thickness gages has made it possible to improve the accuracy and reproducibility of these

Fig. 11—Microprocessor electromagnetic thickness gage.

instruments as well as allowing developments in range, special calibration techniques for rough surfaces, memory of readings, statistical calculation, printouts and data transfer.

In a microprocessor design, the characteristic of the probe voltage output against coating thickness value is stored in the memory of the instrument for many values over the range of the probe. The actual voltage output from the probe is digitized and then compared with the stored values. A thickness value is then calculated from these data and displayed. This is typically achieved in 0.3 s. Using this technique, accuracies of ±3 % of reading are possible. A simple form of this gage is shown as Fig. 10. Note that this gage has no user adjustments and this simple operation is made possible by a factory calibration to the specific requirements of the automotive industry for which it was designed.

As a microprocessor instrument is in effect a dedicated computer, many calculations can be performed on the data, and features such as correction for temperature changes, storage of calibration conditions and corrections to these calibrations, averages, and other statistical values can be included in the instrument's firmware.

Fig. 11 illustrates one of these microprocessor-based electromagnetic thickness gages that have memory-operated features such as a large reading memory, statistics, printout and data transfer.

Fig. 12—Dual microprocessor electromagnetic coating thickness gage.

Fig. 13—Coating Thickness Gage with Hall Effect probe. (Courtesy of DeFelsko Corporation)

Fig. 12 illustrates the current trend in microprocessor design with a dual microprocessor coating thickness gage. This unit has a microprocessor to control the gage, display the readings, perform the calculations, and provide data transfer with a second microprocessor, contained in the separate probe electronics, so that the probe can be individually characterized to thickness standards for optimum accuracy, ±1 % or ±1 μm, whichever is the greater, across the full thickness range of the probe.

Fig. 13 illustrates a coating thickness gage with the Hall effect type probe.

The use of microprocessor electronics also makes it possible for a single gage to make use of a wide variety of probes with different ranges, different formats, and different access capabilities. In general, the greater the thickness range of a probe the larger the physical size of the probe.

EFFECTS OF SURFACE FINISH, CURVATURE, AND SUBSTRATE COMPOSITION ON ELECTROMAGNETIC, EDDY CURRENT, AND HALL EFFECT MEASUREMENTS

The accuracy of coating thickness measurements carried out using the methods described above depends on the technique used in adjusting the gages for the conditions of the measurement. The major influences on the adjustment of these gages are surface finish, curvature, thickness, and material composition of the substrate. In the case of magnetic substrates the substrate material composition will influence the magnetic properties and hence the calibration of the gage. In the case of nonferrous metals the effect is that different materials will have different electrical conductivity, which will influence the generation of eddy currents and the resulting calibration adjustment.

Surface Finish

A variety of surface finishes are to be found on metal to which a protective or decorative coating is to be applied. In some cases the coatings used require an anchor pattern

of profile depth, which forms a part of the specification. Comparators such as the Keane-Tator Surface Profile Comparator or the International Standards Organization ISO 8503 are used to determine the surface finish after shot or grit blasting. Also Testex Tape and the Elcometer Surface Profile Gage can be used to measure peak-to-valley heights of profiles. These instruments are shown in Fig. 14.

Surface finish also influences the calibration adjustment of a coating thickness gage, as the mass of the metal directly beneath the probe is reduced by the effects of shot and grit blasting and the probe tip sits on the highest peaks of the profile. This has the effect of increasing the value of thickness indicated using a gage calibrated on a smooth surface by as much as 1.5 mils (35 μm) at 4 mils (100 μm) coating thickness for the highest values of profile.

It is possible to use a rough surface calibration technique to eliminate this error and make the instrument read the correct value of coating thickness over the peaks by using the statistical power of the microprocessor type gages to calibrate on the profile. This is achieved by using a thin foil 1.0 mil (25 μm) over the profile to set the lower calibration point and a thicker foil 5.0 mils (125 μm) or 10.0 mils (250 μm) to set the upper value over the profile. The instrument will then indicate the thickness over the peaks for the coating between the values of foil chosen.

This method is most accurate and reproducible when 15 to 20 readings are taken on each calibration foil to establish a mean value and the mean value is then reset to the correct value of the foil. Trials have shown that the mean of 15 to 20 readings taken over an area of coating give a mean value within a few percent of the actual value over peaks determined by sectioning.

The method does not, however, take into account situations where access to the substrate is not possible for calibration purposes. In this case, the method described in SSPC PA2 where a correction value is applied to readings taken using a smooth surface calibration in the instrument is more appropriate. This method is also described in EN ISO 19840. For either case it is important to agree with the method before measurements start to avoid discrepancies in reporting.

Curvature

The shape and metal wall thickness can also influence the accuracy of the calibration. The degree to which a particular gage is affected depends on the design of the probe. Most modern instruments exceed the limits identified in SSPC PA2.

The effect of shape is most evident when taking readings on an uncoated sample. With an instrument calibrated on a smooth piece of metal 0.125 in. (3.175 mm) thick, changes of more than 0.2 mil (5 μm) in the reading at zero will be seen on curves with a radius below 0.12 in. (3 mm) convex or 0.96 in. (25 mm) concave on a typical

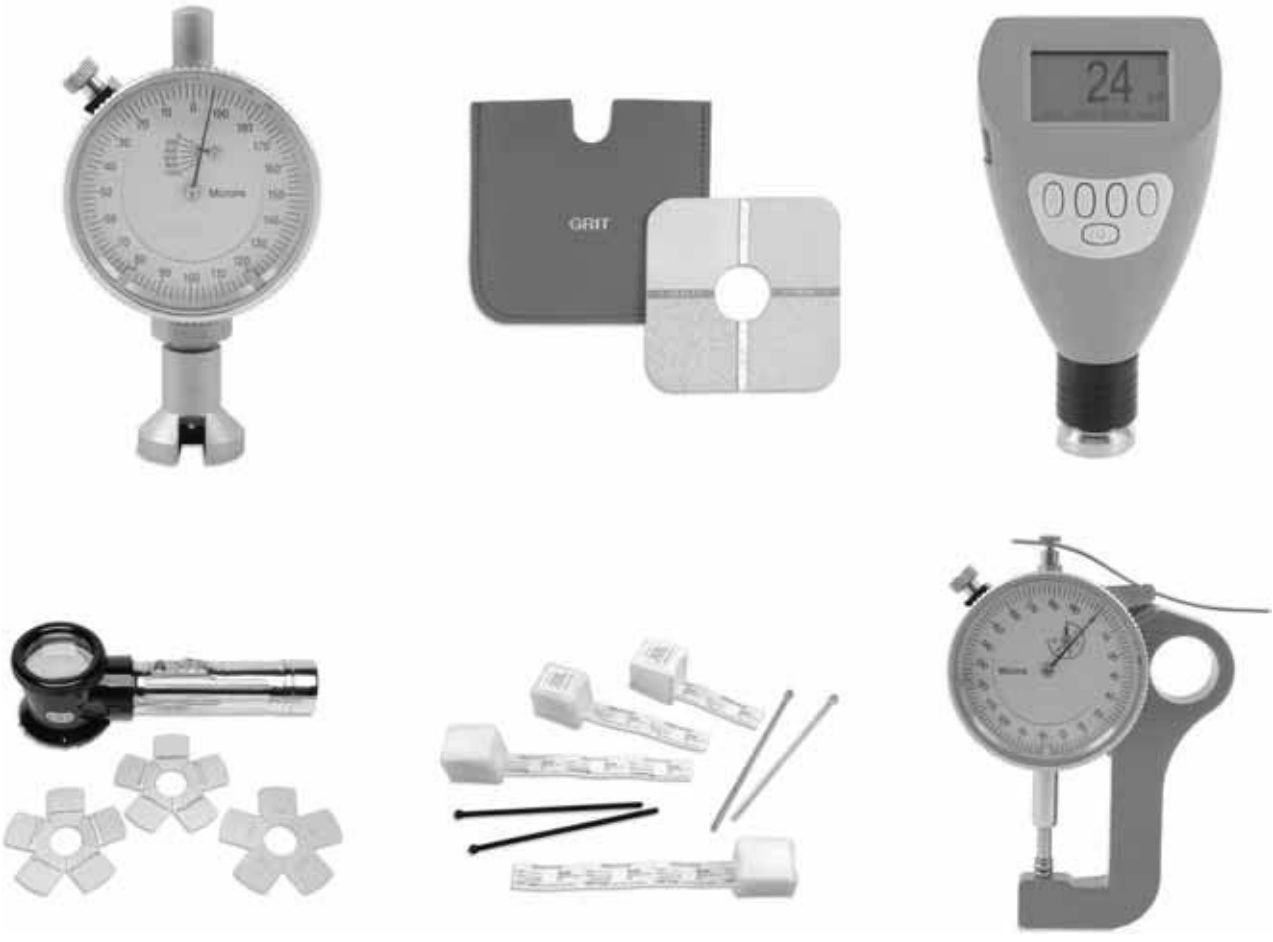

Fig. 14—Surface profile gages.

electromagnetic induction probe. Values will vary between manufacturers and from different probe types.

This error can also be eliminated by calibration on a shape closely representing the specimen to be tested. However, it should be noted that once below the values of curvature indicated in the manufacturer's literature, changes in curvature have a significant effect on calibration, i.e., the calibration on a shape will not be applicable to another shape.

Substrate Thickness

The minimum thickness of substrate required to provide stable readings will vary with the type and design of probe. Typically both F and N probes can be used on substrates down to 6 mil (300 μm). Special gage adjustment techniques can be used to measure on substrates thinner than this value but it should be noted that flexing of these thin substrates also changes the measurement condition and support from a solid nonmetallic base may be required.

Measurement close to the edge of a substrate can also lead to errors. A good rule of thumb for electronic gages is that the area to be measured should be at least the same as the total area of the probe face. The performance of the gage and probe close to an edge can be determined by noting the change in the zero value on an uncoated sample as the probe is brought closer to the edge of the sample. The zero reading will start to increase as the edge effect comes into play.

Substrate Composition

In the case of electromagnetic induction probes, most are insensitive to the differences between the majority of steel specifications in general engineering use. However, when high-carbon steels are coated, the carbon content sufficiently alters the magnetic properties of the steel to cause the normal calibration curve applied within the instruments to be in error with respect to linearity. Thus, an instrument calibrated at zero and say 5 mils (125 μm) may have an error at 2 mils (50 μm) of more than 0.2 mil (50 μm), or 10 %. A similar effect can be seen with some cast irons.

This error can be overcome by calibrating as for the rough surface described in the section earlier in this chapter entitled "Surface Finish." For best accuracy, choose a foil just below the expected coating thickness value for the lower calibration points and a value well above the expected coating thickness value for the upper calibration point.

When coatings applied to nonferrous metals are being measured using eddy current techniques, the composition of the substrate and its effect on electrical conductivity are the important factors with respect to calibration. Materials such as aluminum and copper have very similar characteristics and similar calibration values. However, zinc, brass, and other nonferrous metals and alloys have different characteristics, and calibration on an uncoated sample is essential. Differences of up to 2 mils (50 μm) can be seen between "zero" with an aluminum calibration and zero on a brass component.

D7091 explains calibration, adjustment, and verification for dry film thickness gages. Calibration of a coating thickness gage is normally carried out by the manufacturer of the gage or an authorized laboratory using a documented procedure and thickness standards that are traceable to a National Metrology Institute. The frequency of such calibration is determined by the quality assurance procedure of the user, particularly when operating to a quality management system that is independently audited such as ISO 9001. The re-calibration period for gages within such a system will be specified and is typically 12 months.

The adjustment of a dry film thickness gage is a procedure to minimize the errors caused by the conditions under which the measurements are to be made. These include the topics covered in the paragraphs above, surface finish, curvature, substrate thickness, and substrate composition but may also include issues such as the temperature of the substrate or the prevailing climatic conditions.

The verification of a coating thickness gage should be carried out by the user before the gage is used to measure the work in hand by checking the accuracy of measurements on known thicknesses standards, preferably on a sample of the substrate that is typical for the work that is being coated. The gage must be verified for the range of thickness for which it is to be used and if the gage readings are outside the combined accuracy of the coating thickness standards and the manufacturer's accuracy specification for the gage, then the gage should be sent for re-calibration and repair should that be required to restore the correct calibration.

STATISTICS IN FILM THICKNESS MEASUREMENT

As many random variations can be expected in a coating process, it is appropriate to classify the thickness of the coating using a statistical analysis. In fact, many national specifications utilize a statistical approach in recognition of these variations, e.g., SSPC PA2.

The sources of these variations are many, and only a few examples can be cited here—operator error in taking the measurement, recording error, variation due to surface or curvature or composition, local variation in substrate due to local heat treatment or due to forming or working the metal, inclusions in the metal or in the coating, etc.

The influence of these factors can be greatly reduced by taking a statistically significant number of readings for each area of the coating to be tested. This group of readings can then be summarized using mean and either standard deviation or range to show the average and the spread of readings about the average.

A statistically significant number of readings would be 20 to 50; however, if the process is under statistical control as defined, five readings in each group or subgroup are sufficient.

Many of the microprocessor-based coating thickness instruments are capable of calculating and recording mean values (X), standard deviation (σ), and highest and lowest values (range) within a batch of readings.

It is important to establish the method of evaluating the information before embarking on an evaluation of a coating system so that the correct disciplines are applied to collecting the data and evaluating it for further decisions.

DATA MANAGEMENT

Some gages have memory and data transfer features such as RS 232 serial data transfer by cable or wireless communication via Bluetooth. These features used together allow readings for a project to be collected in a batch or batches in the gage and then this data can be transferred to a

computer running Data Management software for analysis, reporting, and archiving and fulfilling the requirements of Paperless Quality Assurance systems.

One of the major benefits of this approach is the removal of any potential transcription errors that can arise when manual records of coating thickness readings are kept in an inspector's notebook and are then transcribed into a report or a spreadsheet for further analysis.

It is possible to transfer data directly from the memory of the coating thickness gage into a spreadsheet if a suitable function is included either in the gage or in the supporting software. The spreadsheet can then be used in the normal way to provide statistical values and charts. There are Data Management systems that also allow supporting data such as paint datasheets, inspection procedures, photographs and other project-related information to be associated with the specific gage data from an inspection. This then allows detailed reports to be prepared for clients in a semiautomatic fashion.

FILM THICKNESS MEASUREMENT USING ULTRASONICS

Thickness measurements of certain dry films can be made using ultrasonic energy, measuring the time of flight of a pulse through the coating and back from the coating/substrate interface. ASTM D6132, Nondestructive Measurement of Dry Film Thickness of Applied Organic Coatings Using an Ultrasonic Gage, describes this method.

The pulse echo layer thickness measurement technique using an ultrasonic transducer with a scan display is capable of measuring individual layer thickness in a multiple layer system but calibration is sensitive to the differences in these layers and a change of pigment may be sufficient to change the calibration conditions.

A rigid substrate is required to obtain a good reflection of the ultrasonic energy and the coating must be able to transmit the sound energy without attenuation or dispersion. Coatings that include bubbles of air or that have certain types of fillers or pigments cannot be measured using this technique as they absorb the ultrasonic energy. Some substrates exhibit characteristics that tend to disperse the ultrasonic energy, as they are rough or are not sufficiently different to the material of the coating to adequately reflect the energy, e.g., certain coating on plastic substrates.

UNCURED POWDER COATING THICKNESS TO PREDICT FINAL FILM THICKNESS

ASTM D7378, Standard Practice for Measurement of Thickness of Applied Coating Powders to Predict Cured Thickness, describes three procedures. Procedure A uses a rigid metal notched (comb) gage (see Fig. 15).

Procedure B uses a special magnetic or eddy current probe, depending on the substrate material. The probe is designed to minimize the damage to the uncured coating and measures the actual coating thickness of the uncured powder film.

For both Procedure A and Procedure B a correction value has to be applied to the uncured powder thickness readings to predict the cured coating thickness.

Procedure C describes noncontact ultrasonic powder gages (see Fig. 16). These gages use a characterization of the reflected sound energy from the uncured coating to predict the final thickness of the coating after cure. Calibration can be checked by measuring the powder before the cure using the ultrasonic gage and after the cure using a dry film coating thickness gage as described earlier in this chapter. This procedure is awaiting a round robin test to be carried out.

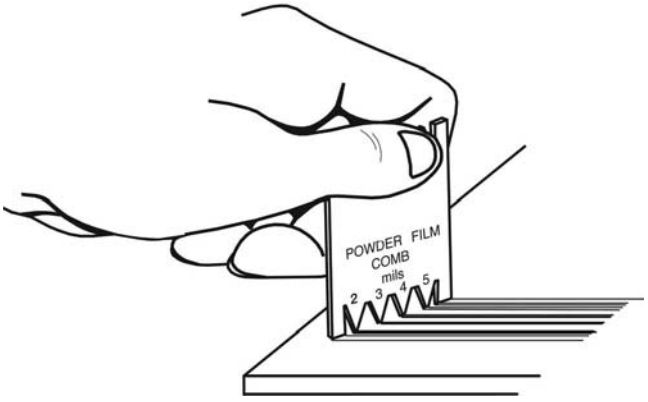

Fig. 15—Notch Gage for uncured powder thickness measurement—schematic diagram.

X-RAY FLUORESCENCE (XRF)

Recent developments in performance and reductions in cost have pushed X-ray fluorescence to center stage, particularly for metal coatings on metal substrate applications and smaller parts, such as fasteners. Beta-ray backscatter (BBS) techniques had been widely used to measure plated coatings; however, limitations in performance—e.g., a minimum of 20 % difference in atomic number between the coating and the substrate is required—mean that while gold over nickel, copper, or Kovar can be measured, nickel

Fig. 16—Noncontact ultrasonic coating thickness gage for uncured powder coatings.

TABLE 2—Thickness ranges for some common coating materials using X-ray fluorescence [7]

Coating	Substrate	Approximate thickness range (μm)
Aluminium	Copper	0–100.0
Copper	Aluminium	0–30.0
Copper	Iron	0–30.0
Copper	Plastic	0–30.0
Gold	Ceramics	0–8.0
Gold	Copper or nickel	0–8.0
Lead	Copper or nickel	0–15.0
Nickel	Aluminium	0–20.0
Nickel	Ceramics	0–20.0
Nickel	Copper	0–20.0
Nickel	Iron	0–20.0
Palladium	Nickel	0–40.0
Palladium-nickel	Nickel	0–20.0
Platinum	Titanium	0–8.0
Rhodium	Copper or nickel	0–50.0
Silver	Copper or nickel	0–50.0
Tin	Aluminium	0–60.0
Tin	Copper or nickel	0–60.0
Tin-lead	Copper or nickel	0–25.0
Zinc	Iron	0–40.0

over copper or Kovar cannot be measured using BBS techniques. Other disadvantages exist, such as limits in the aperture/component geometry, and measurement times have led to the further development of XRF techniques and technology.

Principle of XRF Measurement

If sufficient light energy collides with an electron, it is possible for the electron to be driven out of its atomic orbit, a process known as the photoelectric effect [6]. An atom with an electron removed from its orbit is unstable, so to restore equilibrium, an electron from a higher shell must drop into the vacant orbit. This transition causes an emission of energy in the form of a light wave or photon.

When the inner shell electrons are ejected from an atom, the emitted photon has high energy, and they fall into the region of the electromagnetic spectrum called X rays. X rays have characteristic energy levels determined by the element, which is emitting and can therefore be used to identify the elements in a sample.

In XRF instruments an X ray source or tube is used to produce photon emissions as they have an energy distribution capable of fluorescing all elements commonly used in plating. The X ray beam can be accurately illuminated to provide a small focal spot and high-intensity energy suitable for noncontact measurement of complex layers on small components. The characteristic X rays emitted by the target materials are detected using a gas-filled "proportional counter" in which the passage of the X ray ionizes the gas and produces a pulse of electrical charge proportional to the energy of the X ray.

The XRF instruments' electronics convert the charge pulse into a digital signal that can be interpreted as thickness or analyzed for composition and produce the measurement information by comparison with standards of known thickness. XRF instruments have developed with optical alignment systems and motor-driven sample stages to position the sample and computerized analytical equipment to store calibration data to calculate and present data to the user in a suitable format. Table 2 shows some of the applications, which can be successfully measured using XRF.

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Drying Time

Thomas J. Sliva[1]

THE PROCESS OF DRYING INVOLVES SEVERAL physical and/or chemical changes, such as solvent evaporation, oxidation, and polymerization, all of which are time dependent. The various stages of drying that occur in organic films may be subjective, difficult to measure reproducibly, and are influenced by many factors such as film thickness, substrate, temperature, humidity, light, and air circulation. Therefore, it is essential that most of these variables must be minimized in order to make drying time determinations more quantitative.

PREPARATIONS OF SPECIMENS

Substrate Preparation

It is essential that the substrate to be used and the applied wet film thickness be agreed upon in advance, preferably to conform to the intended use of the coating. Flat glass panels are typically the substrate of choice. Ground and polished glass plates are more suitable for low-viscosity coatings that may tend to crawl. All panels must be thoroughly cleaned, dried, and placed in a horizontal position on a level surface.

Application

The test coating should be filtered to remove any dirt or contamination. Test films are typically prepared, in duplicate, using a drawdown bar or doctor blade adjusted to obtain a uniform film thickness. Films should be drawn down at a uniform rate of application to avoid drag on the coating. It is recommended that all test films should be prepared and tested by one operator properly skilled in the method to be used and that a control (known) coating be run alongside the test coating. All testing should be done within an area, any point of which is not less than 1/2 in. (~ 15 mm) from the edge of the test film.

Table 1 can be used as a general guide for film application when nothing more specific is agreed upon between the purchaser and the seller. The dry film thicknesses shown in Table 1 are suggested. Other methods of application, such as spraying, dipping, or flood coat, may be used provided the film thickness obtained is consistent with that recommended under actual usage. Other substrates, such as metal, may be used provided they are smooth and flat.

ENVIRONMENT

When determining drying time, a controlled environment is essential. Variations in temperature, relative humidity, circulation of air, and light will have an effect on the drying time of a coating. The typical standard environment used for determining the drying time of air dry coatings is a temperature of 73.4° ± 3.6°F (23° ± 2°C) and a relative humidity of 50 % ± 5 % under diffuse daylight (about 25 fc).

Relative humidity should be strictly controlled for moisture-cure and two-package urethane coatings since their cure is greatly affected by the existing relative humidity. The effect of variation in temperature was discussed by Algeo and Jones [1], who observed a difference of 4 h for a particular paint dried at 73 and 77°F (22.7 and 25°C), both at 50 % relative humidity.

All testing should be conducted in a well-ventilated room free from direct drafts and dust. Airflow is important in determining drying time. For films that dry by oxidation, the rate of drying is a function of the concentration of oxygen at the interface. Since oxygen can reach the surface only by diffusion, the rate of drying is a function of the thickness of the stationary air layer. For films that dry by solvent evaporation, the continuous removal of solvent-laden air hastens drying [2].

TEST METHODS

ASTM D1640, Test Methods for Drying, Curing, or Film Formation of Organic Coatings at Room Temperature

Method D1640 is the most commonly used method to determine the various stages and rates of film formation in the drying of organic coatings normally used under conditions of ambient room temperature. The method describes eight stages of the drying process:

1. *Set-To-Touch Time*
   The test film is lightly touched with the tip of a clean finger, and the finger tip is immediately placed against a piece of clean, clear glass to determine when the film does not adhere to the finger or transfer to the glass.
2. *Dust-Free Time*
   This test is generally performed to determine when dust or cotton fibers lightly dropped on the test film can be removed by blowing over the test film. Individual absorbent cotton fibers are dropped from a height of 1 in. (25 mm). The film is considered to be dust free when the cotton fibers can be lightly blown off the test film.
3. *Tack-Free Time*
   The test film is considered to be tack free when no stickiness is observed under moderate pressure. This can be measured by either of two methods:
   a. *Paper Test Method*
   A special paper (K-4 Power Cable Paper) [3] is placed on the test film under a weight of 2 psi (13.8 kPa). After 5 s, the weight is removed and the test film inverted. If

[1] *Deceased, formerly of DL Laboratories, 116 East 16th St., New York, NY 10003.*

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TABLE 1—Recommended film thickness of material to be tested

Material	Dry Film Thickness, mils
Oil paints	1.8±0.2
Enamels	1.0±0.1
Drying oils	1.0±0.1
Water-based paints	1.0±0.1
Varnishes	0.85±0.1
Lacquers, polymer solutions	0.5±0.1

the paper drops off within 10 s, the film is considered tack-free.

A variation of the above method is used to test the tack-free time of insulating varnishes. The varnish is considered tack free when the paper is placed on the test film under a weight of 1 lb (450 g) for 1 min and tested as above.

b. *Tack Tester*

This is a mechanical device that consists of a strip of metal 1 in. (25 mm) wide, 3 in. (75 mm) long, and 0.016 to 0.018 in. (0.41 to 0.46 mm) in thickness. It is bent to form a base 1 in. (25 mm) square and a vertical length 1 in. by 2 in. (25 mm by 50 mm) angled at 135°. The bottom of the base of the tester is covered with aluminum foil [4] (Fig. 1). A 300 g weight is placed on the center of the base and allowed to set for 5 s. The test film is tack free when the tester tips over immediately after the weight is removed. Occasionally, tack-free time may be longer than dry-hard or dry-through time due to the inclusion of external plasticizers in the coating.

4. *Dry-To-Touch Time*

The test film is considered dry-to-touch when no mark is left when the film is touched by a finger. The following variations are used:

a. *Drying Oils*—The film is considered dry-to-touch when it does not rub up appreciably when a finger is rubbed lightly across the surface.

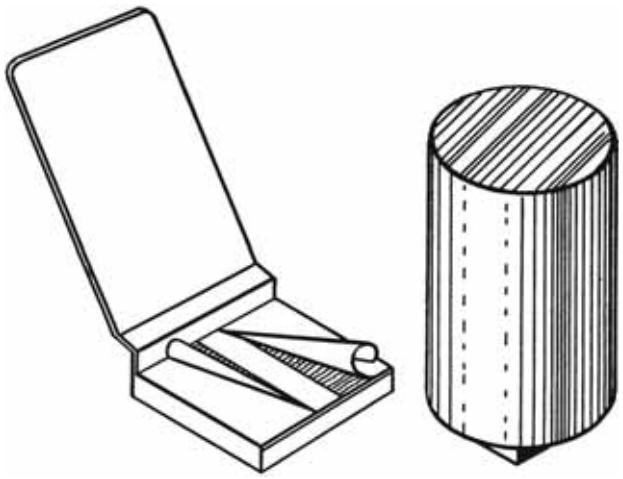

Fig. 1—Zapon Tack Tester. The base of the tester is padded and wrapped with aluminum foil. The weight, at right, is set on the base for a definite interval. After the weight is removed, the time required for the tester to tip over is the measure of tack.

b. *Lacquers* (*and Sealers*)—The film is considered dry-to-touch when no pronounced marks are left by a finger touching the film. Sealers are generally tested on wood or other porous substrates.

5. *Dry-Hard Time*

The test film is considered dry-hard after maximum downward thumb pressure (without twisting) applied to the test film leaves no mark when the contacted area is lightly polished with a soft cloth.

6. *Dry-Through* (*Dry-To-Handle*) *Time*

The test panel is placed in a horizontal position at such a height that when a thumb is placed on the film, the arm of the operator is in a vertical line from the wrist to the shoulder. The operator bears down on the film with the thumb, exerting moderate pressure and at the same time twisting the thumb through an angle of 90°. The test film is considered dry through when the film is not distorted by bearing down with moderate thumb pressure and twisting 90°.

7. *Dry-To-Recoat Time*

The test film meets this requirement when a second coat can be applied without causing any film irregularities, e.g., lifting, wrinkling.

8. *Print-Free Time*

The test film meets this requirement when imprinting fabric under a pressure of 1/2 or 1 lb/in.^{2} (3.5 or 7.0 kPa) shows the coating to be print free. This procedure is similar to ASTM D2091, Test Method for Print Resistance of Lacquers.

An indication of the accuracy of these methods is the precision statement developed in ASTM D1640 in which duplicate determinations within a laboratory should agree within ± 10 % [5].

Federal Test Method Standard 141C, Method 4061.2: Drying Time

This method is similar to ASTM D1640. It includes essentially the above stages of drying with the exception of dry-to-touch. However, it includes a test for free-from-after-tack. This test is applicable to coatings where tackiness persists beyond, or reappears at, the through-dry stage. It is similar to the Paper Test Method, discussed earlier in this chapter, except that a 2.8 kg (6.2 lb) weight is used.

ISO Standard 9117, Paints and Varnishes—Determination of Through-Dry State and Through-Dry Time—Method of Test

This standard describes a method for determining under standard conditions whether a single coat or a multi-coat system of paint or related material has, after a specified drying period, reached the through-dry state, i.e., a pass/fail test. The test procedure may also be used to determine the time taken to achieve that state.

1. *Through-Dry State*

This state defines the condition of a film in which it is dry throughout its thickness as opposed to that condition in which the surface of the film is dry but the bulk of the coating is still mobile. A single coating or a multi-coat system of paint or varnish is considered to be through-dry when a specified gauze attached to a plunger is placed on the test film under specified pressure (1,500 g) for 10 s, after which time the plunger head is turned through an angle of 90° over a period of

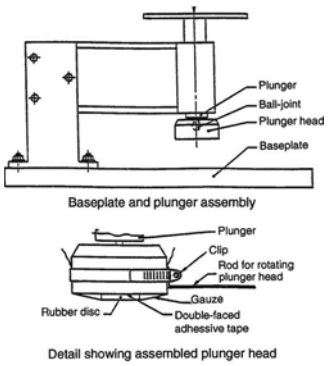

Fig. 2—Through-dry tester.

2 s and removed (Fig. 2). If no damage or markings are noted on the test panel, the film is said to have achieved "through-dry state."

2. *Through-Dry Time*
   This is the period of time between application of a coating to a prepared test panel and the time to achieve the "through-dry state" as outlined above.

British Standard B.S. 3900, Methods of Test for Paints

Parts C-1 thru C-4 of British Standard B.S. 3900 describe drying tests for determining the wet edge time, surface drying, hard-drying, and freedom from residual tack tests. Part C-8 describes a test for determining print-free state or time.

1. *Wet Edge Time* (*BS3900, C1*)
   This procedure is used for determining whether the edge of a film of paint remains "alive" after a specified period of drying. Following a touch-up coat over the film after the specified drying period, the area is evaluated for lack of film continuity, absence of leveling, or variation in color or sheen.
2. *Surface Drying* (*BS3900, C2*)
   This procedure is used to determine the time after which a coating is applied and when approximately 0.5 g of the ballotini (small transparent solid glass spheres) can be poured onto the surface of the film from a height of between 50 and 150 mm and lightly brushed away without damaging the surface.
3. *Hard-Drying Time* (*BS3900, C3*)
   A rubber-faced plunger is covered with cotton twill, rough side outwards, and then loaded to a total weight of 1.8 kg (4lb). The rotating plunger drops into the panel and makes a three-quarter turn while in contact. The paint film is dry-hard when no damage is observed (Fig. 3).

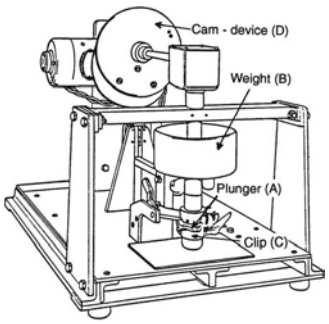

Fig. 3—Hard-drying time apparatus: Assembly.

4. *Freedom from Residual Tack* (*BS3900, C4*)
   After a specified drying period, a paper-backed gold leaf is placed on the test panel and covered with a microscope slide and an 800 g weight. After 10 s, the weight and slide are removed and the panel is held vertically and lightly tapped to detach the gold leaf. The surface of the paint film is examined for adhesion of gold leaf.
5. *Print-Free* (*BS3900, C8*)
   The state of a coating or varnish when gauze of a specified grade, under specified force and after a specified time, does not leave an imprint on the surface of a coating.

DIN 53 150, Determination of Drying Time of Paints

Drying time is determined in this method by the adherence or non-adherence of sand or paper to the film under various loadings. Stage 1 is determined with sand (0.16 to 0.315 mm) or glass beads (ballotini). The sand is allowed to remain on the film for 10 s. The remaining stages are determined using disks of typewriter paper (22 mm in diameter and weighing about 60 g/m^2) and various loads ranging from 5 to 5,000 g/cm^2. Interposed between the load and the test disk is a soft rubber cushion. The load remains on the disks for 60 s. The criteria for the seven stages are as follows:

1. Sand easily removed with a soft brush.
2. Disk under load of 5 g/cm^2 does not adhere.
3. Disk under load of 50 g/cm^2 does not adhere.
4. Disk under load of 500 g/cm^2 does not adhere, but film is temporarily marred.
5. Disk under load of 500 g/cm^2 does not adhere, but film is not marred.
6. Disk under load of 5,000 g/cm^2 does not adhere, but film is temporarily marred.
7. Disk under load of 5,000 g/cm^2 does not adhere, but film is not marred.

MECHANICAL DEVICES

In an attempt to improve the accuracy and reproducibility of the drying time test procedure, various mechanical devices have been developed. The following sections outline these devices and the procedures used in determining drying characteristics.

ASTM D5895, Test Methods for Evaluation Drying or Curing During the Film Formation of Organic Coatings Using Mechanical Recorders

1. *Circular Drying-Time Recorder*
   The device consists of a synchronous motor in a metal case resting on a rubber-tipped tripod and rotating

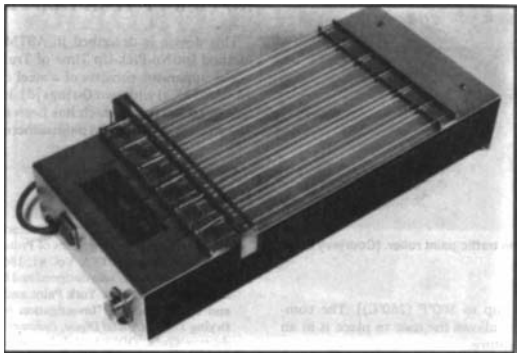

Fig. 4—Straight line recorder. (Courtesy of Byk-Gardner.)

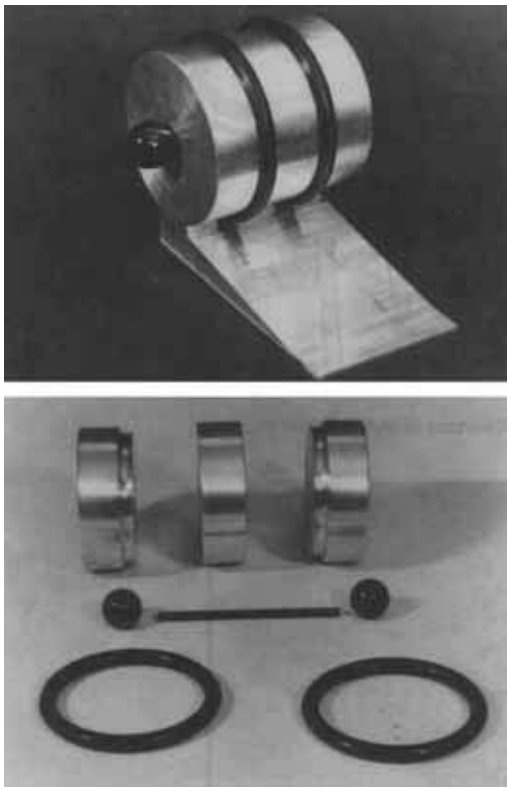

Fig. 5—No pick-up time traffic paint roller. (Courtesy of Byk-Gardner.)

a vertical shaft. A pivotal arm assembly is attached to the shaft, operating a vertical stylus with a Teflon sphere that does not stick to the drying film [6]. Under a 12 g load, the Teflon stylus scribes an arc in the drying film. Programmable units that are designed to control motor speeds and cover drying times of 1 min to 96 h—i.e., one 360° rotation of the stylus.

A transparent, plastic template with time increments can be placed over the dried coating at the end of the test. The appropriate scale number of circular degrees required for the film to cure hard dry is then used to determine the dry time. During the early stages of drying, the coating tends to flow back into the wake of the stylus. When the tendency of the flow has ceased, the film may be considered set. As the drying process continues, a skin will form. Visually, this part of the film formation is seen when the stylus begins to tear the surface of the film. The film may be considered surface dry or dust free when the skin is no longer ruptured by the stylus. It is considered through-dry when the stylus rides above the film.

Circular drying time devices have been developed for use when determining the drying time of bake finishes that cure at elevated temperatures [up to 500°F (260°C)]. The compactness of the instrument allows the user to place it in an oven at a specified temperature.

2. *Straight Line Drying Time Recorder*

This device consists of multiple needles being drawn over multiple (up to six) parallel coated glass strips [7]. Its speed can be varied to cover drying periods of 6, 12, and 24 h (Fig. 4). It defines the following stages in the drying process:

1. The first stage is a pear-shaped depression corresponding to the time it takes for the solvent to evaporate.
2. The second stage is the cutting of a continuous track corresponding to a sol-gel transition.
3. The third stage is an interrupted track corresponding to the surface dry time.
4. In the fourth stage, the needle no longer penetrates the film, indicating the final drying time.

Five-gram brass weights may be added to apply greater pressure on the needles and thus record through drying. The instrument has also been found useful in evaluating gel time of many two-component surface coatings.

NO PICK-UP TIME TRAFFIC PAINT ROLLER

This device is described in ASTM Standard D711, Test Method for No-Pick-Up Time of Traffic Paint. The apparatus consists of a steel cylinder weighing 11 lb, 14 oz (5385 g) with two O-rings [6]. It is rolled along a drying film of traffic paint which has been applied on a glass plate. The paint is dry when no paint adheres to the O-rings (Fig. 5).

References

[1] Algeo, W. L., and Jones, P. A., "Factors Influencing the Accurate Measurement of Drying Rates of Protective Coatings," *J. Paint Technol.,* Vol. 41, 1969, p. 235.

[2] Technical Subcommittee 37 of the New York Paint and Varnish Production Club, "Investigation of Methods for Measuring Drying Time," *Official Digest*, Federation of Paint and Varnish Production Clubs, ODFPA, Vol. 20, 1948, pp. 836–843.

[3] Crocker Technical Papers, Inc., *Grade R 20–34,* Fitchburg, MA.

[4] Bonner, R. E., and Brewster, M. D., "Tack Testing Device," U. S. Patent 2,406,989, Sept. 3, 1946.

[5] Prane, J. W., "A Latin Square Drying Time Study," *Paint Industry Magazine*, 1961, pp. 39–47.

[6] Byk-Gardner, Inc, Gardner Laboratory, Silver Spring, MD; Paul N. Gardner Co., Inc., Pompano Beach, FL 33060.

[7] T. Bell Inc., Akron, OH, as well as manufacturers listed in Ref 6.

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Part 10: Optical Properties

43

Color and Light

Robert T. Marcus[1]

PREFACE

IN PREPARATION OF THIS CHAPTER, THE CONTENTS of the fourteenth edition were drawn upon. The author acknowledges the authors of the fourteenth edition, Fred W. Billmeyer Jr. and Harry K. Hammond III. The current edition will review and update the topics as addressed by the previous authors, introduce new technology that has been developed, and include up-to-date references.

TERMINOLOGY

To understand this chapter and to make the best use of it, the reader should be familiar with the terminology of appearance. The precise definition of terms is becoming increasingly important in today's world community. The paint terminology standard, Definitions of Terms Relating to Paint, Varnish, Lacquer, and Related Products (D16), is the primary source of terms and definitions relating to paint, but it contains very few appearance terms. The reader should refer to Terminology of Appearance (E284) for terms and definitions relating to color and other appearance attributes. All significant terms used in this section are defined in Terminology E284.

An important international source of appearance terms is the *International Lighting Vocabulary* [7], published jointly by the International Commission on Illumination (CIE) and the International Electrotechnical Commission (IEC). However, this is structured from the viewpoint of illuminating engineering. It is less readily available and a much more costly document than Terminology E284.

Because color is a significant factor in the appearance of an object, it is an important characteristic of any paint. Appearance, of which color is a part, is one quality of a product that every customer can judge for himself. No matter how good the physical properties of a paint, if its color does not meet the expectation of the customer, the finished product will be rated as unsatisfactory.

Color, often thought to be a property of the paint itself, depends on three objective aspects: (1) the spectral composition of the light in which the paint is viewed, (2) the spectral reflectance of the paint, and (3) the spectral response of the eye of the observer. The subjective interpretation of the response to these aspects by the brain is also an essential part of color. Describing the color of a paint or other material requires consideration of all of these and not merely the spectral character of the material. The three objective aspects of color are considered in sections entitled "Light Sources," "Reflection and Transmission," and "The Eye." The sciences involved include chemistry, physics, physiology, and psychology. These are broad subjects, and only enough discussion is included to provide a background for understanding the development of test methods. Readers desiring to pursue these subjects in detail should consult an appropriate text [1–6].

LIGHT SOURCES

Light is electromagnetic radiation weighted by the response of the normal human eye. It occupies a small portion of the electromagnetic spectrum between ultraviolet and infrared radiation. Its wavelength range is approximately 380 to 780 nm (Fig. 1).

Natural and Artificial Daylight

Despite modern dependence on interior illumination, daylight is still an important light source since most objects are at some time viewed in it. The spectral composition of daylight, however, is quite variable, depending upon the hour of the day, the season of the year, and the amount of cloud cover. One way of dealing with this variability is to use standard light sources and their spectral power distributions when making visual or instrumental color measurements and calculations (see CIE Standard Sources and Illuminants).

Incandescent Sources

Other light sources must replace daylight when appropriate. For use in homes, incandescent lamplight is generally preferred because it imparts a soft, mellow effect similar to that of candlelight.

Fluorescent Sources

In stores and offices, fluorescent lamps can provide high levels of illumination with low power consumption and heat generation. The most commonly used fluorescent lamp, known as cool white, has a spectral distribution consisting of a relatively smooth curve throughout the visible spectrum. This arises from the fluorescent emission from a phosphor coated on the inside of the lamp tube. The fluorescence is excited by ultraviolet radiation from mercury vapor inside the tube. This lamp is, however, deficient in power in the red end of the visible spectrum. Modifications of it, known as deluxe and super-deluxe versions, have been designed to overcome this deficiency. Fluorescent lamps have also been designed with phosphors emitting only in three rather narrow regions of the spectrum. When these three bands are selected to peak near 450, 530, and 610 nm, light is provided that is especially pleasing to the eye and is energy efficient.

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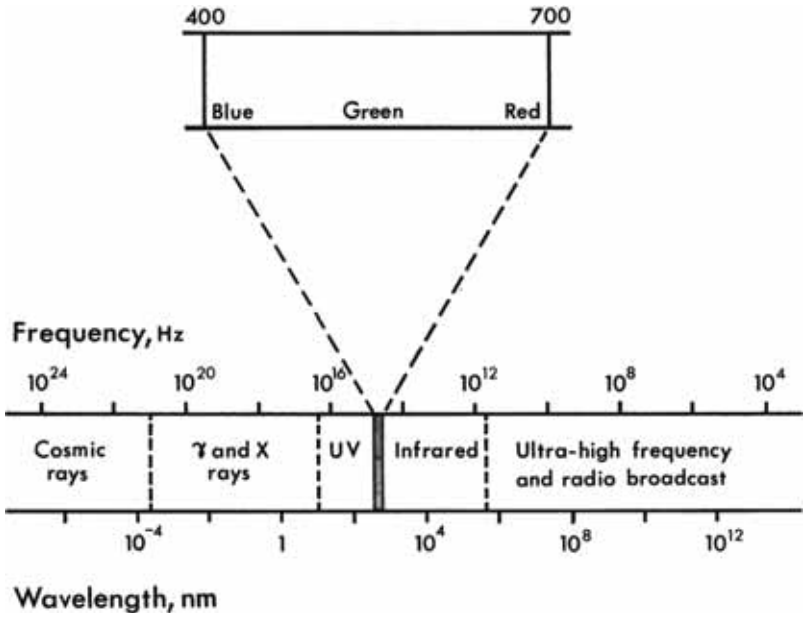

Fig. 1—Electromagnetic spectrum showing the relatively small portion that the visible spectrum occupies.

The color-balance and color-rendering properties among the various types of commercial fluorescent lamps can be vastly different one from another.

Other Sources

Other light sources have been developed for special purposes. They include arc lamps (sodium, mercury, neon, xenon), metal halide lamps, and high-intensity discharge lamps. None of these lamps has been adopted as a standard for use in color measurement.

Color-Matching Booths

Because of the variation in spectral composition of different natural and artificial sources, it is essential that visual color evaluation and matching be done under standardized illumination, such as that provided by a color-matching booth. This device allows the colorist to compare the colors of specimens under controlled and standardized illumination. Carefully manufactured and maintained light booths permit a colorist to make a visual match with confidence that the illumination duplicates that used at another time or place. However, the spectral power distribution of daylight illumination in color-matching booths is not the same as that of natural daylight.

REFLECTION AND TRANSMISSION

Opaque, Transparent, and Translucent Films

When light strikes an object, some of it may be reflected, some may be absorbed, and if the object is not opaque, some may be transmitted. The reflected light may be concentrated in a glossy, mirror-like, specular reflection, scattered uniformly in all directions (diffuse reflection), or distributed between these two extremes. A highly polished metal can reflect as much as 99 % of the incident light in the specular direction. A white powder, such as barium sulfate, scatters light uniformly in all directions, and it, too, can reflect as much as 99 % of the incident light. Specular reflection is related to the visual perception of gloss; diffuse reflection is related to the visual perception of lightness and, when it is wavelength dependent, to that of color.

Transmission can also be diffuse or regular, depending on whether or not light is scattered in passing through a material. Specimens that both transmit and reflect light are called translucent.

A spectrophotometer is used to provide information on the spectrally selective character of a material. Fig. 2 shows typical spectral reflectance curves of some paints. A trained colorist can obtain valuable information from such curves, but spectral data alone are unsatisfactory as a means for color identification.

Among the ASTM standards on reflectance and transmittance measurement [8], the most useful are shown in Table 1[2].

Retroreflection

Retroreflection is defined in Terminology E284 as "reflection in which the reflected rays are preferentially returned in directions close to the opposite of the direction of the incident rays." It is important in paints and coatings used for signs viewed at night, pavement and pedestrian markings, and other safety devices. The measurement of retroreflection requires special instrumentation and special test methods for the determination of daytime and nighttime colors of retroreflecting materials. Table 2 lists the ASTM standards dealing with this subject. The last two items in the table are standards in preparation and may never become official ASTM standards.

[2]As noted in Terminology E284, in the Discussion under *reflectance,* "The term *reflectance* is often used in a general sense or as an abbreviation for *reflectance* factor...." This simplifying convention is used in this chapter, as it is in many textbooks. The reader should refer to Terminology E284 for the definitions of *reflectance, transmittance,* and *radiance,* and the corresponding factors. Note that commercial instruments measure *reflectance factor,* not *reflectance*.

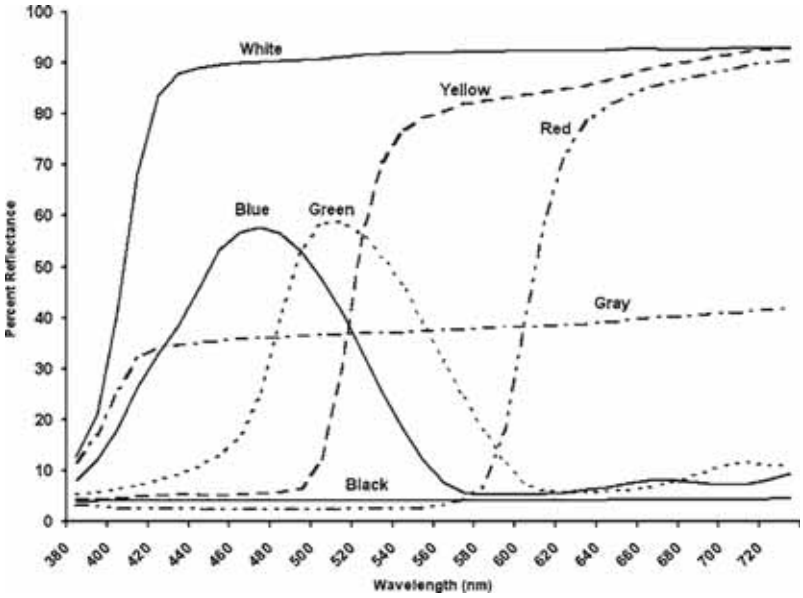

Fig. 2—Spectrophotometric curves typical of those measured on paint films. Note the sharp drop in the curve for rutile titanium dioxide (white) as the violet end of the spectrum is approached. The drop continues in the ultraviolet, where this pigment absorbs light strongly.

Gonioappearance

Gonioapparent coatings change one or more attributes of color with a change in the illuminating or viewing angle. Coatings containing metallic flakes exhibit a change in lightness, while coatings containing mica-based interference pigments or other effect pigments change their hue and chroma. Often metallic flakes are combined with other effect pigments so that the coating will change hue, lightness, and chroma with a change in the illuminating and viewing angles. Multiangle spectrophotometers, sometimes called goniospectrophotometers, are used to measure gonioapparent coatings. These are bidirectional instruments that have the capability of measuring with a variety of illuminating and/or viewing angles. More than one illuminating angle is required to characterize interference pigments, whereas only one illuminating angle can be used to satisfactorily characterize materials containing only metallic flakes. Practice for Multiangle Color Measurement of Metal Flake Pigmented Materials (E2194) describes how to measure gonioapparent materials containing only metallic flake pigments; Practice for Multiangle Color Measurement of Interference Pigments (E2539) describes how to measure gonioapparent materials containing thin film interference pigments; and Practice for Specifying the Geometry of Multiangle Spectrophotometers (E2175) provides a way of specifying geometric properties that are peculiar to multiangle spectrophotometry.

Ultraviolet and Infrared Spectral Regions

Ultraviolet and infrared radiation can have important effects on paint. Ultraviolet radiation, with wavelengths shorter than 380 nm, is the principal stimulus of fluorescence of certain pigments, is an aid to identification and analytical determination of certain ingredients of paint, and may promote decomposition of pigments or binders. Colorless pigments absorbing in the ultraviolet region can impart protection against such decomposition. Rutile titanium dioxide absorbs in the ultraviolet, as its spectral curve shows (see Fig. 2).

Infrared radiation, with wavelengths longer than 780 nm, is associated with heat transfer. It is widely used for the identification and analysis of chemical compounds. The near-infrared region, with wavelengths from 780 to about 1100 nm, is important for camouflage detection. Most paint pigments do not absorb radiation in this region, but some inorganic pigments reflect visible light and absorb radiation in the near-infrared.

TABLE 1—ASTM standards on reflectance and transmittance measurements

Designation	Title
E1164	Practice for Obtaining Spectrometric Data for Object-Color Evaluation
E1331	Test Method for Reflectance Factor and Color by Spectrophotometry Using Hemispherical Geometry
E1347	Test Method for Color and Color-Difference Measurement by Tristimulus (Filter) Colorimetry
E1348	Test Method for Transmittance and Color by Spectrophotometry Using Hemispherical Geometry
E1349	Test Method for Reflectance Factor and Color by Spectrophotometry Using Bidirectional (45:0 or 0:45) Geometry
E805	Practice for Identification of Instrumental Methods of Color or Color-Difference Measurement of Materials
E1345	Practice for Reducing the Effect of Variability of Color Measurement by Use of Multiple Measurements
E2214	Practice for Specifying and Verifying the Performance of Color-Measuring Instruments

TABLE 2—ASTM standards on Retroreflectance

Designation	Title
D4061	Test Method for Retroreflectance of Horizontal Coatings
E808	Practice for Describing Retroreflection
E809	Practice for Measuring Photometric Characteristics of Retroreflectors
E810	Test Method for Coefficient of Retroreflection of Retroreflective Sheeting Utilizing the Coplanar Geometry
E811	Practice for Measuring Colorimetric Characteristics of Retroreflectors Under Nighttime Conditions
E1501	Specification for Nighttime Photometric Performance of Retroreflective Pedestrian Markings for Visibility Enhancement
E1696	Test Method for Field Measurement of Raised Retroreflective Pavement Markers Using a Portable Retroreflectometer
E1709	Test Method for Measurement of Retroreflective Signs Using a Portable Retroreflectometer at a 0.2 Degree Observation Angle
E1710	Test Method for Measurement of Retroreflective Pavement Marking Materials with CEN-Prescribed Geometry Using a Portable Retroreflectometer
E1809	Test Method for Measurement of High-Visibility Retroreflective-Clothing Marking Material Using A Portable Retroreflectometer
E2176	Test Method for Measuring the Coefficient of Retroreflected Luminance of Pavement Markings in a Standard Condition of Continuous Wetting ($R_{L\text{-}Rain}$)
E2177	Test Method for Measuring the Coefficient of Retroreflected Luminance (R_L) of Pavement Markings in a Standard Condition of Wetness
E2302	Test Method for Measurement of the Luminance Coefficient Under Diffuse Illumination of Pavement Marking Materials Using A Portable Reflectometer
E2366	Test Method for Measurement of Daytime Chromaticity of Pavement Marking Materials Using a Portable Reflection Colorimeter
E2367	Test Method for Measurement of Nighttime Chromaticity of Pavement Marking Materials Using a Portable Retroreflection Colorimeter
E2540	Test Method for Measurement of Retroreflective Signs Using a Portable Retroreflectometer at a 0.5 Degree Observation Angle
F923	Guide to Properties of High Visibility Materials Used to Improve Individual Safety (Withdrawn 2006)
WK3833	New Test Method for Determination of the Coefficient of Retroreflection of Pavement Markings Using a 30 Meter Geometry Mobile Retroreflectometer
WK19806	New Test Method for Measuring the Coefficient of Retroreflected Luminance of Pavement Markings in a Standard Condition of Continuous Wetting (RL-Rain)

Fluorescence

Some materials have the property of fluorescing when irradiated by ultraviolet or visible radiation. They typically emit radiation at longer wavelengths in the visible range or even in the near-infrared. The effect of fluorescence is to increase the apparent reflectance since the eye responds to the sum of the fluoresced and the reflected energy. This sum may even exceed the amount of light reflected by an ideal white material at the wavelengths of maximum fluorescent emission. Fluorescent pigments had a reputation for poor lightfastness in outdoor applications, but improved technology is changing this. Some fluorescent pigments can now survive at significant levels for several years.

Most modern colorimeters and spectrophotometers are designed to properly evaluate the colors of fluorescent materials. However, many of these instruments do not have light sources adequately simulating the ultraviolet content of natural daylight. In such a case, the instrument will not produce the same amount of fluorescence as would daylight. While many instruments will measure the color of fluorescent materials, generally it is necessary to use an instrument that both illuminates the specimen monochromatically and also views monochromatically to separate the fluorescence component from the reflection or the total radiance of a material. These instruments are called either spectrofluorimeters or bispectrometers.

Five ASTM standards apply to the measurement of fluorescence. Practice for Color Measurement of Fluorescent Specimens Using the One-Monochromator Method (E991) specifies the instrument geometry required for the measurement and shows how to assess the performance of daylight-simulating instrument light sources. Practice for Detecting Fluorescence in Object-Color Specimens by Spectrophotometry (E1247) provides instrumental methods to supplement simple visual examination of the specimen under ultraviolet light to detect the presence of fluorescence. Practice for Computing the Colors of Fluorescent Objects from Bispectral Photometric Data (E2152) and Practice for Obtaining Bispectral Photometric Data for Evaluation of Fluorescent Color (E2153) specify how to collect and interpret fluorescence data using bispectral, fluorescence-measuring instruments. Test Method for Daytime Colorimetric Properties of Fluorescent Retroreflective Sheeting and Marking Materials for High Visibility Traffic Control and Personal Safety Applications Using 45°:Normal Geometry (E2301) specifies how to collect and interpret fluorescent-retro-reflective materials by bispectral colorimetry using a 45:0 or 0:45 optical measuring system.

Recently, fluorescence has been used for the detection of defects in industrial coatings including fluorescing primer coatings, as well as non-fluorescent top coatings. A Specification for Light Source Products for Inspection of Fluorescent Coatings (E2501) was developed to provide the requirements for light source products intended for the excitation of fluorescent materials used for the detection of defects in industrial coatings. Test Method for Luminance Ratio of a Fluorescent Specimen using a Narrow Band Source (E2630) was developed as a companion to Specification E2501 to support the development and specification of industrial coatings that are used in a system for the detection of coating defects when inspected with a Specification E2501 light source. Specification E2501 establishes

a quantitative measure of the optical property of a coating that correlates to its ability to enhance defect contrast under the specified inspection light source.

Phosphorescence

Phosphorescence is similar to fluorescence. However, while fluorescing materials will stop emitting radiation once the irradiation stops, phosphorescing materials continue to emit. This makes phosphorescing materials ideal for safety markings. Two ASTM standards and one specification apply to phosphorescing materials—Guide for Recommended Uses of Photoluminescent Phosphorescent Safety Markings (E2030), Test Method for Photopic Luminance of Photoluminescent (Phosphorescent) Markings (E2073), and Specification for Photoluminescent (Phosphorescent) Safety Markings (E2072).

THE EYE

The Visual System

The human eye functions in a manner similar to a camera. It has a lens to focus images of objects and an iris to control the amount of light that enters. A complex light-sensitive layer, called the retina, plays a role analogous to that of the film in a camera. Neither the structure of the retina nor its function are fully understood. It contains two different types of light receptors that send information along neural pathways to the visual cortex of the brain. They are called rods and cones because of their shapes. The rods are responsible for black-and-white vision at low light levels, and they are not considered further in this section. At usual daylight levels, the rods are overwhelmed and do not contribute to vision. The cones are responsible for color vision. There are three types of cones, each with a different spectral sensitivity. The exact spectral response of each type of cone is not known, although it is assumed that each cone response function is related to the absorption curve of its pigment. The absorption curves are broad and overlapping (Fig. 3). They peak in the short, middle, and long wavelength regions of the visible spectrum; thus the designations blue, green, and red (sensitive) cones are sometimes used [9-12].

Detailed models of color vision have been proposed [13,14], but they are presently based on incomplete information. What happens to the neural signals from the retina on the way to and in the brain is not well understood, but for most work related to color and appearance, it does not need to be.

Perception

Perception is defined as the translation of retinal images by the observer into meaningful information about the environment. The perception of objects and their colors thus represents the overall response of the visual system, including both the eye and the brain. Vision is called a psychophysical phenomenon—physical in the way light reaches the eye, psychological in how the brain interprets the neural signals. The psychological factor determines, for example, whether a given color combination is interpreted as pleasing or displeasing. The mechanism of seeing is physical; the interpretation of what is seen is psychological.

Objective color measurement is, however, confined to physical aspects. For example, the perceived color of a specimen may be changed by changing the color of the area surrounding it. This phenomenon, called simultaneous contrast, cannot yet be evaluated instrumentally.

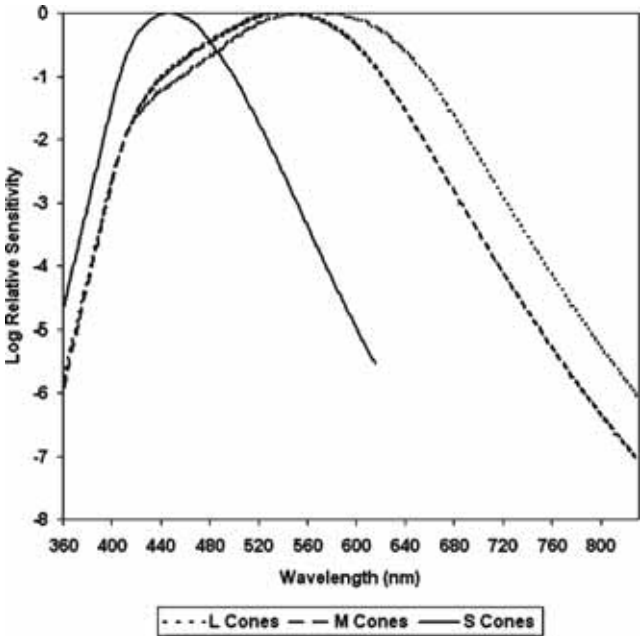

Fig. 3—Spectral curves showing the relative sensitivities of the three types of cones in the eye, peaking in the short (S), medium (M), and long (L) wavelength regions.

Another example of a perceptual phenomenon is chromatic adaptation, defined as the changes in the visual system's sensitivities due to changes in the spectral quality of the illuminating and viewing conditions. These changes tend to compensate, for example, for the effect of the change in illumination from distinctly bluish daylight to distinctly yellowish incandescent lamplight. The perceived colors of familiar objects tend to appear the same (known as color constancy) when the observer goes between environments illuminated by the two kinds of light, while the actual colors have all been shifted because of the change in spectral composition of the incident light.

The Variables of Perceived Color

The fact that the eye perceives color because it has three types of cones with differing spectral sensitivities implies, and experience confirms, that perceived color should have three variables. Several sets of these variables are of interest because of their wide use.

Object Colors: L, C, and H Cylindrical Systems

Of great interest to the paint colorist are the variables applying to the perception of object colors. Hue is always one of the variables. Hue is defined as the attribute of color described by common names such as red, yellow, green, blue, etc. The hues are commonly arranged in a circle in the order of their appearance in the spectrum, with the circle closed by the purples, mixtures of the red and blue at the ends of the visible spectrum (Fig. 4).

A second important variable of object colors is lightness, the attribute by which an object is judged to reflect more or less light. It is often represented graphically by a line through the center of the hue circle and perpendicular to its plane (also shown in Fig. 4). The upper and lower

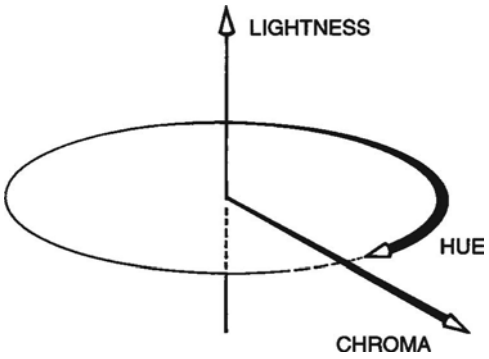

Fig. 4—Arrangement of the hue, lightness, and chroma axes in the usual cylindrical representation of color space.

ends of this line, often called the neutral or achromatic axis, are white and black, respectively.

The third variable in this set has several different names, referring to variations among what we can perceive: Chroma, saturation, and colorfulness are examples. The common factor among these names is a sense of the amount, in contrast to the kind, of hue in the color. In this section we use chroma as the name for this third variable and show it in Fig. 4. This quantity is exemplified by the distance between the point representing the color and the neutral axis. The Munsell system (see Munsell System) is an example of a cylindrical system.

Colored Lights

When we deal with colored lights instead of objects, two changes need to be made in the above system: Lightness is replaced by brightness and chroma by saturation. Brightness in this sense is defined as the attribute by which an area appears to emit more or less light.

Object Colors: L, a, and b Opponent Systems

A widely used alternative to the hue-lightness-chroma system described above is an opponent-color system that mimics the behavior of the neural signals transmitted from the retina to the brain. The lightness axis, often labeled *L,* is retained, but the hue circle is replaced by two opponent-type axes at right angles and perpendicular to the lightness axis (Fig. 5). Commonly they are a redness-greenness and a yellowness-blueness axis labeled *a* and *b,* respectively, as in the figure. Scales of this type are displayed in many color-measuring systems; examples are given later in Color Order Systems.

Color Constancy and Metamerism

Color Constancy

As previously noted under Perception, color constancy is the general tendency of colors to remain constant in appearance when the color of the illumination is changed. Note that this term refers to what happens to the color of a single specimen when the illumination is changed.

Metamerism

Of greater concern to the colorist is what happens to the relationship of two colors when the illumination is changed. This phenomenon is of industrial importance and largely under the control of the colorist. Suppose that two

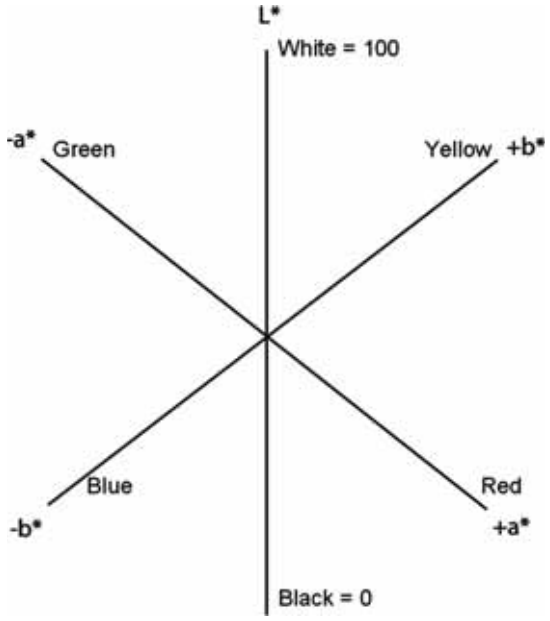

Fig. 5—Arrangement of the lightness, redness-greenness, and yellowness-blueness axes in the usual opponent-color representation of color space.

colors, which match in daylight, are formulated by using different sets of pigments. The two colors may not match under another type of illumination, such as incandescent lamplight, since the two specimens may exhibit different types and degrees of color constancy. This phenomenon is known as illuminant metamerism, and the colors are said to be metameric. Illuminant metamerism is defined as the property of two specimens having different spectral characteristics and having the same color when viewed by a normal observer under a given illuminant, but different colors when viewed under a different illuminant when other conditions remain the same. The metameric samples whose spectral curves are shown in Fig. 6 were created by using different pigments in each specimen. Observer metamerism is the phenomenon in which two specimens having different spectral characteristics match to some observers but not to others under the same illuminating and viewing conditions.

Only when colors have identical spectral curves can they be expected to match under all types of light and to all observers. To avoid metamerism, the same pigment formulation should be used when remaking the color. Correcting a batch by adding pigments that were not in the original formulation can result in metamerism. Whenever pigments used for the match have different spectral characteristics from those used in the target, the resultant color match should be tested for the metamerism by several observers and under several different types of illumination. Daylight, incandescent lamplight, and fluorescent lamplight are commonly used sources for evaluating metamerism. A color-matching booth should be used for making the evaluation. If the match is not satisfactory, spectrophotometric analysis of the two formulations should be carried out to determine their spectral differences, and the formulation should be adjusted to minimize metamerism. Practice for Visual Evaluation of Metamerism (D4086) specifies procedures

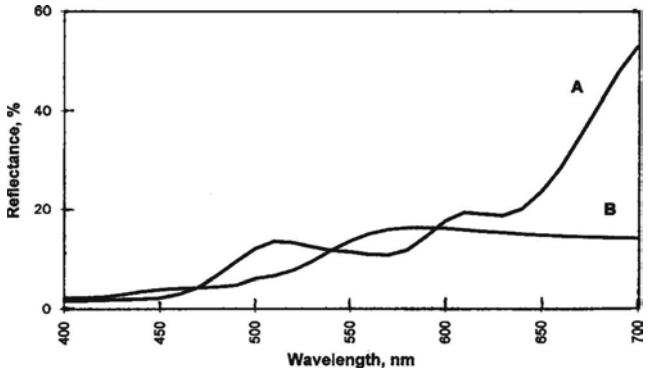

Fig. 6—Spectrophotometric curves of two highly metameric paint films. To most observers, the films match visually and are a dull green color in daylight, but sample A shifts color to a strong reddish brown in incandescent lamp light while sample B exhibits color constancy for this change of illumination.

for identifying the presence of metamerism and evaluating it semiquantitatively. Means of minimizing metamerism in both visual and instrumentally aided color matching are described later in "Color Matching."

COLORIMETRY AND THE CIE SYSTEM

Colorimetry is defined as the science of color measurement. Its modern development began in 1931, when, in the interest of standardization and to focus attention on the properties of material objects such as paint films, international standards and recommendations were established by the International Commission on Illumination (Commission Internationale de l'Éclairage, CIE). These recommendations [15] define standard lights and observers and a methodology for combining their properties with those of the objects to describe color and related appearance parameters.

CIE Standard Sources and Illuminants

Here, it is necessary to note two conventions of CIE terminology [7] reflected in Terminology E284. A source is defined as a real emitter of light, whereas an illuminant is defined as a spectral power distribution.

Incandescent Source and Illuminant

In 1931 the CIE defined a tungsten-filament incandescent lamp of 2856 K color temperature (see "Other Features of the CIE System") as Source A. Later, when measurement of spectral power distributions became easier, the fundamental definition was changed to the lamp's spectral power distribution, known as Illuminant A. The spectral power distribution of Illuminant A is given in Ref. [15], in a CIE/ISO standard [16], and in abbreviated form in Practice for Computing the Colors of Objects by Using the CIE System (E308).

Daylight Source and Illuminants

The CIE also recommended standard Source C in 1931, consisting of liquid filters used in combination with Source A, representing north-sky daylight. Later, the fundamental definition was changed to that of Illuminant C [15].

Source and Illuminant C do not duplicate the ultraviolet content of natural daylight and thus do not provide correct daylight color rendition of fluorescent materials. In 1968 the CIE adopted the D series of illuminants, which duplicate the spectral power distributions of various phases of natural daylight. They are designated by their correlated color temperatures (see "Other Features of the CIE System"). The most important of these daylight illuminants [15,16] is D65, with a correlated color temperature of 6500 K. The spectral power distributions of Illuminant C and several of the D series are tabulated in Practice E308. Unfortunately, very few real sources, whether for visual or instrumental use, simulated any of the D illuminants satisfactorily. The CIE has recommended procedures for assessing the quality of daylight simulators [17]. The relative spectral power distributions of CIE Standard Illuminants A, C, and D65 are shown in Fig. 7.

Fluorescent Illuminants

In 1986, the CIE defined [15], but did not recommend as standard illuminants, a series of 12 spectral power distributions representative of various types of fluorescent lamps, including cool white lamps simulating daylight well, and three-band lamps. These data should be used when calculations involving fluorescent lamps are required.

CIE Standard Observers

1931 CIE Standard Observer

In order to evaluate colors consistently, a standard observer was defined by the CIE in 1931 [15,18] by evaluating the spectral responses of a small group of well-trained individuals. The spectral responses of the CIE 1931 Standard Observer were determined by means of experiments, like those described later in Additive Mixing of Lights, in which the observer determined the amounts of three primary colors (red, green, and blue) required to match the colors of all wavelengths of the visible spectrum. These sets of three values are called tristimulus values. For convenience, the data were transformed mathematically to correspond to the use of imaginary primary lights designated *X, Y,* and *Z*. The Standard Observer is defined by the amounts, $\bar{x}(\lambda)$, $\bar{y}(\lambda)$ and $\bar{z}(\lambda)$, of these primaries required to match the spectrum colors; these are plotted in Fig. 8. The symbol (λ) indicates that the quantity depends on the wavelength, λ. The quantities $\bar{x}(\lambda)$, $\bar{y}(\lambda)$ and $\bar{z}(\lambda)$, are known as the color-matching functions of the 1931 CIE Standard Observer.

The transformation from real primaries to *X, Y,* and *Z* was made so that the color-matching function $\bar{y}(\lambda)$ is equal to the spectral luminous efficiency function $V(\lambda)$, that is, the effectiveness of radiation to stimulate the perception of light. This choice means that the tristimulus value *Y* of a given color, called its luminance, contains all the information about the lightness of the color.

1964 Supplementary Standard Observer

The data for the CIE 1931 Standard Observer were obtained with a visual colorimeter in which the field of view subtended an angle of only 2° at the eye of the observer. This was selected to correspond to the size of the fovea, which is that part of the retina containing only cones used in color vision. Later, the CIE studied color vision in a 10° field, with the central 2° portion disregarded. This corresponds to sample sizes more like those used in commerce, but for which the spectral sensitivity of the eye is somewhat differ-

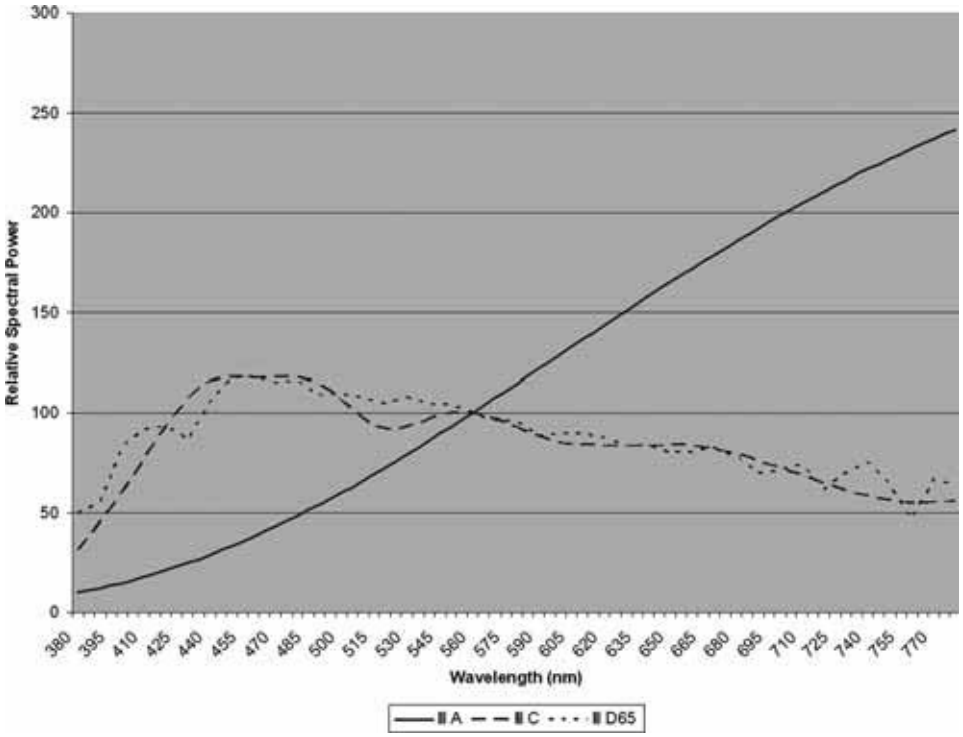

Fig. 7—Relative spectral power distributions of CIE standard illuminants A (incandescent lamp light), C (north-sky daylight), and D65 (actual daylight).

ent from that for the 2° field. With the newer data, the CIE established the 1964 Supplementary Standard Observer [15,18]; see also Practice E308. Where confusion might result, quantities referring to the 1964 Supplementary Standard Observer are given the subscript 10; for example, its color-matching functions are $\bar{x}_{10}(\lambda), \bar{y}_{10}$ and $\bar{z}_{10}(\lambda)$.

Calculation of Tristimulus Values

The tristimulus values *X, Y,* and *Z* of a color can, in principle, be obtained by direct matching, as were the tristimulus values of the spectrum colors defining the standard observers. But this is impractical, and one of two other methods is always used. One of these involves the design and use

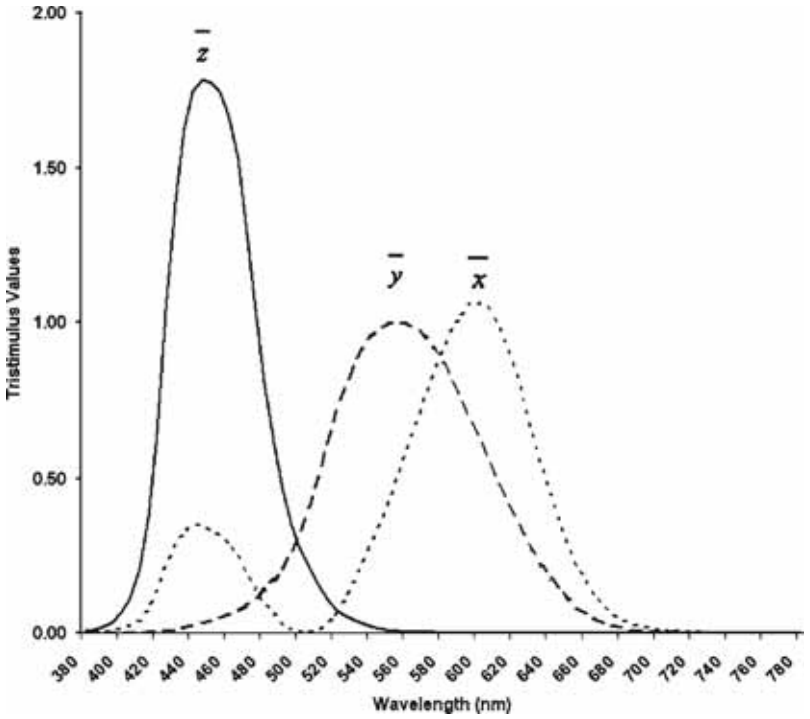

Fig. 8—The color-matching functions of the CIE 1931 standard observer; they are the tristimulus values of the colors of the spectrum.

of tristimulus (filter) colorimeters and is discussed later in "Tristimulus (Filter) Colorimeters." The other requires knowledge of the spectral reflectance curve of the specimen, obtained by spectrophotometry, and the following procedure.

At any wavelength, the contribution to a tristimulus value is given by the product of the relative spectral power of the illuminant, $S(\lambda)$, the reflectance of the specimen, $R(\lambda)$, and one of the color-matching functions of the observer, for example, $\bar{x}(\lambda)$. These products are summed over the visible wavelengths, then normalized by multiplication by a normalization factor k; for example

$$X = k\sum S(\lambda)R(\lambda)\bar{x}(\lambda)$$

(and similar equations for Y and Z), where Σ indicates the summation over the visible wavelength region. The quantity k is chosen to make Y for perfect white equal to 100

$$k = \frac{100}{\sum S(\lambda)\bar{y}(\lambda)}$$

The CIE had defined perfect white as the perfect reflecting diffuser, the ideal reflecting surface that neither absorbs nor transmits light, but reflects all of it. Most textbooks, Practice E308, and Ref. [15] provide examples of the use of these equations. Because the fundamental process is integration, for which summation is an approximation, the process is usually referred to as tristimulus integration.

If a large number of sets of reflectance data are to be integrated for the same illuminant and observer, it is convenient to combine quantities such as $S(\lambda)\bar{x}(\lambda)$ by multiplying them together and normalizing the products so that $k = 1$. The resulting tristimulus weighting factors can then be stored and used by multiplying them by whatever function $R(\lambda)$ is desired. The CIE has not tabulated or recommended specific sets of tristimulus weighting functions, but a substantial number can be found in Practice E308. They may be used for wavelength intervals of 10 or 20 nm. For closer intervals, such as 5 or 1 nm, the tables in Practice E308, Ref. [15], or Refs. [16,18] should be used. For the wavelength intervals of 10 or 20 nm, the raw spectral data acquired by the instrument are affected by the spectral bandpass error. This error is introduced because the spectral bandpass must be of significant bandwidth to allow sufficient energy to reach the detector. However, the spectral data being reported has a theoretical zero bandwidth. ASTM developed a Practice for Rectification of Spectrophotometric Bandpass Differences (E2729). This Practice outlines the methods that can be used to deconvolve, at least in part, the spectral bandpass error of raw spectral data acquired by abridged spectrophotometry.

Chromaticity Coordinates and Diagram

An important use of the CIE tristimulus values *X, Y,* and *Z* is the calculation of coordinates describing the chromaticity of a color, that is, its hue and chroma, ignoring its luminance or lightness. The CIE chromaticity coordinates *x, y,* and *z* are computed from the tristimulus values *X, Y,* and *Z* by dividing each of these by the sum *X*+*Y*+*Z*. Thus

$$x = \frac{X}{X+Y+Z}$$

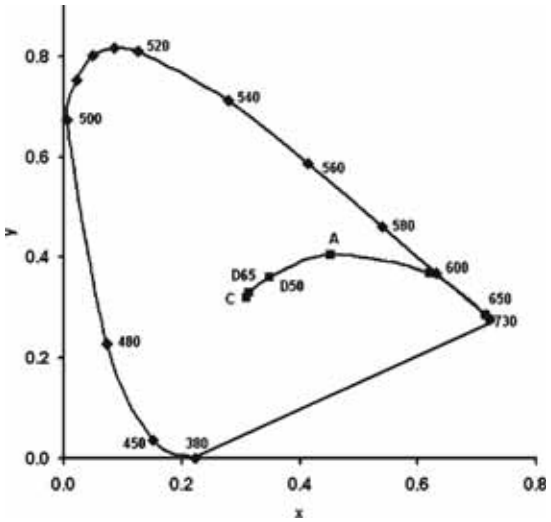

Fig. 9—The CIE 1931 *x, y* chromaticity diagram showing the various features described in the text.

$$y = \frac{Y}{X+Y+Z}$$

$$z = \frac{Z}{X+Y+Z}$$

Since $x + y + z = 1$, only two chromaticity coordinates need be given; usually they are *x* and *y*. These chromaticity coordinates can be plotted to yield the 1931 CIE *x, y* chromaticity diagram, shown in Fig. 9, or the 1964 CIEx_{10},y_{10} diagram for the Supplementary Standard Observer; the two are quite similar.

Features of the chromaticity diagrams include: (1) the locations of the spectrum colors around the horseshoe-shaped spectrum locus, from 400 nm (violet) at the lower left to 700 nm (red) at the right; (2) the straight line along which purples lie joining these two ends of the spectrum locus; and (3) the location of whites (illuminant points) near the middle of the diagram. As an alternative to the three tristimulus values, colors can be specified by the chromaticity coordinates *x* and *y* together with the luminance *Y* (or their equivalents in the 1964 system). These can be arranged in a three-dimensional color space.

Other Features of the CIE System

Dominant Wavelength, Complementary Wavelength, and Purity

Dominant wavelength is defined as the wavelength along the spectrum locus at the end of a line drawn from the white point (usually Illuminant C**)** through the sample point to the spectrum locus. For purple colors where the line would end at the purple locus, it is extended back through the white point to the spectrum locus, and the wavelength at that point is designated as the complementary wavelength of the sample. The fractional distance from the white point to the sample point relative to the distance to the spectrum or purple locus is called the (excitation) purity of the sample. Dominant wavelength correlates well with the hue of the sample, but purity does not correlate well with any perceived quantity and is rarely used today.

Blackbody Locus, Color Temperature, and Correlated Color Temperature

When a metal, such as a lamp filament, is heated, it first radiates heat in the infrared region, then light with a chromaticity at the red corner of the diagram. As it gets hotter, the chromaticity shifts through the oranges and yellows. The line along which these chromaticities lie for perfect absorbers and emitters of radiation is called the blackbody locus and is shown in Fig. 9. If the metal did not melt, its color would continue along this locus through white to light blue at infinitely high temperature. The temperature of a perfect blackbody can be correlated with its chromaticity and is called the color temperature of the body. It is measured in kelvins, K; the color temperature of Illuminant A is, for example, 2856 K. Many light sources, including the phases of daylight and fluorescent lamps, have chromaticities that are close to, but not on, the blackbody locus. In that case, the color temperature closest to the chromaticity of the source is used and called its correlated color temperature. An example is Standard Illuminant D65, with a correlated color temperature of 6500 K.

Uniform Color Spaces

From almost the beginning of the CIE system, it was recognized that distances in the CIE space did not correlate well with visual estimates of the magnitudes of color differences. Many proposals have been made for deriving quantities that are more uniformly visually spaced. In 1976, the CIE recommended two more nearly uniform color spaces that, although not perfect, have been widely used. Here we describe the one that is most widely used in the paint and related industries and mention briefly the second, more useful, when colored lights are considered. The equations for these two spaces, known by official acronyms CIELAB and CIELUV, are found in Refs. [1,6,15] and in the Practice E308.

CIE 1976 L* ,a*, b* (CIELAB) Space

CIELAB is an opponent-type color space, with a lightness axis L^*, a redness (positive values)-greenness (negative) axis a^*, and a yellowness (positive)-blueness (negative) axis b^*, all mutually perpendicular, as illustrated in Fig. 5. The transformations from Y to L^*, from X and Y to a^*, and from Z and Y to b^* are all nonlinear, using cube-root functions.

The equations for these transformations are

$$L^* = 116(Y/Y_n)^{1/3} - 16$$

$$a^* = 500[(X/X_n)^{1/3} - (Y/Y_n)^{1/3}]$$

$$b^* = 200[(Y/Y_n)^{1/3} - (Z/Z_n)^{1/3}]$$

$$\frac{X}{X_n}, \frac{Y}{Y_n}, \frac{Z}{Z_n} \geq 0.008856$$

where X_n, Y_n, and Z_n are the tristimulus values of the illuminant or white point. See Practice for Calculation of Color Tolerances and Color Differences from Instrumentally Measured Color Coordinates (D2244) for alternate equations *when* $X/X_n, Y/Y_n, \cdot Z/Z_n < 0.008856$.

Because CIELAB does not have tristimulus values or chromaticity coordinates as defined for the 1931 and 1964 CIE systems in Chromaticity Coordinates and Diagram, it does not have a chromaticity diagram.

An alternative set of CIELAB coordinates results in an LCH cylindrical color space. L remains the same but a^* and b^* are combined to give a chroma C^* and a hue angle h (measured in degrees)

$$C^* = (a^{*2} + b^{*2}); \quad h = \tan^{-1}(b^* / a^*)$$

These correlate well with visual judgments of lightness, chroma, and hue, respectively. Perhaps the widest use of CIELAB is in the calculation of color differences (see "Color Difference Calculations").

CIE 1976 L*,u*,v* (CIELUV) Space

The CIELUV space has a chromaticity diagram with coordinates u' and v', which are linear transformations of x and y, respectively. The linearity is important for the additive mixing of colored lights (see Additive Mixing of Lights). For the three-dimensional CIELUV space, these are combined with the (nonlinear) L^* transformation to give opponent-type axes u^* and v^*, whose meanings are the same as those of CIELAB a^* and b^*, respectively. An alternative set of hue angle and chroma coordinates, like those in CIELAB, and a color-difference equation, much less widely used than the CIELAB equation, are also part of this system.

COLOR ORDER SYSTEMS

A color order system is a rational method or plan of ordering and specifying all producible object or display colors, or all within a limited domain, by means of a set of physical standards selected and displayed so as to represent adequately the whole set of such colors under consideration. In this section the major color order systems, which have physical exemplifications or atlases illustrating underlying systems, are briefly discussed. References [19, 20] provide useful general coverage.

Munsell System

Dating from the early 1900s, the Munsell system is accepted by most users as the standard for equal visual spacing. It is described in the Practice for Specifying Color by the Munsell System (D1535). Its color solid is like that of Fig. 4 with the sole exception that lightness is called *value* in the Munsell system. Munsell Hue is designated by position around the hue circle in a notation combining letters designating five major hues (red, yellow, green, blue, purple) and their pairs (R, YR, Y, GY, G, BG, B, PB, P, RP) with numbers from 1 to 10. Munsell Value, to which CIE lightness L^* is a good approximation, runs from zero for black to 10 for white. Munsell Chroma, which expresses the degree of departure of the color from the gray of the same lightness, starts at zero and is open-ended. To describe a color in the Munsell system, the hue, value, and chroma are noted in a prescribed sequence, as for example, 8R 4/10. This designation indicates that the hue is red (toward yellow-red, i.e., an orange color), the value is 4, and the chroma is 10.

In 1943, the underlying Munsell system was defined in colorimetric terms [21], and since 1968 the chips in the glossy editions of the *Munsell Book of Color* have been produced to match these specifications. Fig. 10 shows contours of equal Munsell Hue and Chroma at value 5 on the 1931 CIEx,y chromaticity diagram.

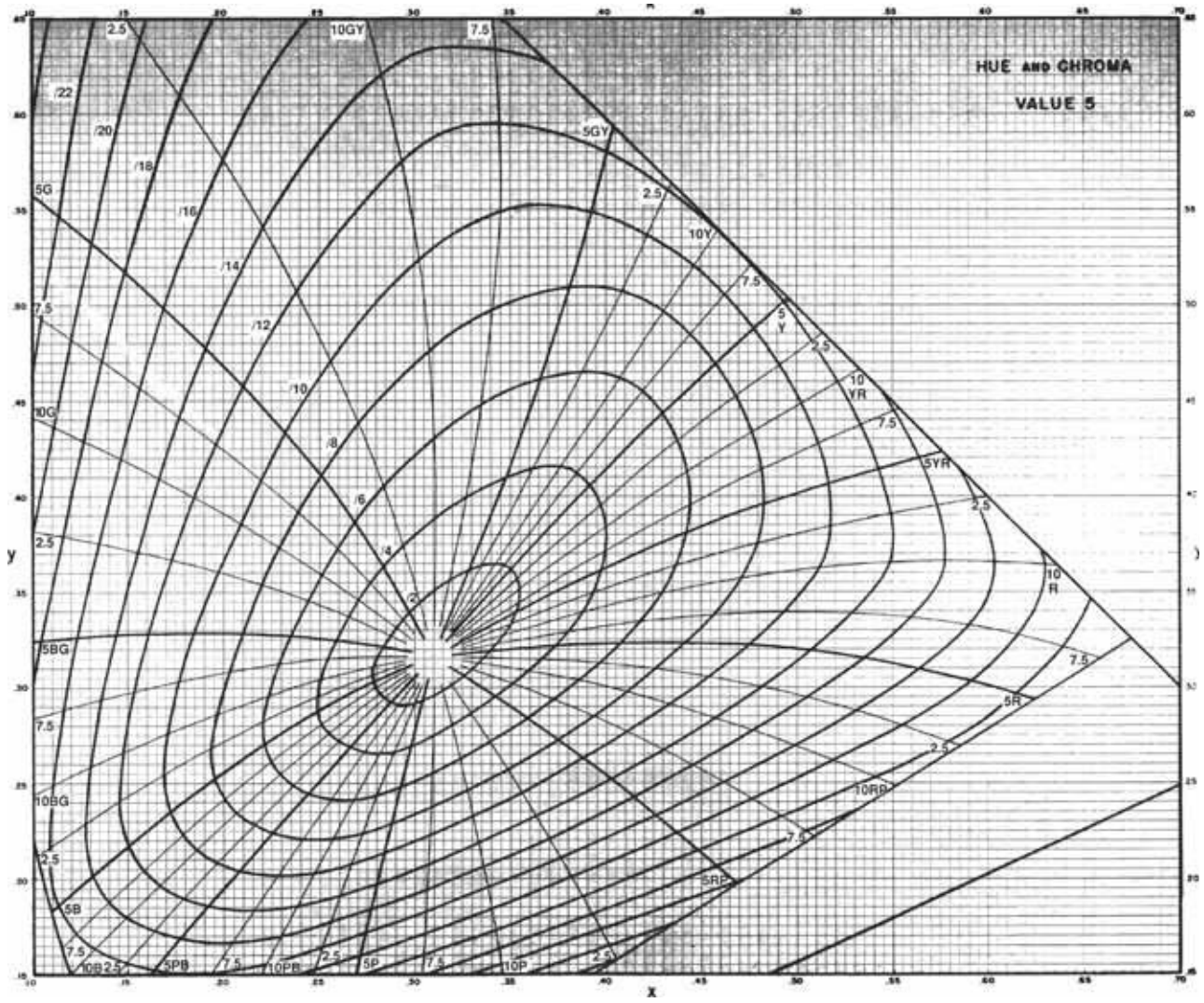

Fig. 10—Lines of constant Munsell Hue and closed curves of constant Munsell Chroma, at Munsell Value 5 plotted on the CIE 1931 chromaticity diagram.

The *Munsell Book of Color* [22], which is available in the United States, exemplifies the Munsell system.

ISCC-NBS System

In the 1950s the Inter-Society Color Council (ISCC) and the National Bureau of Standards (NBS) developed the ISCC-NBS Method of Designating Colors [23] based on the Munsell system but grouping similar colors to produce a smaller number (267) of categories. These are designated by descriptive color names, for example, dark reddish orange for the group containing 8R 4 /10.

Universal Color Language

The Munsell system and the ISCC-NBS system are both parts of a Universal Color Language [23], a six-level system for describing color to any desired degree of accuracy. Level 1 consists of the use of 13 hue and neutral names. At this level, the color with Munsell notation 8R 4/10 would be described as orange. In Level 2, which has 29 categories, intermediate hue names are added. Here the color would be described as reddish orange. Level 3 is the ISCC-NBS system, and Level 4 is the Munsell system as used in the *Munsell Book of Color;* designations at these levels are given above. Level 5 uses interpolated Munsell notations based on visual comparison of the color with *Munsell Book* chips. With practice it is possible to interpolate accurately to 1/10 value step, 1/4 chroma step, and from 1 hue step at chroma /2 to 1/4 hue step at chroma near /10 and above. Thus, at this level the color might be designated very accurately as 8.25 R 4.1/9.75. The final stage, Level 6, of the Universal Color Language is based on the results of color measurement, expressed as CIE chromaticity coordinates x,y, and Luminance Y. Now the color might be specified with greatest accuracy as $x = 0.527, y = 0.343, Y = 12.5$.

DIN System

The DIN Color System is the official German Standard Color System [24]. Its coordinates are hue (for which dominant wavelength is used), saturation (like chroma except representing difference from black instead of from gray of the same lightness), and relative darkness. From time to time, atlases of DIN samples have been available in glossy and matte finish and in transparent films. In the former

two, chips are arranged on pages of constant hue, similar to the Munsell arrangement.

NCS

Developed in the late 1960s and 1970s, the Natural Color System (NCS) [25] is the national standard color order system in Sweden and several other European countries. It is based on an entirely different principle from that of the other systems discussed, namely the resemblances of colors to six imaginary elementary colors, unique red, yellow, green, and blue, and black and white. The four hues are placed 90° apart on the hue circle. This does not lead to visually equal hue spacing. Two opponent-type axes result, perpendicular to the black-white lightness axis. The third variable of the system is chromaticness.

In terms of resemblances, hue is defined as the resemblance of a color to the two nearest chromatic elementary colors. For example, orange might be said to have 80 % resemblance to red and 20 % to yellow; its hue notation would be Y80R. Chromaticness is the resemblance of the color to the (imaginary) color of the same hue having the maximum possible chromatic content. Lightness is not an explicit variable in the system; the third resemblance can be to either white or black. Scales of resemblances to white, black, and the aforementioned maximally chromatic color are chosen so that these three add to 100 %, so only one of the resemblances to white or black need be specified. For the notation, resemblance to black has been selected, so that the three variables of the system are blackness, chromaticness, and hue. The complete NCS notation for the orange sample considered above in the Munsell system is approximately 3070 Y80R.

In the NCS atlas, pages of constant hue notation contain chips arranged on a grid in the form of an equilateral triangle. The corner points of the NCS triangles are imaginary elementary colors.

OSA-UCS System

The Optical Society of American Uniform Color Scales (OSA-USC) system [26,27] was developed by a committee of the OSA between 1947 and 1976. Although the committee concluded that no perfectly equally visually spaced system can exist because color space itself is not Euclidean, it attempted to achieve the best possible compromise and is generally thought to have succeeded. The axes of the color solid are lightness, L (with both positive and negative values around zero at middle gray) and two opponent axes, j (from the French *jaune* for yellow), with positive values toward yellow and negative values toward purple-blue, and g (for greenness), with blue-greens at the positive end and pinks at the negative end.

The OSA-UCS system in described in Practice for Specifying Color by Using the Optical Society of America Uniform Color Scales System (E1360). The 558 samples of the OSA atlas are arranged in a rhombohedral lattice in which each sample, except those at the edges, has 12 nearest neighbors.

COLORCURVE SYSTEM [28]

This new color order system was introduced in the United States in 1989. It is based on a color space similar to CIE 1964 tristimulus space [29]. Aim points are laid out according to additive mixing (see "Additive Mixing of Lights") of CIE 1964 tristimulus values X_{10}, Y_{10}, Z_{10} for Illuminant D65, starting from eight specified CIELAB points. The CIELAB lightness axis L (designated only as L) is retained, but coordinates along the CIELAB-type opponent axes are replaced by a simple numbering system, giving the sample location in terms of the number of lattice steps between it and the neutral axis in the directions of two adjacent major axes directed toward reds, yellows, greens, and blues. A typical Colorcurve notation would be L40 R1Y3 representing at lightness level 40 the lattice point one step away from neutral toward the reds and three steps toward the yellows. This is an orange, only slightly different from the sample discussed above.

Another feature of the Colorcurve system is that spectral reflectances are furnished for the aim points. These can be additively mixed like tristimulus values to obtain the spectral curve corresponding to any Colorcurve notation; this can be the basis for computer colorant formulation (see "Instrumental and Computer-Aided Color Matching") to provide a match with minimum metamerism to the surrounding Colorcurve samples. Practice for Specifying and Matching Color Using the Colorcurve System (E1541) describes the system in more detail, including a tabulation of spectral reflectances, tristimulus values, and CIELAB coordinates for the sample aim points.[3] The Colorcurve atlas [30] contains about 2,200 painted samples.

Color Collections

For each of the color order systems described above, atlas samples consist of painted chips individually matched to the specified aim points with a mean accuracy of about one CIELAB unit. A number of color collections have been produced by coating paint on paper, printing, molding plastic chips, and dying textiles. A colorist may be required to match these collections. Painted samples are probably the easiest to match because of the similarity of pigments and resins. Plastic samples can present problems because they are often translucent. However, many of the pigments used in plastics are similar to paints and may be fairly easy to match. Printed samples are often very difficult to match. Most are at incomplete hiding and have high chromas because they are printed over white (possibly fluorescent) paper. It may be impossible to achieve the high chromas in a conventional paint system at complete (or nearly so) hiding. The color reproducibility achieved by printing is usually significantly lower than can be achieved with a paint system. Textile samples are made by dying fabric. It may not be possible to match the spectral curve of a dyed fabric with the pigments used in a paint system.

Single-Number Color Scales

Occasions arise in which the colors of samples vary along a single direction in color space. In such a case the color can be described adequately by a single scale value. Three cases are of interest: whiteness, yellowness, and series ranging from colorless to highly colored as the concentration of a colored component increases.

[3]E1541 was withdrawn in 2007 after production of the Colorcurve atlas and related materials ceased. This section is included for historical purposes.

TABLE 3—Coefficients for the Equations for CIE Whiteness Index and Tint						
	CIE Standard Illuminant and Observer					
Value	C, 1931	D_{50}, 1931	D_{65}, 1931	C, 1964	D_{50}, 1964	D_{64}, 1964
x	0.3101	0.3457	0.3127	0.3104	0.3477	0.3138
y_n	0.3161	0.3585	0.3290	0.3191	0.3595	0.3310
WI,x	800	800	800	800	800	800
WI,y	1700	1700	1700	1700	1700	1700
T,x	1000	1000	1000	900	900	900
T,y	650	650	650	650	650	650

Whiteness and Tint Indices

Whiteness scales start at the point corresponding to an ideal white, which may be the perfect reflecting diffuser (see "Calculation of Tristimulus Values") or some other industry standard, often assigned a whiteness of 100.

Practice for Calculating Yellowness and Whiteness Indices from Instrumentally Measured Color Coordinates (E313) extends the equations recommended by the CIE [15] to Illuminants C and D50. The equation for the whiteness index is

$$WI = Y + (WI,x)(x_n - x) + (WI,y)(y_n - y)$$

where:

Y,x,y = the luminance factor and the chromaticity coordinates of the specimen,

x_n and y_n = the chromaticity coordinates for the CIE standard illuminant and source used, and *WI,x* and *WI,y* = numerical coefficients.

The whiteness index is valid only for specimens with $40 < WI < (5Y–280)$.

E313 also includes a tint index

$$T = (T,x)(x_n - x) - (T,y)(y_n - y)$$

where the symbols have meanings analogous to those for the whiteness index.

The tint index is valid only for specimens with $-3 < T < +3$.

Values for all the coefficients, except those measured for the specimen, are given in Table 3.

Yellowness Indices

Yellowness indices show the departure of a specimen from achromatic toward yellow. The yellowness index described in Practice E313 is calculated using the equation

$$YI = \frac{100(C_X X - C_Z Z)}{Y}$$

Values for all the coefficients, except those measured for the specimen, are given in Table 4.

This equation supercedes the one given in the ASTM Test Method for Yellowness Index of Plastics (D1925), which has been withdrawn.

Scales for Liquids

When only a limited range of color is involved, for example, in the testing of the color of oil, clear varnish, lacquer, or solvents used in the paint industry, simple methods are used consisting of comparison of the specimen with standard colored solutions or glasses ranging from colorless to highly colored. A standardized series of these colors is used to provide a specialized color scale. The color is often a measure of concentration of an ingredient. One difficulty in the use of these special color scales is that the color of the specimen may not match that of the standard; this can make rating on a single-number scale difficult. Nevertheless, their simplicity, low cost, and adaptability to special situations has resulted in wide use of single-number scales for certain applications. Scales useful to the paint industry are shown in Table 5.

Test Method D6045 is an instrumental version of Test Methods D1500 and D156. Practice E313 can be used to determine the whiteness and yellowness indices of transparent liquids. A number of single-number color scales were compared by Johnston [31].

INDUSTRIAL COLOR MEASUREMENT

Instruments Using the Eye as Detector

The eye is the ultimate arbiter in color evaluation because, of course, it is the means for making the final judgment on the acceptability of a color. The first color-measuring instruments used the eye as a detector. This practice is still followed when use of a simple color comparator suffices, as in many of the test methods for single-number color scales described in the preceding paragraph. But there are many factors, such as fatigue, poor color memory, and subjectivity, as well as the perceptual phenomena described earlier under

TABLE 4—Coefficients of the Equation for Yellowness Index				
	CIE Standard Illuminant and Observer			
Value	C, 1931	D_{65}, 1931	C, 1964	D_{64}, 1964
C_X	1.2769	1.2985	1.2871	1.3013
C	1.0592	1.1335	1.0781	1.1498

TABLE 5—ASTM standards on scales for liquids

Designation	Title
D156	Test Method for Saybolt Color of Petroleum Products (Saybolt Chromometer Method)
D365	Guide for Soluble Nitrocellulose Base Solutions
D1209	Test Method for Color of Clear Liquids (Platinum-Cobalt Scale)
D1500	Test Method for ASTM Color of Petroleum Products (ASTM Color Scale)
D1544	Test Method for Color of Transparent Liquids (Gardner Color Scale)
D1686	Test Method for Color of Solid Aromatic Hydrocarbons and Related Materials in the Molten State (Platinum Cobalt Scale)
D5386	Test Method for Color of Liquids Using Tristimulus Colorimetry
D6045	Test Method for Color of Petroleum Products by the Automatic Tristimulus Method
D6166	Test Method for Color of Naval Stores and Related Products (Instrumental Determination of Gardner Color)

"Perception," that make the eye at least suspect for close color evaluation work. Therefore, the use of the eye as a detector has been almost entirely replaced by the use of two types of photoelectric instruments developed since the 1940s for color measurement.

Spectrophotometers

Spectrophotometers provide the spectral reflectances (or transmittances) required for the calculation of CIE tristimulus values and derived color coordinates, which were described earlier under "Colorimetry and the CIE System" and in Practice E308.

When radiation strikes a sample, it may be reflected, absorbed, or transmitted. Each of these can be measured by most spectrophotometers. All spectrophotometers consist of a light source, a monochromator, arrangements for illuminating and viewing the sample, a photodetector, and an output device. In modern instruments, the latter consists of a computer that processes the signals from the detector and provides for the calculation of tristimulus values and a wide variety of other color-related quantities. Each of these components is described briefly.

The Illuminator

The illuminator is that part of a spectrophotometer that provides the illuminating beam on the specimen, including the source, occasionally a monochromator or spectral filters, a diffuser such as an integrating sphere, if used, and associated optics. In most cases the exact nature of the light source in a spectrophotometer is of little importance as long as it has adequate power and stability at all wavelengths in the visible spectrum. Incandescent lamps or xenon flash tubes are widely used. When fluorescent samples are measured (see "Fluorescence"), the source must illuminate the sample directly and may be filtered to simulate a standard source, such as CIE daylight D65. Most color measuring spectrophotometers are designed with these features. Practice E991 provides more information on the measurement of fluorescent samples.

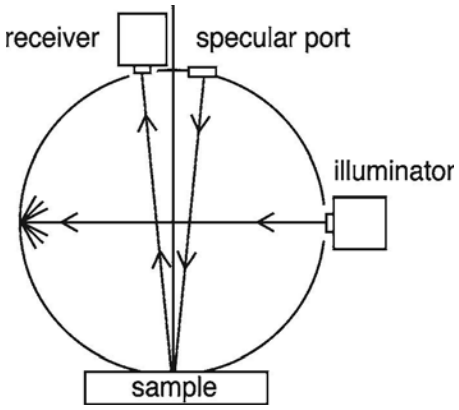

Fig. 11—A representation of the CIE hemispherical geometry. Light illuminates the integrating sphere to diffusely illuminate the sample. The receiver is placed slightly off of the normal so that the specular reflection can be either included or excluded during the measurement.

Illuminating and Viewing Geometry

In most spectrophotometers, the geometry of sample illumination and viewing follows CIE recommendations [15]. Two standard geometries are widely used. In hemispherical geometry, light from the source usually illuminates the white interior of a hollow, approximately spherical cavity called an integrating sphere, and the diffused light from the sphere illuminates the sample from all angles in the hemisphere bounded by its surface. The sample is viewed at an angle near the normal or perpendicular to its surface. If the sample is glossy, the specular or mirror reflection from its surface will result in a portion of the wall of the integrating sphere also being viewed. The user is given the option of making this part of the sphere white, thus including the specular component, or black, excluding it (Fig. 11).

In bidirectional geometry, illuminating and viewing are at angles along the normal to the sample surface (designated 0°) and 45° from the normal, or the reverse (Fig. 12). The use of bidirectional geometry with the specimen illuminated by white light is recommended when fluorescent samples are measured. Hemispherical and bidirectional geometries are described in the Guide for Selection of Geometric Conditions for Measurement of Reflection and Transmission Properties of Materials (E179) and in Practice E1164, as well as by the CIE [15].

In typical 45/0 or 0/45 geometry, several illuminating or viewing beams, distributed around the azimuth at 45° to the normal, may be used. When a specimen exhibits directionality, that is, its reflectance changes when it is rotated in its own plane, the use of an instrument with multiple beams provides data that average over the directionality, giving a single number characteristic of the average properties of the specimen. If it is desired to measure the directionality, an instrument with one illuminating (or viewing) beam, or two 180° apart in azimuth, should be used and measurements made at several different specimen orientations.

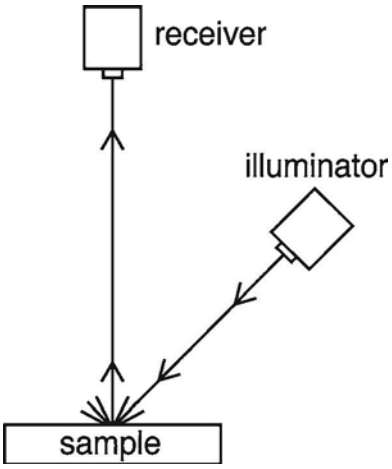

Fig. 12—A representation of the CIE 45/0 bidirectional viewing. Light illuminates the sample from an angle of 45° and the receiver views the light reflected from the sample along its normal. The positions of the illuminator and receiver can be reversed to obtain the 0/45 illuminating/viewing geometry. For non-directional specimens, the two measurements will be equivalent.

For the measurement of specimens exhibiting gonioappearance, in which the reflectance changes when the illuminating or viewing angles are changed, the use of special instruments capable of measuring at different combinations of these angles is required. Several such multiangle instruments, known as goniospectrophotometers, are commercially available (Fig. 13). See the earlier section on "Gonioappearance."

The Receiver

The receiver converts the light reflected or transmitted by the specimen into an electrical signal and includes all the optics necessary to focus the light onto a photodetector. The optics in the receiver direct the light to the spectral analyzer in which a narrow (typically 10 to 20 nm) band of wavelengths is selected from the full spectrum of the incident light. The spectral analyzers in modern instruments usually use holographic diffraction gratings or interference filters to isolate the narrow wavelength range. Spectral light is received by the photodetector, usually a silicon photodiode. The photo-detector may consist of an array of diodes, each positioned permanently to receive light of a given wavelength, thus eliminating the need for a spectrum scanning device. The electrical signal from the detector is usually amplified, digitized, and entered in an interfaced computer. In addition to Practice E1164, the following ASTM test methods cover the operation of modern spectrophotometers: Test Method E1331, Test Method E1348, and Test Method E1349.

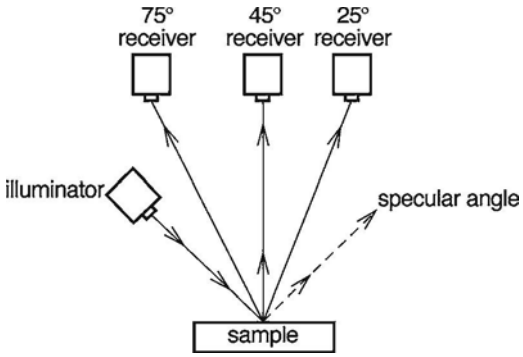

Fig. 13—A representation of a multiangle instrument (goniospectrophotometer) for measuring materials containing metallic flake pigments. One illuminating angle and three viewing angles are sufficient for these materials. To characterize interference pigments, at least two illuminating angles are required.

Spectroradiometers

Instruments closely related to spectrophotometers but made to measure light incident from external sources are known as spectroradiometers. They could be used in the paint industry when, for example, the specimen must be sensed remotely after being illuminated externally to the instrument. Methods for making such measurements are described in Test Method for Obtaining Colorimetric Data From a Visual Display Unit by Spectroradiometry (E1336), Practice for Obtaining Spectroradiometric Data from Radiant Sources for Colorimetry (E1341), and Practice for Obtaining Colorimetric Data from a Visual Display Unit Using Colorimeters (E1455).

Obtaining Tristimulus Values from Spectral Data

The first step in utilizing spectral data is the calculation of CIE tristimulus values, as described earlier under Calculation of Tristimulus Values. This step is performed automatically as part of the measurement sequence in all modern spectrophotometers designed for color measurement. It is usual that the spectral bandpass of the monochromator and the measurement interval are selected to be the same. For highest accuracy, the correct set of tristimulus weighting factors, corresponding to the instrument bandpass, selected from among those added to the Practice E308 in 1994 (Table 6), must be used in calculating tristimulus values. In addition, the user must select the standard illuminant and the standard observer used.

Spectrocolorimeters

Some spectrophotometers are designed so that the measured spectral reflectances or transmittances cannot be accessed for examination; only the resulting tristimulus values and other color coordinates can be printed out. Such instruments are designated spectrocolorimeters.

Tristimulus (Filter) Colorimeters

Among the earliest photoelectric color-measuring instruments were those in which the source-filter-photodetector combinations duplicate the tristimulus functions of the Standard Observer and a CIE Standard Illuminant, usually Illuminant C [32]. How well their filters are designed and matched to the spectral characteristics of the source and of the detector determines how accurately the instrument performs. Today a high degree of accuracy is attained in the resulting tristimulus values.

Because of their ease of operation, good precision, and relatively low cost, tristimulus (filter) colorimeters had found wide application for industrial control. They are used primarily as color-difference meters to evaluate the difference in color between a production specimen and a standard of similar spectral character. This last limitation is important for most colorimeters. Because of their design,

TABLE 6—Standards pertinent to calibration and maintenance of color-measuring instruments

Designation	Title
D3964	Practice for Selection of Coating Specimens and Their Preparation for Appearance Measurements
D5531	Guide for Preparation, Maintenance, and Distribution of Physical Product Standards for Color and Geometric Appearance of Coatings
E1164	Practice for Obtaining Spectrometric Data for Object-Color Evaluation
E1331	Test Method for Reflectance Factor and Color by Spectrophotometry Using Hemispherical Geometry
E1345	Practice for Reducing the Effect of Variability of Color Measurement by Use of Multiple Measurements
E1348	Test Method for Transmittance and Color by Spectrophotometry Using Hemispherical Geometry
E1349	Test Method for Reflectance Factor and Color by Spectrophotometry Using Bidirectional (45°:0° or 0°:45°) Geometry
E2214	Practice for Specifying and Verifying the Performance of Color-Measuring Instruments

most colorimeters provide colorimetric data for only one combination of illuminant and observer and therefore cannot detect metamerism. When specimens are metameric, a colorimeter can give incorrect data on the differences among them. Filter colorimeters should not be used to evaluate pairs of specimens that may be metameric. This limitation should be clearly understood. As a result of improved technology and lower costs, most tristimulus colorimeters have been replaced by spectrophotometers.

The use of colorimeters is described in Test Method E1347.

Selection and Calibration of Instruments

The potential user of color-measuring instrumentation must carefully consider the selection of the proper instrument(s), depending on his samples and measurement needs. Guide E179 and Practice E805 address this topic. They should be consulted, if possible, before the purchase of a new instrument.

The user of any color-measuring instrument must give regular attention to its calibration. Appropriate calibration standards, available from instrument manufacturers and, in some cases, national standardizing laboratories, should be obtained, maintained in good condition, and used at frequent intervals in an established routine [33]. A collaborative reference program [34] is available by means of which a user's instrument performance can be compared to that obtained for the same samples by the color community as a whole and by national standardizing laboratories.

With proper calibration and maintenance, modern color-measuring instruments are capable of a repeatability and reproducibility far greater than the repeatability with which the samples themselves can normally be prepared for industrial measurement. Thus, special care must be taken to establish a highly reproducible method of paint sample preparation and to establish by careful measurement and periodic verification the uncertainties associated with this step in the measurement process. ASTM standards pertinent to this topic are shown in Table 6.

The following two subsections apply mainly to spectrophotometers.

Precision

The modern age of computer-interfaced color measuring spectrophotometers began in the mid-1970s. By then it had been clearly demonstrated that such instruments could surpass the eye in the precision of color measurement. In 1981 the short-term repeatability of instrumental color measurement was reported to be about 0.1 CIELAB unit of color difference [35] (see "Color Difference Calculations"). By 2002 instrument manufacturers were specifying the short-term repeatability for top-of-the-line benchtop instruments to be in the neighborhood of 0.01 CIELAB units. In 1979 the average reproducibility within a group of similar instruments was reported to be about 0.2 CIELAB units [36]. By 2002 instrument manufacturers were specifying the inter-instrument agreement for top-of-the-line benchtop instruments as less than 0.10. It should be noted that the very low repeatability and reproducibility numbers can only be achieved with stable standards at a tightly controlled temperature. Note that 0.5 CIELAB unit is approximately the smallest difference that can be detected visually. Repeatability and reproducibility values are published in the Precision and Bias section of Practice E1164 and Practice for Calculation of Color Tolerances and Color Differences from Instrumentally Measured Color Coordinates (D2244).

Bias

This quantity, the difference between a measured result for a standard sample and the result when it is measured in a reference laboratory, is difficult to quantify for color measurement where there are no absolute values. It is usual to accept the results obtained in a national standardizing laboratory as the reference. On this basis, when instruments are selected to minimize differences in measuring geometry and are properly calibrated and used, the average bias for a group of standard samples can be as low as 0.5 CIELAB unit [37]. In addition, the differences between the two sets of measurements can be utilized effectively to model and correct the systematic spectrophotometric errors leading to the bias [38].

Commercial Instruments

Specific information about instruments published in a manual such as this would almost certainly become obsolete by the time the manuscript is printed. For this reason, detailed information on suppliers and their instrumentation is not included. Such information, including types of instruments manufactured, their design features and performance characteristics, can best be found by first consulting buyers' guides [39,40] that are revised annually. Another useful source of information is the lists of exhibitors at paint shows, such as the descriptions published annually in the *JCT Coating Tech.* An additional source of information on commercial instruments is the internet.

Most color instrument suppliers maintain internet sites with current information on their products and services. Registered users can also obtain product updates and support. In contacting suppliers of instrumentation, the user might request that they send literature, measure samples sent them, or have a representative visit the user to demonstrate the instrument. Another procedure is to negotiate a rental-purchase contract. While some suppliers are reluctant to negotiate such contracts, the procedure provides users the opportunity to evaluate the instrument with their own operators at their own facilities.

1. *Portable instruments*. In earlier times, production samples had to be taken to a quality-control laboratory for evaluation. This procedure is still desirable in some instances to permit control of such variables as ambient light, temperature and humidity, and atmospheric contamination. However, time can be saved by making measurements on the production floor using portable instruments. Many manufacturers now supply portable spectrophotometers and colorimeters that provide small size and light weight. Some portable instruments perform nearly as well as benchtop instruments. In many, the precision is good, but limitations related to measurement geometry may increase bias. If very small illuminated and viewed areas are used, there may be an advantage in that smaller portions of samples can be measured, but averaging of multiple measurements (see Practice E1345) may be required to obtain representative values for nonuniform samples.
2. *Multiangle Evaluation*. Several manufacturers now supply instruments with multiangle geometry for the measurement of gonioapparent samples, such as those containing metal flake or pearlescent pigments. For research in this field, a goniospectrophotometer is required. For quality control, however, use of one angle of illumination with several angles of view, or several angles of illumination with one angle of view, may suffice.
3. *Location and Type of Use*. For continuous processes, online instrumentation is finding greater use. In addition, color measurement and computer-aided color matching (see Instrumental and Computer-Aided Color Matching) are used extensively at point-of-purchase locations such as retail paint stores.

COLOR DIFFERENCE EVALUATION FOR COLOR CONTROL

The color control of industrial paint products is generally aided by color measurement, as described in the last section. The instruments provide color coordinates of sample and standard from which accurate measures of color difference may be derived. These data can also be used to establish color tolerances. Of course, color differences may also be judged visually, and several ASTM standards address this topic: Practice for Visual Appraisal of Colors and Color Differences of Diffusely-Illuminated Opaque Materials (D1729), Test Method for Evaluation of Visual Color Difference With a Gray Scale (D2616), and Guide for Selection, Evaluation, and Training of Observers (E1499). This guide also describes materials and methods for the testing and evaluation of the observer's color vision.

Color-Difference Calculations

In the 1931 and 1964 CIE systems, equal distances in different parts of color space do not represent equally perceived color differences. Although many proposals for more uniform color spaces have been made, an ideal uniform space has not been and may not ever be devised. Sets of color coordinates can be derived from tristimulus values that correlate better with perceived color differences than do the original CIE tristimulus values.

Modifications of CIE tristimulus values have been proposed for more uniform color spaces. Those proposed by Hunter [32], MacAdam [41-43], and the CIE [15] had been widely use in the paint industry. The color-difference equation based on the CIE 1976 $L^*a^*b^*$ (CIELAB) space discussed earlier in Uniform Color Spaces and color-difference equations based on that equation perform significantly better than the Hunter and MacAdam equations when compared to experienced visual color judgments. As a result, the Hunter and MacAdam equations can no longer be recommended.

The total CIELAB color difference, ΔE^*_{ab}, is given by

$$\Delta E^*_{ab} = [(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2]^{1/2}$$

where

$$\Delta L^* = L^*_{\text{TRIAL}} - L^*_{\text{STANDARD}}$$

$$\Delta a^* = a^*_{\text{TRIAL}} - a^*_{\text{STANDARD}}$$

$$\Delta b^* = b^*_{\text{TRIAL}} - b^*_{\text{STANDARD}}$$

It is convenient to express ΔE^*_{ab} in terms of differences in the Munsell-type coordinates hue, chroma, and lightness, but the hue angle h defined earlier in Uniform Color Spaces does not have the same dimensions and scaling as chroma C^* and lightness L^*. Instead of using h, it is necessary to define CIELAB hue difference ΔH^* to combine with ΔC^* and ΔL^*

$$\Delta H^*_{ab} = \left[\left(\Delta E^*_{ab}\right)^2 - \left(\Delta C^*_{ab}\right)^2 - \left(\Delta L^*\right)^2 \right]^{1/2}$$

Then

$$\Delta E^*_{ab} = \left[\left(\Delta H^*_{ab}\right)^2 - \left(\Delta C^*_{ab}\right)^2 - \left(\Delta L^*\right)^2 \right]^{1/2}$$

This method of computing ΔH^*_{ab} loses the information about the sign of the hue difference (positive or negative) and can be unstable for pairs of colors near the neutral axis. Alternative equations for determining ΔH^*_{ab} and its sign have been proposed [44] that corrects both problems

$$\Delta H^*_{ab} = s\left[2\left(C^*_{ab,B} C^*_{ab,S} - a^*_B a^*_S - b^*_B b^*_S \right) \right]^{1/2}$$

where

$$s = 1 \text{ if } a^*_S b^*_B > a^*_B b^*_S, \qquad \text{else } S = -1$$

in which the subscript B indicates the trial and the subscript S indicates the standard. The unit of CIELAB color difference is two to three times the just perceptible color difference.

In the use of color differences, it is important to examine the components of the color difference, such as ΔL^*, Δa^* and Δb^*, or ΔL^*, ΔC^*_{ab}, and ΔH^*_{ab}, as well as ΔE^*_{ab} itself. The magnitudes and signs of these components can provide valuable information on remedial action needed to bring a production batch on shade. For near-neutral and pastel colors, there are advantages to using the ΔL^*, $\Delta^* a$, and $\Delta^* b$ forms of the color-difference equation.

The interpretation of measured color differences becomes more complex when the specimens are gonioapparent and measurements are made at several combinations of illuminating and viewing angles. The quantitative meaning of color differences as the angles change has not yet been thoroughly studied.

Since the adoption of the CIELAB equations, a number of new color-difference equations have been developed. One of these, known as the CMC (l:*c*) equation [45,46], is a modification of CIELAB that has improved uniformity of visual perception of its color differences. The CMC (l:c) equation has found widespread use in the coatings industry. The CMC (l:c) equation modifies the ΔL^*, ΔC^*, and ΔH^* components of the CIELAB color difference

$$\Delta E_{\mathrm{CMC}}(l:c) = cf * \sqrt{\left(\frac{\Delta L^*}{l * S_L}\right)^2 + \left(\frac{\Delta C^*}{c * S_C}\right)^2 + \left(\frac{\Delta H^*}{S_H}\right)^2}$$

$$S_L = \frac{0.040975 * L^*}{1 + (0.01765 * L^*)} \quad \text{for} \quad L^* \geq 16$$

$$S_L = 0.511 \quad \text{for} \quad L^* < 16$$

$$S_C = \frac{0.0638 * C^*}{1 + (0.0131 * C^*)} + 0.638$$

$$S_H = S_C\{(T * f) + 1 - f\}$$

where

$$f = \left\{\frac{(C^*)^4}{(C^*)^4 + 1900}\right\}^{1/2}$$

$$T = 0.56 + \mathrm{abs}\left|0.2\ \cos(h + 168\ ^\circ)\right| \quad \text{if } 164\ ^\circ < h < 345^\circ$$

else

$$T = 0.36 + \mathrm{abs}|0.4 * \cos(h + 35^\circ)|$$

in which "abs" indicates the absolute, i.e., positive value, of the term inside the brackets.

The parameters *l* and *c* are to compensate for systematic bias or parameteric effects such as texture and sample separation. The most common values for *l:c* are 2:1. The parameter *cf* is a commercial factor [47] used to adjust the total volume of the tolerance region so that accept/reject decisions can be made on the basis of a unit value of the tolerance.

In 2001 the CIE recommended an improved color-difference equation, CIEDE2000, based on the CIELAB color space [48]. This equation has been shown to outperform the CMC (l:c) equation [49]. CIEDE2000 is calculated from

$$L' = L^*$$

$$a' = (1 + \mathrm{G}) \cdot a^*$$

$$b' = b^*$$

$$C' = \sqrt{(a')^2 + (b')^2}$$

If $b' \neq 0$, then $h' = 180 - (180/\pi)\ \arctan(a'/b') - 90\ \mathrm{sign}(b')$

If $b' = 0$, then $h' = 90\ \mathrm{sign}((a')^2) - 90\ \mathrm{sign}(a')$

where *sign* is a function that returns the sign of the argument and *arctan* is the inverse tangent function returning angles in units of radians

$$G = 0.5 * \left(1 - \sqrt{\frac{(\bar{C}^*)^7}{(\bar{C}^*)^7 + 25^7}}\right)$$

where $\bar{C}^*$ is the arithmetic mean of the CIELAB C^* values for the pair of specimens (standard and batch).

$$\Delta L' = L'_B - L'_S$$

$$\Delta C' = C'_B - C'_S$$

$$\Delta H' = s * \sqrt{2\left[\left(C'_{\mathrm{B}} * C'_{\mathrm{S}}\right) - \left(a'_{\mathrm{B}} * a'_{\mathrm{S}}\right) - \left(b'_{\mathrm{B}} * b'_{\mathrm{S}}\right)\right]}$$

where

$$s = 1 \text{ if } a'_S\, b'_B > a'_{B^*} b'_S, \quad \text{else s} = -1$$

$$\Delta E_{00}^{\ 2} = \left(\frac{\Delta L'}{K_L \cdot S_L}\right)^2 + \left(\frac{\Delta C'}{K_C \cdot S_C}\right)^2 + \left(\frac{\Delta H'}{K_H \cdot S_H}\right)^2 + R_r \cdot \left(\frac{\Delta C' \cdot \Delta H'}{K_C \cdot S_C \cdot K_H \cdot S_H}\right)$$

$$\Delta E_{00} = \sqrt{\Delta E_{00}^2}$$

The factors K_L, K_C and K_H are correction terms for variation in perceived color-difference due to the viewing conditions. To obtain color-differences similar to CMC (2:1), set $K_L = 2$ and $K_C = K_H = 1$.

$$S_L = 1 + \frac{0.015\ *\ \left(\bar{L}'\ -\ 50\right)^2}{\sqrt{20 + \left(\bar{L}'\ -\ 50\right)^2}}$$

where $\bar{L}'$ is the arithmetic mean of the CIELAB L' values for the pair of specimens (standard and batch).

$$S_C = 1 + (0.045\ *\ \bar{C}')$$

where $\bar{C}'$ is the arithmetic mean of the CIELAB C' values for the pair of specimens (standard and batch).

$$S_H = 1 + (0.015\ *\ \bar{C}' * T)$$

$$R_T = -R_C * \sin(2 * \Delta\theta)$$

$$R_C = 2 * \sqrt{\frac{(\bar{C}')^7}{(\bar{C}')^7 + 25^7}}$$

$$\Delta\theta = 30 * \exp - \left\{\left[\frac{\bar{h}' - 275^\circ}{25}\right]^2\right\}$$

$$T = 1 - [0.17 * \cos(\bar{h}' - 30°)] + [0.24 * \cos(2\bar{h}')] + [0.32 * \cos(3\bar{h}' + 6°)] - [0.20 * \cos(4\bar{h}' - 63°)]$$

where $\bar{h}'$ is the arithmetic mean of the CIELAB L' values for the pair of specimens (standard and batch). All angles are in degrees. Take care calculating the mean hue-angle if the color-difference pair has samples in different quadrants. For example, a color-difference pair has hue angles of 30° and 300°. The mean hue-angle for this example is 345°. To determine the mean correctly, calculate the absolute difference of the hue angles. If the absolute difference is larger than 180° then add 360 to the smaller hue angle and divide that sum by 2.

Color Tolerance

A valuable means of recording the experience gained in the production of a given color is through the use of color tolerances, expressed as numerical limits to ΔE^* and its components or as color-tolerance charts. Because no color space is entirely uniform, industrial color tolerances are often based on acceptability, not perceptibility, considerations between buyer and seller. General color differences should be used only as a guide until enough experience has been accumulated for each color to allow specification of a firm tolerance limit.

Tolerance Charts

Color-tolerance charts are usually enlarged sections of a nearly visually equally spaced diagram, such as the CIELAB a^*,b^* diagram. A color-tolerance chart is set up with the coordinates of the standard at the center, and the differences Δa^* and Δb^* of production batches are entered as they are made (Fig. 14(*a*)). The process is described in Practice for Establishing Color and Gloss Tolerance (D3134). As experience is gained, it should be possible to draw a tolerance-limit curve enclosing most, if not all, of the acceptable batches and excluding most, if not all, of the unacceptable batches. Because no known diagram is perfectly visually uniform or if there is a preferred direction for the batches relative to a standard, then the tolerance limit figure may not be a circle or an ellipse and may not be centered on the location of the standard.

Lightness differences between the standard and batch must also be taken into account. This can be done by use of a separate tolerance for ΔL^*, but better practice is to use a second chart (Fig. 14*(b)*), in which ΔL^* is plotted against either Δa^* or Δb^*, depending on the data. The batch readings should fall within the tolerance figure on both charts.

It must be emphasized that the final criterion for acceptance of a color is always its visual appearance, to which instrumental measurements, color differences, and tolerance charts provide only clues. Instrument malfunctions, miscalibrations, miscalculations, and operator errors can be revealed only by use of confirming visual observations.

Indices of Metamerism

Another important use of color-difference equations is to quantify indices of metamerism as an aid in reducing this defect between standard and batch. The CIE [15,50] has recommended that indices of metamerism be calculated as the color differences between two samples that match under a standard illuminant or to a standard observer when measured for a test illuminant or a test observer. For illuminant metamerism, the standard illuminant is usually daylight. The second observer is selected by the user and is usually incandescent light. Often a third illuminant is specified, which is usually a fluorescent lamp. For observer metamerism, the standard observer is either the CIE 1931 or 1964 observer. To determine the index of metamerism, a corresponding second standard deviate observer is provided [50] based on the range of normal color vision found in the human population.

COLOR MIXING

Additive Mixing of Lights

When a white card is illuminated, its apparent color is the color of the incident light; a red light, for example, makes it appear red. Three colored lights (red, green, and blue), if carefully chosen, would, when placed to overlap on the same area of the card, produce white again (Fig. 15). In this area, the reflected lights from the three sources add together. These three lights are called the additive primaries. By adjusting the intensities of each of the three lights, a wide range of colors can be produced.

The procedure just described can provide an analytical tool for color measurement. If an adjacent spot on the white card is illuminated by light of an unknown color, it could be matched visually, in principle, with the three-light combination by adjusting their intensities. This is the basis for color matching by addition of lights. The additive principle is used to produce the colors in television and computer monitors [51].

The analytical device described above is also a simple version of the visual colorimeter used to generate the tristimulus values of the spectrum colors that form the basis for the CIE Standard Observers (see CIE Standard Observers). At each wavelength, the total light reflected is the sum of the power reflected from each of the three primary lights. Since tristimulus values are obtained by adding such sums across the spectrum, they too are produced by additive mixing. It is not necessary to know the spectral nature of the additive primaries to predict the resulting colors.

Subtractive Mixing in Transparent Films

Now consider the light falling on a white card after passing through a film that contains three transparent colorants, yellow, cyan (blue-green), and magenta (red-purple). This might be the situation with a free-standing transparent plastic film, for example. If the three colorants are ideally chosen, all the light would be absorbed when all three colorants are present, and the result would be black (Fig. 16). These three colorants are called the subtractive primaries. If varying quantities of them were combined in subtractive mixing, a wide variety of colors could be produced. However, these mixture colors cannot be predicted from the colors of the primaries alone, as in the additive mixing described above. One must also know their spectral character and compute, wavelength by wavelength, how much light is removed by each primary through absorption, using the well-known Beer's law relationship. From what is not absorbed, tristimulus values can be calculated in the usual way.

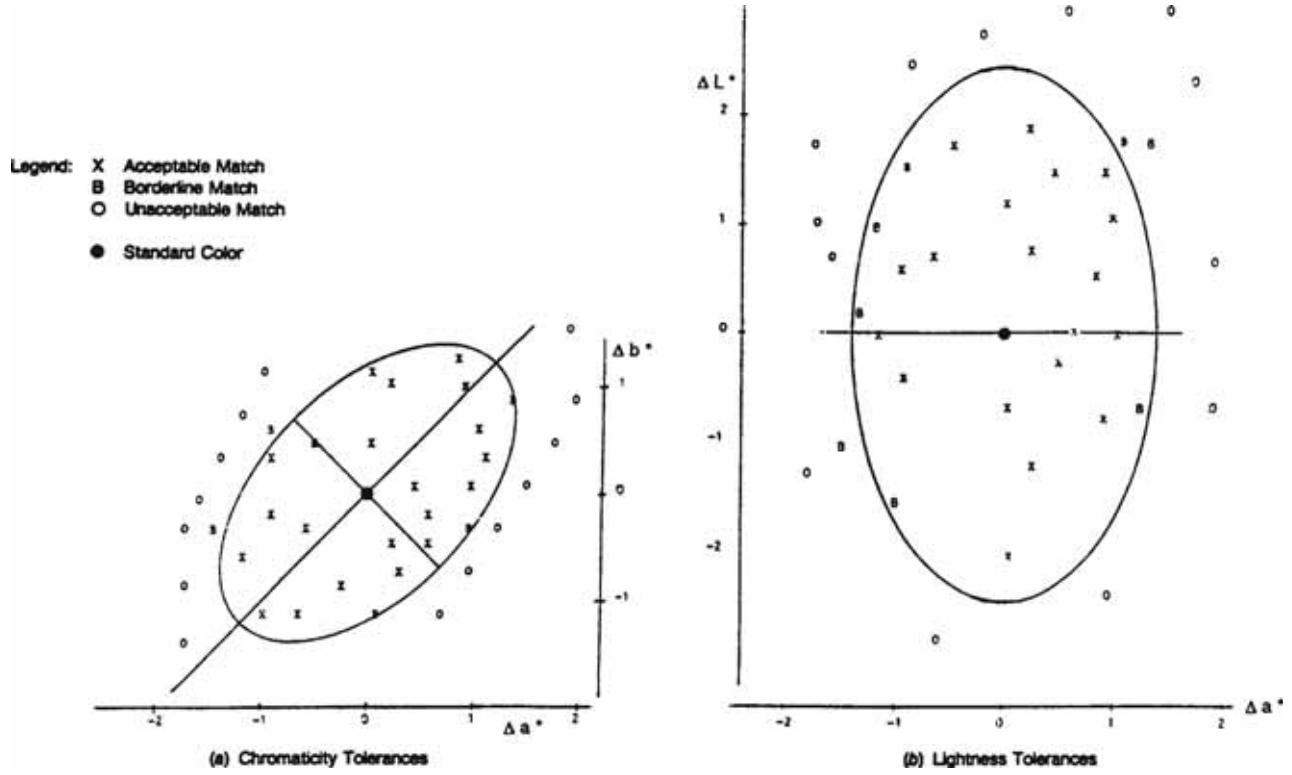

Fig. 14—Color tolerance charts plotted in the CIELAB system: (a) chromaticity tolerance figure on a Δ*a**, Δ*b** diagram; (b) lightness tolerance figure on a Δ*L**, Δ*a** diagram. In this case, a plot of Δ*L** versus Δ*b** would have served as well. (Based on ASTM D3134.)

Pigment Mixing

Pigments are added to paints to produce a wide variety of colors. The pigmentation is chosen to control the three components of color—hue, lightness, and chroma. Four pigments are needed to control the components. Generally two pigments are used to control the hue, one (a black or umber) to control the chroma and usually a white to control the lightness. The white pigment is also used as an opacifier. Mixing of colors using pigments is more complex than simple subtractive mixing in transparent films because of the scattering of light caused by the pigments. Again, it is necessary to know the spectral character of all the colorants present. The Beer's law calculation of the transparent case is replaced by the Kubelka-Munk relation: For opaque films, as is often the case in the paint industry, there are simple equations relating the reflectance $R(\lambda)$ of the film at each wavelength to the ratio of two constants describing what happens to the light in the film

$$K(\lambda)/S(\lambda) = [1 - R(\lambda)]^2 / 2R(\lambda)$$

$$R(\lambda) = 1 + K(\lambda)/S(\lambda) - \left\{[K(\lambda)/S(\lambda)]^2 + [2K(\lambda)/S(\lambda)]\right\}^{1/2}$$

in which $K(\lambda)$ is the Kubelka-Munk absorption coefficient, and $S(\lambda)$ is the Kubelka-Munk scattering coefficient. Here, $R(\lambda)$ must be expressed as a decimal instead of the usual percentage. The quantities $K(\lambda)$ and $S(\lambda)$ refer to the mixture of pigments in the paint film. These are calculated by adding the separate contributions of each pigment, using its $K(\lambda)$ and $S(\lambda)$ weighted by its concentration C in the mixture

$$\frac{K(\lambda)_{\text{MIXTURE}}}{S(\lambda)_{\text{MIXTURE}}} = \frac{[C_1 * K_1(\lambda)] + [C_2 * K_2(\lambda)] + \ldots}{[C_1 * S_1(\lambda)] + [C_2 * S_2(\lambda)] + \ldots}$$

in which there are as many terms as there are pigments used. These equations form the basis for computer color

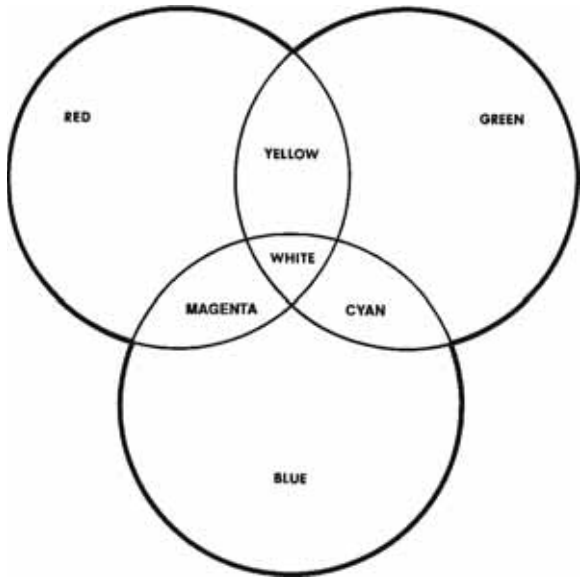

Fig. 15—Representation of the additive mixing of colored lights showing the additive primaries red, green, and blue forming the mixture colors yellow, cyan, and magenta where the primaries overlap in pairs and white where all three overlap.

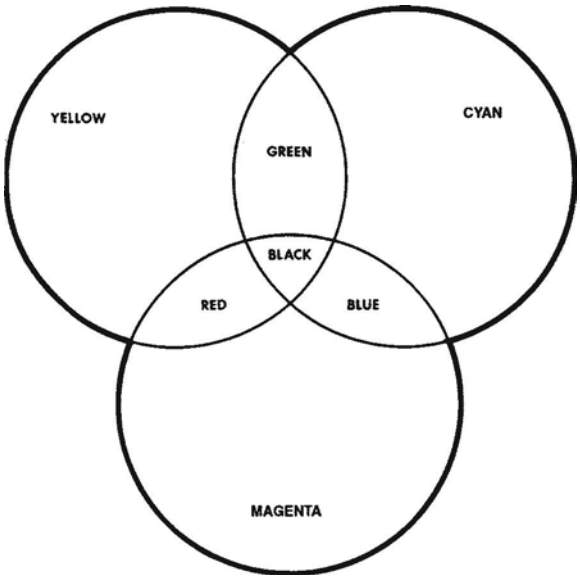

Fig. 16—Representation of the subtractive color mixing of transparent colorants showing the subtractive primaries yellow, cyan, and magenta forming the mixture colors green, blue, and red where the primaries are mixed in pairs and black where all three are mixed together.

matching described in the next section. The equations for dealing with translucent films are more complex [52].

COLOR MATCHING

One of the major objectives of industrial coloring is to match the color a customer wants. Whether this is done visually or with the aid of instruments and computers is often a matter of work load and economics. Therefore, we address both visual and instrumental matching. In either case, a major objective of color matching in paint systems is the formulation of a nonmetameric match to a given paint sample. The difference in spectral character of the samples of a metameric pair is the property determining their metamerism, and achieving a nonmetameric match places several requirements on the formulation.

First, the same pigments must be used. This requires identification of the pigments in the sample to be matched. Second, the pigments must be used in the same resin system since the spectral properties of pigments can depend upon the choice of binder. Finally, the same degree of dispersion must be achieved since the absorption and scattering properties of pigments that determine their spectral character change with degree of dispersion. This usually means that the same method of dispersion must be used.

Visual Color Matching

The selection of visual color matchers should be made with great care, and reference should be made to Guide E1499 for details of how to make the selection, test the color vision of the candidates, and train them in making visual judgments.

Beyond this there is no substitute for the experience of the visual color matcher. He or she must learn the skill by practice. This should include becoming familiar with one of the better color order systems and atlases and learning how to use it, coupled with knowledge of the behavior of the paint system and pigments available, to predict the colors that result from mixing them under carefully controlled conditions. Careful record keeping to document the results is essential. Visual methods of recognizing and controlling metamerism have been described [53,54]. These require no more than knowledge of the behavior in mixtures of the pigments used and a good color matching booth (see "Color Matching Booths").

Instrumental and Computer-Aided Color Matching

The importance of eliminating metamerism dictates that the instrument of choice is clearly a spectrophotometer. Display of the spectral curves of samples, and the computer-aided color-matching operations that lead to spectral curve shapes minimizing metamerism, cannot be achieved by the use of other types of instruments. The spectrophotometer can also be used in a simple but powerful method of organic pigment identification [55] based on extraction of the pigments into solution followed by spectrophotometry. This can be an important aid to selecting the same pigmentation for the match as was used in the standard.

Many modern color-measuring spectrophotometers can be obtained with computer software for color matching. Most of these systems work very well, but it must be emphasized that the investment in building up the database that is essential for their use, and in taking all the steps necessary to bring the coloring process under precise control, is not a small one.

The details of how computer color matching works are beyond the scope of this chapter. In summary, most systems call for measurement of the sample to put its spectral data into the computer. These data are usually matched at each of 16 or 31 wavelengths across the spectrum by Kubelka-Munk-type calculations [56] using stored values of $K(\lambda)$ and $S(\lambda)$ for the useful pigments in the product line. The results are the pigment concentrations in the formulation. Several formulations arising from mixing different pigments are usually produced. Additional calculations of metamerism indices and pigment costs allow the selection of the most suitable results.

Computer color matching has been discussed in a book [57], and some textbooks [1,2,5,58,59] provide useful summaries. The underlying Kubelka-Munk theory, applied to paint systems, has been the subject of a number of articles [56,60-65] directed to paint colorists. More complex theory appears to be needed only in special cases, such as matching automotive paints containing metal flake or pearlescent pigments. The development of such theories is still in its early stages.

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Gloss

Gabriele Kigle-Böckler[1] and Harry K. Hammond III[2]

THE APPEARANCE OF THE SURFACE OF AN OBJECT or material can be described by its color and gloss characteristics. Like color, gloss can be subdivided into several aspects depending on viewing conditions. In 1937, Hunter identified five aspects of gloss [1] and the functions of reflectance by which they could be evaluated. Later studies by Lex [2] expanded Hunter's gloss terms and divided them into two groups. One group is based on visual observation with the eye focused on the surface of the material (Fig. 1). For the other group, the eye is focused on the image of the object reflected by the material (Fig. 2). However, investigations have shown that no single objective measurement of gloss will provide perfect correlation with the integrated subjective appraisal of glossiness that the eye so quickly renders. For this reason, the gloss evaluation requirement of an object or material should first be examined and the most useful gloss measurement aspects then selected.

ASPECTS OF GLOSS AND THEIR DEFINITION

The simple term "gloss" is defined in ASTM E284, Terminology of Appearance [3] as "angular selectivity of reflectance, involving surface-reflected light, responsible for the degree to which reflected highlights or images of objects may be seen as superimposed on a surface." To indicate specific types of "angular selectivity," such as those involving specular gloss (see below), sheen, or haze, and to illustrate the difference between an evaluation where the focus is on the surface and one where the focus is on the reflected image, the complexity of the phenomenon "gloss" is illustrated in Fig. 3.

By focusing on the reflected image of an object, an observer obtains information on the image forming capabilities of the surface. A reflected light source may appear brilliant or diffuse depending on the specular gloss of the surface. The outline of a reflected object may appear distinct or blurred depending on the distinctness-of-image. A halo surrounding the image of the reflected object is an indication of haze. Focusing on the surface of an object provides information on the size, depth, and shape of surface structures contributing to such things as waviness or directionality of brush marks.

Specular Gloss

Specular gloss is defined in ASTM E284 [3] as the "ratio of flux reflected in specular direction to incident flux for a specified angle of incidence and source and receptor angular apertures" (Fig. 4). This aspect of gloss has been measured most frequently because it is the one for which an instrument is most easily constructed. In practice the divergence angles of source and receptor are precisely specified in ASTM Test Method for Specular Gloss [4], D523, as are the directional angles of incidence and reflection. Tolerances are specified for all angles. For simplicity, glossmeter geometries are identified by reference to the incidence angles, most frequently 20°, 60°, and 85°. However, the associated source and receptor aperture angles and their tolerances play a vital role in determining the reproducibility of instrument readings. The measurement result is dependent on the amount of light reflected in the specular direction and the refractive index of the surface. ASTM D523 Test Method for Specular Gloss [4] lists the gloss values in dependence of the refractive index. A polished glass with a refractive index of n = 1.550 has a maximum 20° gloss value of 95.4. If the refractive index changes to n = 1.510, the 20° gloss value will decrease to 84.7. Therefore, gloss readings of materials with different refractive indices, such as 1 and 2 K clear coat systems, will not correlate with the visual perception (Fig. 5). As long as the refractive index of the material does not change, a glossmeter will give objective measurement results.

Sheen

Sheen is defined in ASTM E284 [3] as "the specular gloss at a large angle of incidence for an otherwise matte specimen." The usual angle for sheen measurement is 85°; from the perpendicular to the specimen. This is about the maximum angle that can be used without encountering difficulty in positioning the optics to illuminate and view the specimen at near-grazing angles.

Haze

Haze of opaque products is called reflection haze, while haze of transparent products is encountered as near-forward scattering in transmission that is designated transmission haze. ASTM E284 [3] defines haze in reflection as "percent of reflected light scattered by a specimen having a glossy surface so that its direction deviates more than a specified angle from the direction of specular reflection."

Distinctness-of-Image

This aspect of gloss is also referred to as "image clarity." ASTM E284 [3] defines distinctness-of-image gloss as "the

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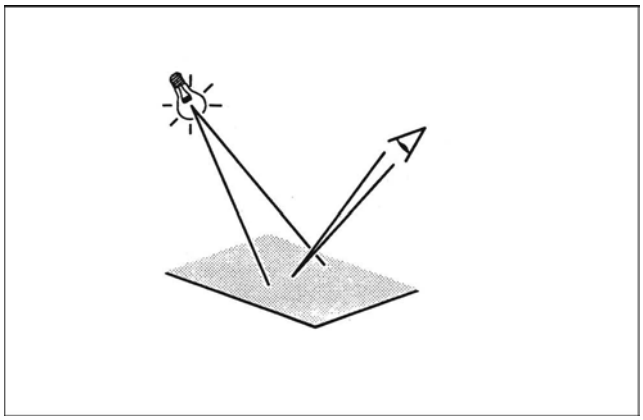

Fig. 1—Observer focuses on the image of reflected object.

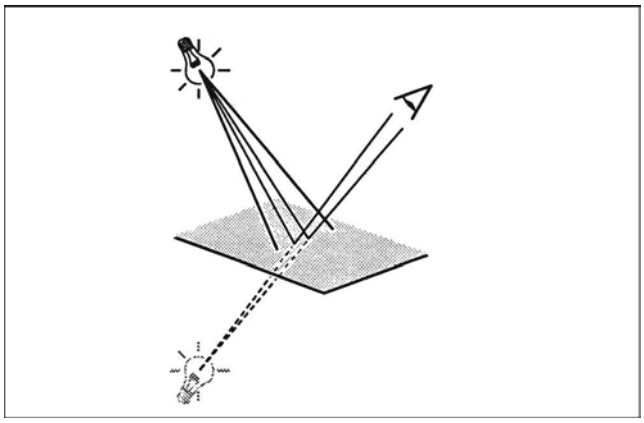

Fig. 2—Observer focuses on the illuminated surface of object.

aspect of gloss characterized by the sharpness of images of objects produced by reflection at a surface." During visual observation, the sharpness of the light-dark edge of a reflected object can be observed.

Waviness

One obvious type of waviness is designated "orange peel." ASTM E284 [3] defines orange peel as "the appearance of irregularity of a surface resembling the skin of an orange." A surface may be described as exhibiting orange peel when it has many small imperfections that are perceived as a pattern of both highlighted and non-highlighted areas. This pattern is interpreted by an observer as a three-dimensional structure of peaks and troughs.

Directionality

ASTM E284 [3] defines directionality, perceived as "the degree to which the appearance of a surface changes as the surface is rotated in its own plane, under fixed conditions of illumination and viewing." A surface exhibits directionality when specular gloss measurements are a function of the direction for which measurements are made. When paint is applied by brushing in one direction, the brush marks can cause the surface to have a directional characteristic. Metallic materials frequently exhibit directionality when the surface is polished in one direction.

VISUAL GLOSS EVALUATION

Early investigations of gloss were carried out by observing differences in the characteristics of images reflected in the surfaces of specimens. In 1932, the Detroit Paint and Varnish Production Club [5] reported on investigations carried out with their distinctness-of-image gloss comparator. In 1936, Hunter [6] reported an investigation where reflected images of a target pattern were observed.

Only in comparatively recent times has there been a major effort to investigate visual scaling of gloss and to endeavor to develop correlation between visual and instrumental measurements. O'Donnell did a doctoral thesis on visual gloss scaling at Rensselear Polytechnic Institute, Troy, New York. Results were first presented, in part, at an ASTM Symposium in 1984 [7] and more fully in a journal article in 1987 [8]. In 1997, the DFO (Deutsche Forschungsgesellschaft für Oberflachenbehandlung) started a research project to investigate which of the physically measurable parameters influence the visual assessment of gloss. The conclusion of this study was that the visual perception is influenced by scattered light reducing the contrast and microstructures distorting an object's outlines, which results in a lower sharpness. Specular gloss measurement is dependent on the refractive index of the material and the curvature of the sample. Therefore, the visual assessment of gloss requires

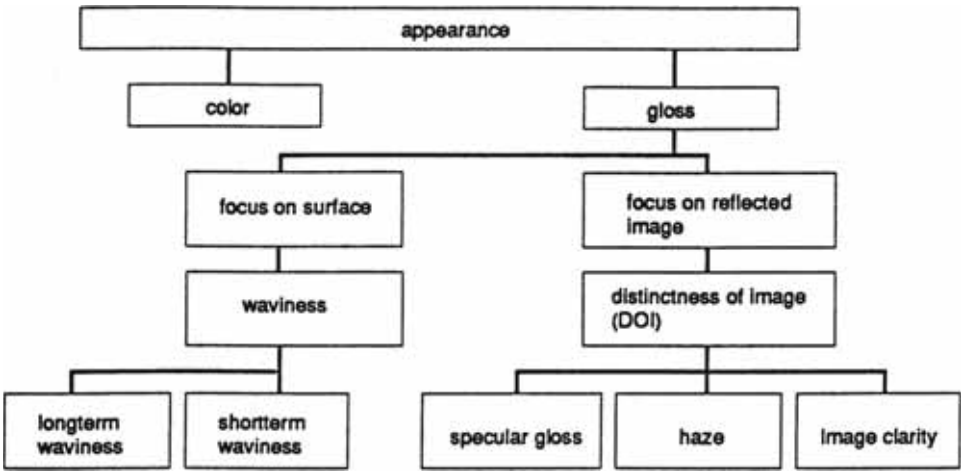

Fig. 3—Block diagram depicting relationships of various appearance characteristics.

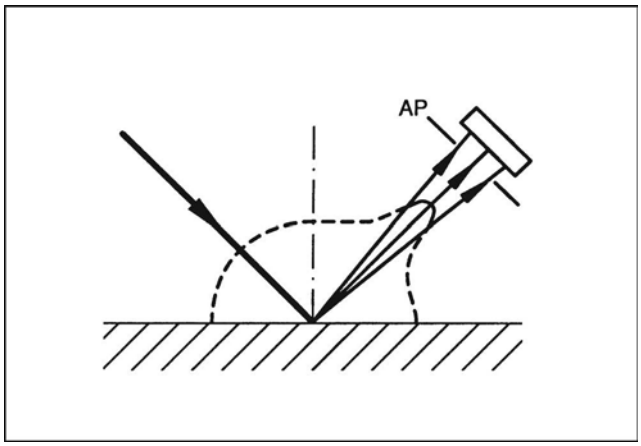

Fig. 4—Reflected light flux distribution from a semigloss surface is depicted by a broken curve. Three lines are shown proceeding from the specimen surface. The center one depicts the specular direction, the image of a ray reflected from a mirror-like surface. The two other rays represent the range of angles passing through the aperture (AP) to the detector (shown as a rectangle).

a multi-dimensional description [9]. At about the same time the ASTM committee E12 on Color and Appearance started a new subcommittee, E12.14, on Multidimensional Characterization of Appearance. The scope of this subcommittee is to develop standards for visual and instrumental assessment of appearance that address the multiple dimensions of appearance. In the first step the committee has conducted several round robin experiments to judge distinctness of image both visually and instrumentally [10].

Development of a Documentary Standard

In 1990, ASTM Committee D-1 on Paint and Related Coatings and Materials published ASTM D4449, Method for Visual Evaluation of Gloss Differences Between Surfaces of Similar Appearance [11], for making visual evaluations of gloss between surfaces of similar appearance. It uses two types of light sources. One source consists of a tubular fluorescent desk lamp modified by placing a matte-black reflecting material behind the tubes and a coarse wire-mesh screen in front. The directions of illumination and view can be adjusted to be 20°, 60°, or 85° as desired for comparing specimens having high gloss, intermediate gloss, or sheen. The other light source is a clear-bulb incandescent lamp. Light from the selected source illuminates the specimens at the chosen angle. The sharpness of reflected images permits a subjective comparison of the relative gloss of similar surfaces.

Use of Landolt Rings to Visually Analyze Distinctness of Image

Landolt rings have been used by ophthamologists to evaluate visual acuity for nearly a hundred years [12]. The test consists of locating the gaps in a graduated series of sizes of incomplete rings whose radial thickness and gap are equal to one fifth the diameter of the ring. For gloss evaluation of trans-illuminated rings, reflections are viewed on a Mylar polyester film. Rings have different sizes and different gap orientations. An image-gloss scale is associated

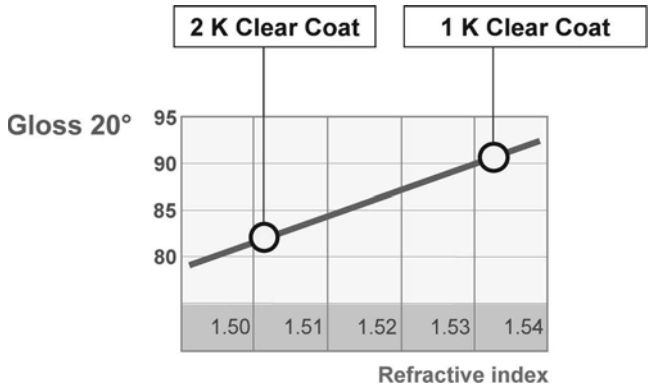

Fig. 5—Specular gloss is dependent on the refractive index of the material: The 1 K and 2 K clear coat system look the same. Due to the difference in refractive index the 2 K clear coat system has a lower specular gloss value than the 1 K clear coat system.

with the different sizes of rings. An image-gloss scale ranging from 10 to 100 in steps of 10 was established for 11 sizes of rings from the largest to the smallest. The development of the scale is not documented, but it ostensibility took place in the General Motors Automotive Division about January 1977. Visual observers select the smallest size of ring for which they can call the gap orientation correctly. The visual judgment is influenced by the loss of contrast and sharpness of the outlines. The numerical size of the rings is used as an inverse index of distinctness-of-image gloss (Fig. 6). ASTM has not published a method for visually evaluating distinctness-of-image gloss by using Landolt rings, but equipment for this purpose is available.[3]

Visual Evaluation of Orange Peel

The automotive industry established a physical standard for orange peel consisting of ten high-gloss panels with various degrees of orange peel structure.[4] The panels are visually ranked from 1 to 10 with Panel Number 1 depicting very pronounced orange peel and Panel Number 10 illustrating no orange peel. The visual observer can use these panels as a supportive tool to evaluate degree of orange peel.

In order to understand this visual ranking it is important to realize that our visual impression is influenced by the structure size and the observing distance (Figs. 7–9)

INSTRUMENTAL MEASUREMENT TECHNIQUES

Specular Gloss Measurement

The design of many gloss meters is based on the precise measurement of the specular component of reflected light [13]. A light source, simulating CIE illuminant C, is placed at the focal point of a collimating lens. The axis of the collimated beam is set to the desired angle of illumination. A receptor lens with an aperture in the focal plane followed by an illumination detector completes the basic optical design (Figs. 10 and 11). The size of the receptor aperture and the size of the source image in that aperture are the elements that complete the optics and that

[3] Apparatus for evaluating distinctness of image using Landolt rings, available from Paul N. Gardner Co., Pompano Beach, FL.

[4] Set of orange-peel panels can be obtained from Advanced Coatings Technology, 273 Industrial Dr., Hillsdale, MI 49242.

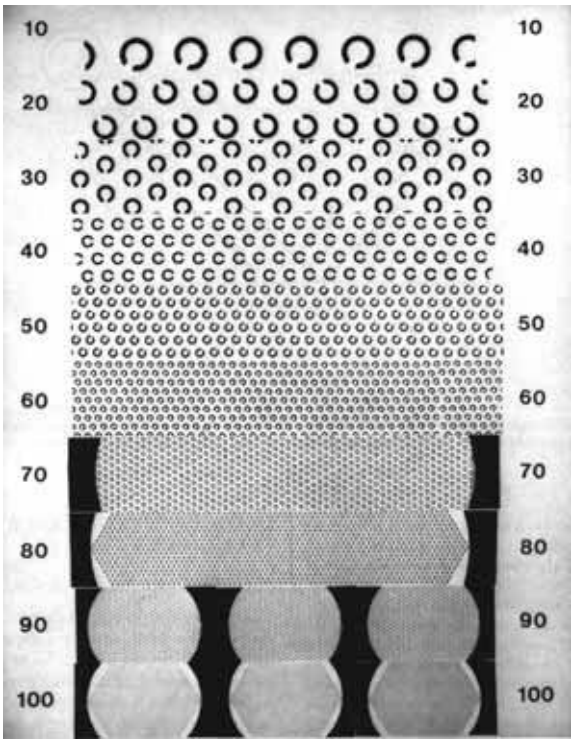

Fig. 6—"Landolt Rings." Broken rings of various sizes are used to provide a scale for visual evaluation of the distinctness of surface-reflected images.[3]

determine the high, low, and intermediate gloss scale readings. The specular angle largely determines the magnitude of the reflected light. However, the tolerances assigned to the source and receptor apertures are what determine the accuracy and reproducibility of measurements made with instruments having the same angles of illumination and view.

Periodic calibration or verification of instrument performance requires the use of calibrated gloss standards. For permanence they should be made of glass or ceramic material. ASTM D523 recommends the use of a primary standard of polished black glass of known refractive index for which the Fresnel (specular) reflectance [14] has been computed for the angle of incidence of the geometry for which the instrument is designed. Since about 1990, national standardizing laboratories have preferred a primary reference standard made of a wedge of clear quartz. Polished black glass working standards can be calibrated by direct comparison of their reflectances with that of a quartz wedge.

A single measurement geometry, such as 60°, may not provide instrument readings of gloss that correlate well with visual observations when comparing different gloss levels. This is why ASTM D523 [4] provides for measurement at three different angles of incidence, namely 20°, 60°, and 85° (Fig. 12). Each of the three geometries uses the same source aperture, but a different receptor aperture. The choice of geometry depends on whether one is: (1) making a general evaluation of gloss, (2) comparing high-gloss finishes, or (3) evaluating low-gloss specimens for sheen. ASTM D523 [4] states that the 60° geometry is used for intercomparing most specimens and for determining when

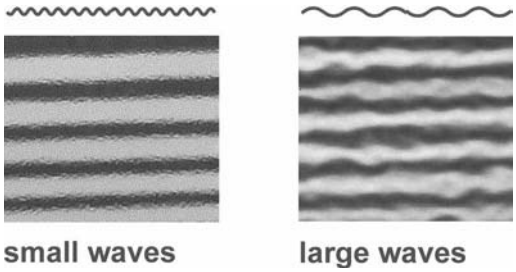

Fig. 7—Appearance changes with structure size.

the 20° or 85° geometry may be more applicable. The 20° geometry is advantageous for comparing specimens having 60° gloss values higher than 70. The 85° geometry is used for comparing specimens for sheen or near-grazing shininess. It is most frequently applied when specimens have 60° gloss values lower than 10.

The ASTM documentary gloss standard originally published in 1939 contained only the 60° geometry [15]. The desirability of using an auxiliary geometry of 85° for sheen evaluation was recognized shortly afterward. However, the use of another geometry with smaller angles of incidence and view, such as 20°, and a smaller receptor aperture to provide improved differentiation of high-gloss finishes was not published until 1947 [16]. The three geometries, 20°, 60°, and 85°, were originally published as separate ASTM standards. In 1953, ASTM D523 was revised to incorporate all three geometries, and it still does.

Meanwhile, the Paint Committee of the International Organization for Standardization, ISO TC-35, was investigating gloss measurements with various commercial instruments prior to drafting an international standard. A paper documenting what the committee had been doing was published in 1976 by the Chairman of the Gloss Task Group, Dr. Ulrich Zorll [17]. In 1978, the ISO Paint Committee published ISO 2813, essentially an international version of ASTM D523 [18]. In keeping with the usual ISO procedure, the standard was made available in English, French, and German.

Instrument manufacturers report that measurement precision, reproducibility, and data handling capabilities of gloss meters have been improved markedly in recent years. New instruments have been designed that are smaller, more portable, and more convenient to use. Data storage and analysis are frequently included as well as the capability of electronically transferring data to a personal computer [19,20].

Goniophotometry

"Gonio" means angle, and a photometer measures radiance; so a goniophotometer is an instrument for measuring the angular distribution of reflected or transmitted light intensity. This type of instrument is often used in the research laboratory to investigate the distribution of light flux (Fig. 13). A goniophotometer with appropriate apertures can also be used to provide gloss data for a wide variety of angles and apertures. When goniophotometric measurements are desired, reference should be made to ASTM E167, Practice for Goniophotometry of Objects and Materials [21]. Analysis of goniophotometric curves was treated by Nimeroff [22].

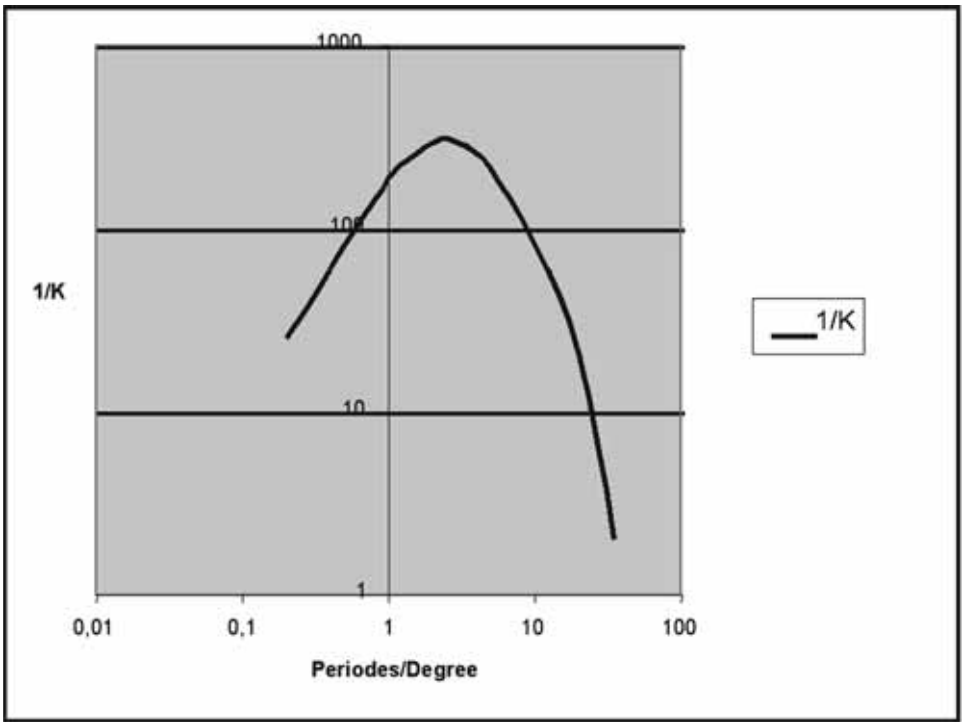

Fig. 8—Contrast sensitivity of our eyes is highest at three periods per cycle. Therefore, our visual assessment is dependent on the observing distance.

Measurement of Reflection Haze

Haze is a gloss parameter that causes a high-gloss surface to appear milky and lighter, thereby losing contrast. When visually evaluating the reflected image of a hazy object, one observes halos around distinct reflection outlines caused by scattered light. Haze can result from various material or process parameters such as degree of dispersion, flocculation, incompatibility of raw materials (pigment-additive-resin), or from poor application procedures.

Haze is most often associated with high-gloss surfaces when small amounts of reflected light are scattered in a region 1° to 4° from the direction of specular reflection. Therefore, it is useful to place apertures several degrees wide on each side of the specular receptor aperture (Fig. 14). ASTM E430, Test Methods for Measurement of Gloss of High Gloss Surfaces by Goniophotometry [23], describes two methods for evaluating reflection haze, one at 20° and another at 30°. The instrument using a 30° angle is no longer commercially available.[5] Since about 1992, a 20° laboratory gloss meter[6] was equipped with auxiliary apertures for haze evaluation, thus permitting measurement of 20° specular gloss and haze with the same instrument (Fig. 15).

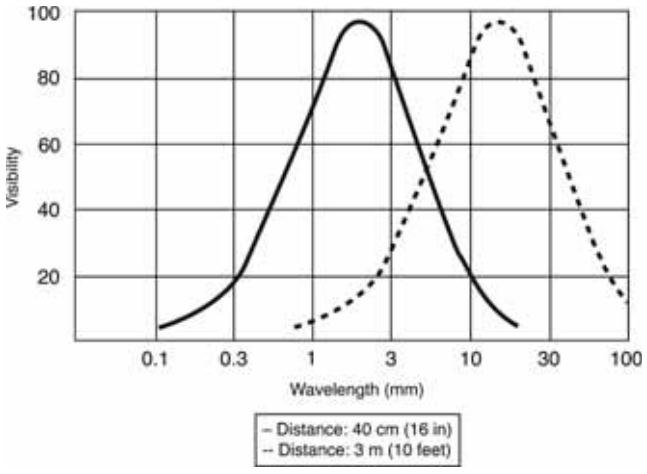

Fig. 9—At a 40 cm observing distance structures with a wave length size of 3–5 mm can be best seen. While at a 3 m observing distance structures with a wave length size of 10–15 mm can be best seen: Typical orange peel.

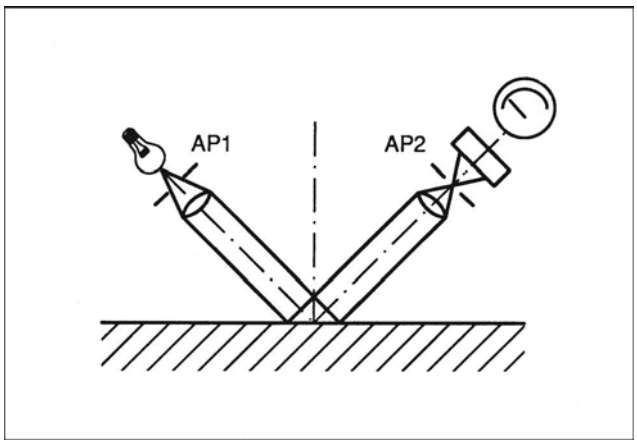

Fig. 10—Schematic diagram of a gloss meter. Source is on the left, detector on the right. Lenses are used to provide beam control. Source aperture is designated AP1, receptor aperture AP2.

Fig. 11—Photograph of a modern miniature glossmeter[5] (courtesy of BYK-Gardner).

Measurement of Distinctness-of-Image

A variety of different technologies is commercially available to measure Distinctness of Image (DOI) [24–28]. The two most-often used principles are: (1) evaluation of the steepness of the reflection indicatrix or (2) measurement of contrast in dependence of the structure elements.

ASTM E430 [23] describes the design of an instrument based on the evaluation of the reflection indicatrix (Fig. 16). The instrument illuminates the specimen at a 30° angle and measures the light reflected at 0.3° from the specular angle with an aperture of 0.3° width. This instrument[7] is no longer commercially available.

Based on the DFO research project the visual perception of DOI is influenced by loss of contrast and microstructures distorting outlines. Therefore, in 1999 a new measurement technology[8] [29] was developed to measure light scattering caused by structure sizes smaller than 0.1 mm. This new measurement parameter was named "Dullness." A light emitting diode light source and a CCD detector are used to detect the reflected image of the source aperture (Fig. 17).

In Fig. 18 two different surfaces are compared. Surface A is a polished black glass standard without dullness. In this case the camera will detect a perfectly sharp image—no light scattering outside the aperture. Surface B shows some light scattering, which results in a lighter image outside the aperture. The dullness measurement determines the amount of light scattering within and outside the aperture in a defined range. The dullness value is a ratio of these two values. Therefore, this measurement parameter is independent of the refractive index. In addition, an adaptive filter is used to separate between the inner and outer image, which minimizes the influence of curvature.

[5] Apparatus designated "micro-TRI-gloss," available from BYK-Gardner USA, Columbia, MD.

[6] Apparatus designated "haze-gloss," available from BYK-Gardner USA, Columbia, MD.

[7] Apparatus designated "Dorigon," Hunter Associates Laboratory, Inc. VA.

[8] Apparatus designated "wave-scan" available from BYK-Gardner USA, Columbia, MD.

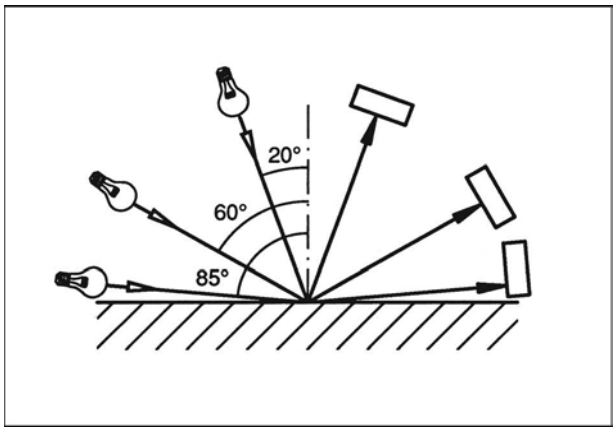

Fig. 12—Diagram depicting the positions of source and receptor for the three geometries of ASTM D523.

Microstructures larger than 0.1 mm also influence our impression of DOI. They are in the wavelength range of 0.1–1 mm and can be objectively detected with the same measurement principle as used for orange peel measurement.

Measurement of Waviness (Orange Peel)

The phenomenon of waviness is most observable on a glossy surface, a critical appearance phenomenon in the automotive industry. Waviness has been evaluated by visual means and by use of a profilometer. The correlation between pro-filometry measurements and visual perception is satisfactory for surfaces with similar optical properties. The operation of a profilometer, however, is very time consuming and limited to laboratory use. When the eye of an observer is focused on a painted surface, various types of waviness can be identified that involve size, structure, and shape. Variations in process or material parameters can cause differences in surface structure. For example, poor flow or leveling properties of a coating will usually cause a long wave structure often called orange peel. Changes in substrate roughness, on the other hand, will exhibit a short wave structure of higher frequency. Because waviness is often caused on the production line, it is important to control it there.

After considerable research, an instrument was introduced in 1992 to provide an objective evaluation of waviness with structure sizes between 0.3 and 12 mm [30]. In 1999 the measurement principle of this instrument was further developed to increase the resolution and expand the measurement range from 0.1 to 30 mm (Fig. 19).

A diode laser source is used to illuminate the specimen at 60°. The reflected light intensity is evaluated at the specular angle. During the measurement the instrument is moved along the surface for a distance of about 10 cm. The intensity of the reflected light is a maximum when coming from a concave structure element. The detector receives less light from a convex structure element. The human eye cannot resolve the actual heights of the structural elements of a painted surface, but the contrast between light and dark areas provides an impression of depth. The contrast of a surface structure can be expressed by use of the statistical parameter "variance." The final measurement results

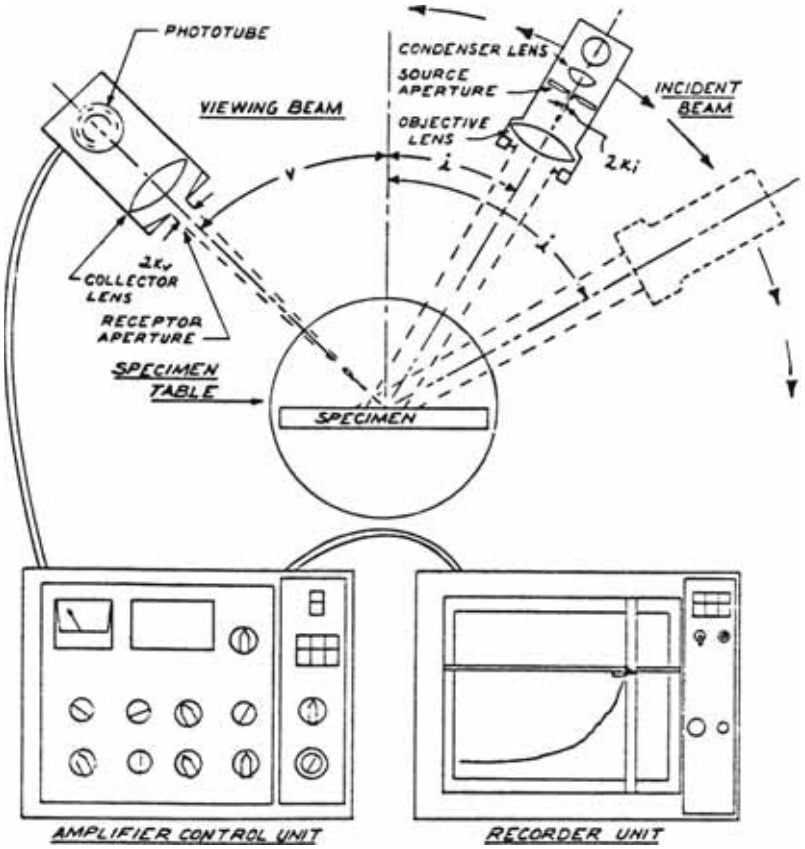

Fig. 13—Schematic diagram of a goniophotometer.

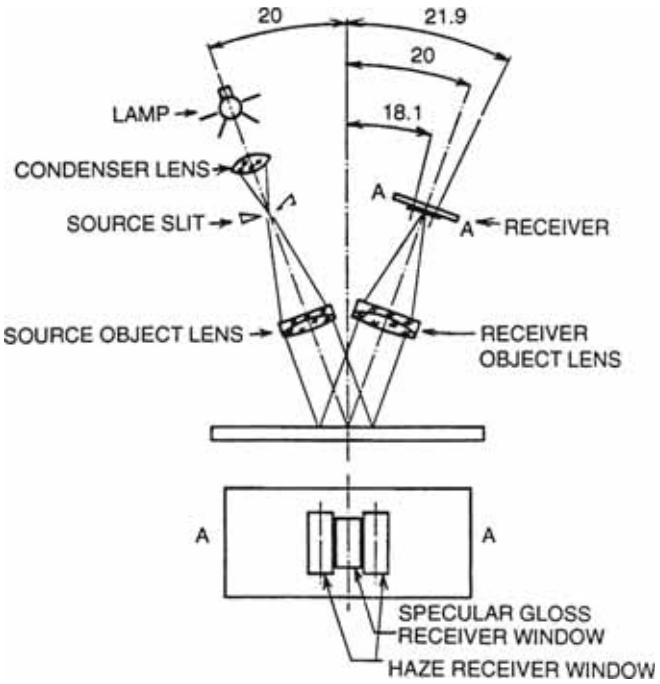

Fig. 14—Schematic diagram of an instrument for reflection haze measurement.

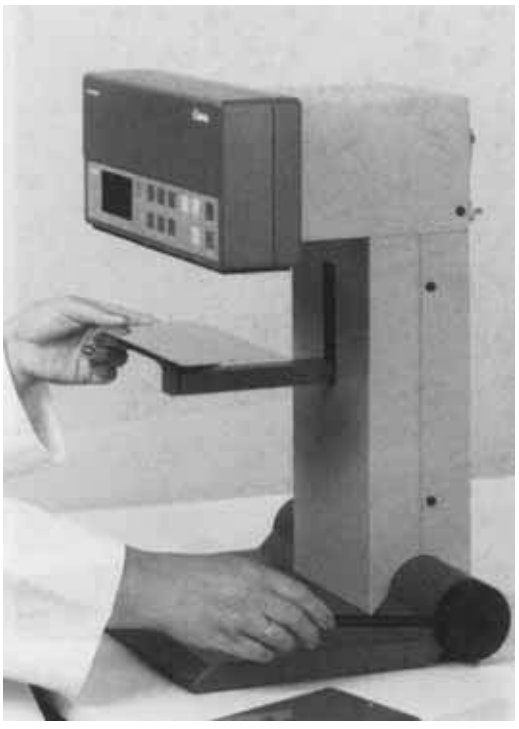

Fig. 15—Photograph of a haze-and-gloss-measuring instrument.[6]

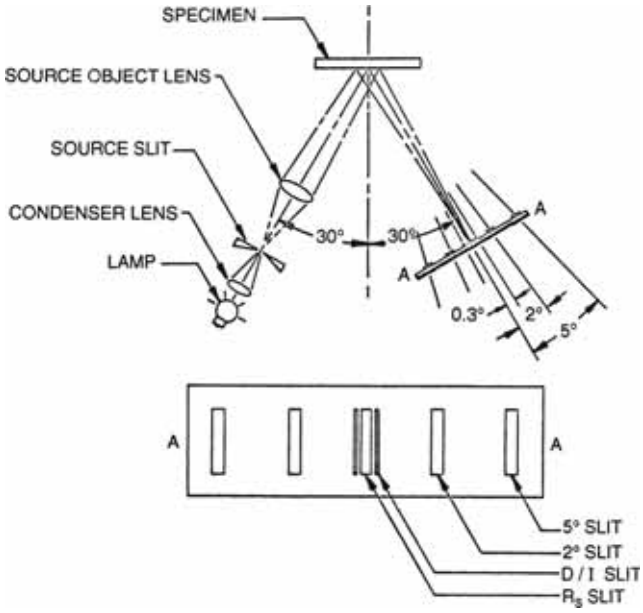

Fig. 16—Schematic diagram of an instrument for DOI measurement.[7]

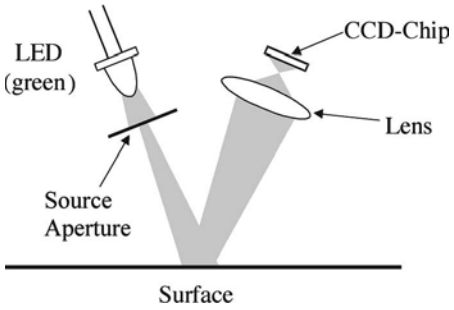

Fig. 17—Schematic diagram of an instrument for dullness measurement.

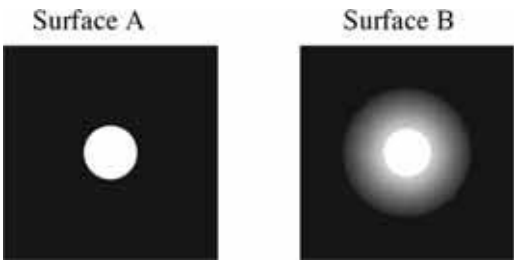

Fig. 18—Surface A without dullness; Surface B with dullness.

Fig. 19—Photograph of an orange-peel-measuring instrument.[8]

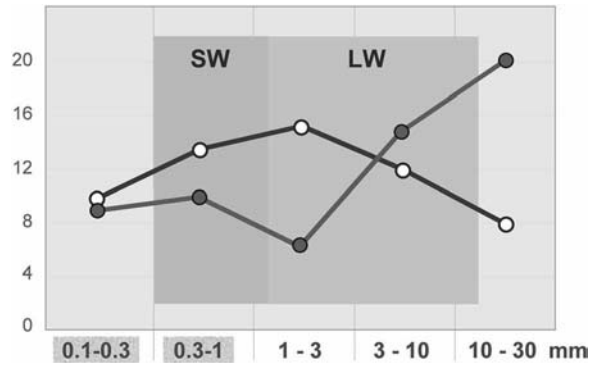

Fig. 20—Structure spectrum helps to understand appearance of surface finishes

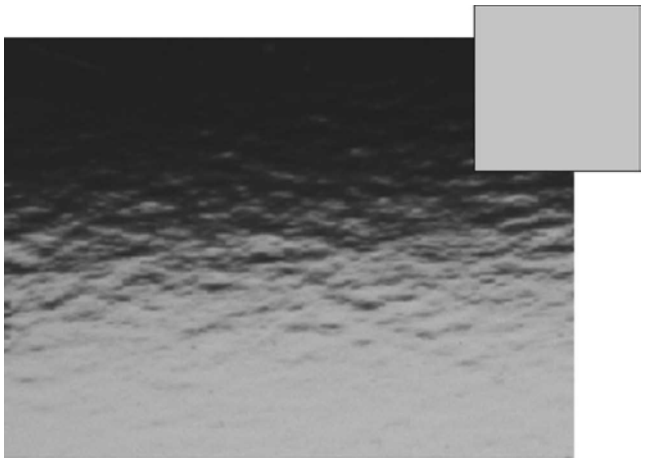

Fig. 21—Original surface with high amount of long-, short- and microstructures: Equivalent to the color gray.

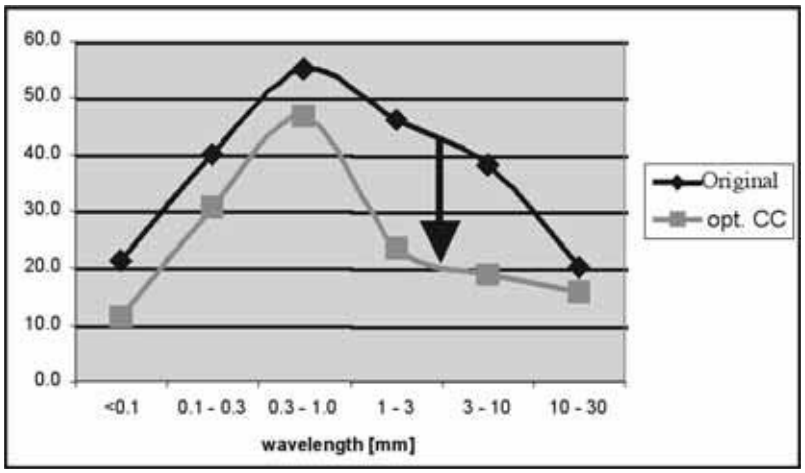

Fig. 22—Structure spectrums of original surface and first improvement step: reduction of longer waves.

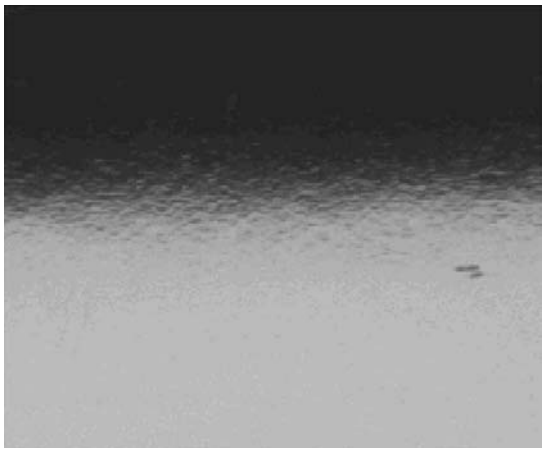

Fig. 23—Surface appearance is dominated by short waves after longer waves were reduced: Surface appears "dull."

are divided into five wave length ranges (Wa–We) using electronic filtering procedures. As a final result a structure spectrum is obtained for structure sizes between 0.1 and 30 mm (Fig. 20).

In order to get a complete picture of the surface appearance, this new instrument also includes the measurement principle for dullness. The combination of two measurement principles in one instrument simulates the visual perception at different distances and permits categorizing structure sizes with their causes.

Changes in Structure Spectrum Compared to Changes in Color Measurement

For better understanding of how various structure sizes influence the visual perception, changes in the structure spectrum can be compared to color measurement. The visible spectrum of color measurement is between 400 and 700 nm (blue → red). For simplicity three colors can be allocated to three structure sizes: Long waves correspond to the color red, short waves correspond to the color green, and micro-structures (DOI) correspond to the color blue.

The ideal surface would be perfectly smooth, i.e., no waves. In colorimetric terms we would be dealing with

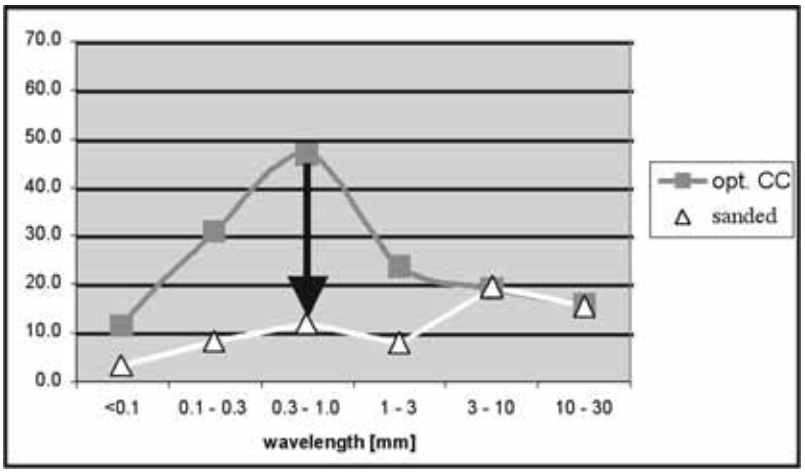

Fig. 24—Structure spectrum with reduced short waves by, e.g., sanding primer surfacer.

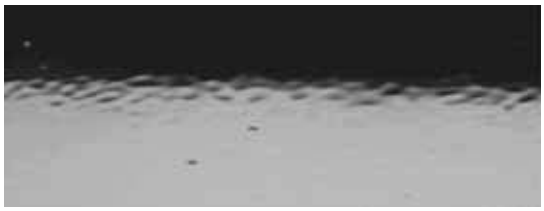

Fig. 25—Very brilliant surface with a low amount of short waves makes long waves very apparent.

the color black (no waves = no color). In the following example a coating with severe waviness is to be improved whereas the main target is to reduce the longer waves. The original surface has a high amount of long, short, and microstructures corresponding to the color gray (Fig. 21).

The structure spectrum of the original surface is shown in Fig. 22. A reduction of the longer waves can be achieved by optimizing the basecoat/clearcoat application (e.g., higher clear coat film thickness).

As a result the new look will be dominated by the shorter waves, which would be equivalent to a blue/green color (Fig. 23). In practice dominance in shorter waves can be caused by, e.g., a poor-quality primer.

This high amount of shorter waves can be reduced by, e.g., sanding the primer. In our example the shortened microstructures were reduced below the amount of longer waves (Fig. 24).

In color measurement the color red would be dominating the look. And the same is true in appearance measurement: The very low levels of shorter waves will make the surface very brilliant with a high DOI and consequently the small amounts of long waves will be very obvious (Fig. 25).

It is important to realize that the impression of gloss is a multi-dimensional phenomenon. By changing the ratio of different structure sizes, the visual appearance can be dramatically changed. The structure spectrum is like the fingerprint of a surface and can be compared to the spectral curve of colorimetry. Currently the correlation of the different wavelength ranges to the visual perception is under investigation. The goal is to obtain a measurement system for appearance similar to the L*, a*, b* system of color measurement [31].

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45

Hiding Power

Leonard Schaeffer

CONCEPTS, RELATIONSHIPS, TERMINOLOGY

Opacity

WHEN LIGHT ENTERS A PAINT FILM, SOME OR ALL of it is absorbed or reflected by the film before reaching the substrate, thereby hiding the substrate to a lesser or greater degree. The light that reaches the substrate is partly absorbed by it and partly reflected back in conformance with the substrate's visual pattern. Reflection from the substrate eventually emerges from the film carrying the substrate reflectivity information perceived as visibility or lack thereof, and referred to as *hiding*. Opacity may be qualitatively defined as the property of a paint film that enables it to prevent the passage of light and thereby to hide the substrate on which it has been applied. Note that *opacity* is a film property, whereas *hiding power* is a property of the whole paint. *Hiding* is a more general term used frequently to refer to either opacity or hiding power (HP).

Light Absorption

If most of the light is absorbed by the film before reaching the substrate, the film is dark in color and hides the substrate well, in which case hiding has been produced by light absorption.

Light Scattering

If most of the light entering the film is reflected back and reemerges without having reached the substrate, the film is white or light in color and hides the substrate well. The reflection mechanism of the film involves multiple internal refractions and reflections that scatter the light to produce a net reversal in its direction. Hiding in this case is produced by light scattering.

Incomplete Hiding

In all cases, the light-absorbing and light-scattering properties of the film act together to produce its opacity. If the film is low in both light-absorption and light-scattering ability, much of the light reaches the substrate. Such a film, therefore, hides poorly and is characterized as being low in opacity.

Test Substrates

An opacity test substrate generally has an ordered pattern of contrasting colors or shades, usually black and white, although black and gray and gray and white are also used. Juxtaposition of contrasting areas permits both visual observation and photometric measurement of film opacity. Sealed paperboard charts are the most commonly used substrates of this description. For photometric measurements only, individual black glass and white glass panels are sometimes employed to take advantage of their excellent planarity. Clear plastic can also be used as an opacity test substrate by placing it over black-and-white backgrounds. Black and white painted metal panels are commercially available for use with powder coatings. Standard black-and-white opacity test substrates are defined in paint technology as having CIE-Y reflectances of 0.01 (1 %) maximum and 0.80 (80 %), respectively.[2] White test areas are seldom exactly 80 %, but equations are available for correction of photometric values to that and any other standard (see "Kubelka–Munk Equations for Correcting Reflectance and CR_n Measurements to a Standard White Substrate Reflectance").

CR

The extent to which a paint film obscures or hides the contrasting features of the test substrate on which it is uniformly applied is the measure of its opacity. This is expressed photometrically as the ratio of the luminous (CIE-Y) reflectance over the darker, to that over the lighter, area of the substrate, which is referred to as the CR (CR). The *Y*-reflectance is employed because this CIE parameter is designed to match the sensitivity of the human eye. The CR and the reflectance are expressed as a percentage or as a decimal fraction, the latter to be assumed unless otherwise indicated. A CR value of unity indicates that too little light has reached the substrate for the substrate reflectance characteristics to have a measurable effect on the emergent light flux; thus, there is complete absence of contrast, or complete hiding. Lesser CR values define intermediate levels of contrast, or incomplete hiding. The CR of a given paint film varies with substrate reflectances, and therefore has significance only with respect to a known substrate and primarily to a standard black-and-white substrate as defined in Test Subtrates. In practice, the white area of a commercially available black-and-white substrate normally deviates somewhat from the ideal reflectance of 80 %, whereas the black area is normally 1 % or less, which has no measurable effect on test results, and is therefore treated mathematically as having zero reflectance. Conventional symbols used in this connection are as follows:

W = the reflectance of the white area of the test substrate,

[1] *The Leneta Company, 15 Whitney Road, Mahwah, NJ 07430. (Author deceased 2002.)*
[2] CIE = Commission Internationale d'Eclairage. Reflectances are measured with specular (mirror) reflection excluded.

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R_w = the reflectance of the paint film over a white area of reflectance W,
R_0 = the reflectance of the paint film over the black area,
$C_w = R_0/R_w$, the CR of the applied paint film,
$C_{0.80} = R_0/R_{0.80}$, the CR when $W = 0.80$, and
$C = C_{0.80}$, the abbreviation sometimes used in equations.

In careful HP measurements, if the white substrate reflectance deviates more than 0.01 from the standard value of 0.80, one of the following correction equations[3] is employed. Correction equations[3] for normalizing CR values to a standard white substrate reflectance are given in "Calculation of Hiding Power from Tinting Data."

$$C_{0.80} = f(R_0, R_w, W) = \frac{WR_0(1-0.80R_0)}{R_0(W-0.80)+0.80R_w(1-WR_0)} \quad (1)$$

$$C_{0.80} = f(C_w, R_0, W) = \frac{WC_w(1-0.80R_0)}{C_w(W-0.80)+0.80(1-WR_0)} \quad (2)$$

Visual Observations of Contrast

Although intermediate levels of contrast cannot be directly quantified by visual means, the eye is qualitatively very sensitive to contrast variations. It can identify equalities or nearly complete absence of contrast with considerable precision, which is the basis for the original, as well as several current, HP methods to be described. Indeed, such visual observations are the basic criteria of what constitutes hiding and HP, to which all instrumental hiding measurements trace their validity.

Film Thickness

This is usually expressed in thousandths of an inch (mils) or in micrometres (μm). A liquid paint usually contains a substantial quantity of volatiles, so that its dry film thickness (DFT) is substantially less than the original wet film thickness (WFT). The WFT of architectural paints applied in the field are typically in the neighborhood of 3 to 4 mils (75 to 100 μm). With other coating types, it might be as low as 1 mil (25 μm) or as high as 60 mils (1500 μm). With volatile-free liquid coatings, the WFT and DFT are the same except for a possible small increase in density during curing. With powder coatings, for which film formation and curing are concurrent, the term WFT is inapplicable and DFT redundant, so that it is appropriate to refer simply to *film thickness*.

SR

When paint is applied, whether for test purposes or in actual usage, the area covered per unit quantity of paint is called the spreading rate (SR) for that particular application. When the quantity of coating is expressed volumetrically, as is usual with liquid paints, the SR is usually expressed in square feet per gallon (ft²/gal) or square metres per litre (m²/L). When the quantity is expressed gravimetrically, the SR is usually expressed in square feet per pound (ft²/lb) or square metres per kilogram (m²/kg). SR is inversely related to the film thickness; thus, for a given paint, the lower the SR, the higher the film thickness and film opacity.

[3] Derived from Eq (41) by equating to $W = 0.80$.

SR and Film Thickness Relationships

Let

H = SR of the coating (equivalent to SR),[4]
T = wet film thickness (equivalent to WFT),[4]
D = coating density (prior to loss of volatiles),
t = DFT (exclusive of air)[5] (equivalent to DFT),
d = dry film density (displacement density),[5]
N = Nonvolatile fraction by weight (equivalent to nonvolatile fraction by weight (NVW)), and
N_v = nonvolatile fraction by volume (equivalent to nonvolatile fraction by volume (NVV)).

U.S. UNITS

$$H(\text{ft}^2/\text{gal}) \times T(\text{mil}) = 1604.2 \quad (3)$$

$$H(\text{ft}^2/\text{gal}) \times t(\text{mil}) = 1604.2ND \div d \quad (4)$$

$$H(\text{ft}^2/\text{lb}) \times T(\text{mil}) = 1604.2 \div D(\text{lb/gal}) \quad (5)$$

$$H(\text{ft}^2/\text{lb}) \times t(\text{mil}) = 1604.2N \div d(\text{lb/gal}) \quad (6)$$

METRIC UNITS[6]

$$H(\text{m}^2/L) \times T(\mu\text{m}) = 1000 \quad (7)$$

$$H(\text{m}^2/L) \times T(\mu\text{m}) = 1000 \quad (8)$$

$$H(\text{m}^2/\text{kg}) \times T(\mu\text{m}) = 1000 \div D(\text{kg/L}) \quad (9)$$

$$H(\text{m}^2/\text{kg}) \times t(\mu\text{m}) = 1000N \div d(\text{kg/L}) \quad (10)$$

U.S.—METRIC UNIT CONVERSIONS

$$H(\text{ft}^2/\text{gal}) = H(\text{m}^2/\text{L}) \times 40.746 \quad (11)$$

$$H(\text{ft}^2/\text{lb}) = H(\text{m}^2/\text{kg}) \times 4.8882 \quad (12)$$

$$T(\text{mil}) = T(\mu\text{m}) \div 25.4 \quad (13)$$

$$D(\text{lb/gal}) = D(\text{kg/gal}) \times 8.3454 \quad (14)$$

DRY VERSUS WET FILM RELATIONSHIPS[7]

$$ND = N_v d \quad (15)$$

$$t = N_v T \quad (16)$$

$$T = td \div ND \quad (17)$$

DEFINITION OF HP

Qualitatively, HP is the property of a paint that is manifested as opacity in its films. Quantitatively, it is the SR at

[4] Note that WFT and SR, when the latter is expressed by volume, are inverse ways of stating the same information.
[5] Refers to films containing no air or hypothetically compressed to exclude air.
[6] The following metric notations are identities: kg/L = g/mL = g/cm³ = g/cc.
[7] These are applicable to both common and metric units since the units all cancel.

which the film opacity is just sufficient to give complete hiding over the specified standard black-and-white substrate (see "Test Substrates"). The "complete hiding" point is determined visually in some test procedures and photometrically in others.

Visual HP End-Point

In the visual determination of HP, the operator increases the film thickness gradually and records the amount of paint applied at the supposedly exact point of complete hiding. In practice, instead of perceiving such a point, a range of uncertainty is reached beyond which, when hiding seems unquestionably complete, it also seems that the true end-point has been exceeded. To resolve this dilemma and to obtain repeatable results, the operator chooses an end-point at which it seems that only a negligible increase in film thickness is required to completely obscure the contrasting features of the substrate. This so-called *complete hiding* end-point is therefore more accurately described as just short of complete hiding.[8]

Photometric HP End-Point

Uncertainty as to the end-point also exists when measuring HP photometrically. A curve of film thickness versus CR approaches CR = 1 asymptotically, so in theory there is no point at which the contrast is completely obscured. Thus in practice the CR end-point for HP measurements must be less than unity. A CR value of 0.98 is generally accepted in paint technology as representing the point of photometric *complete hiding* because it is in fact very close to being visually complete, and a higher CR end-point could not be identified with as much precision. The concept of 98 % as the CR for complete hiding was originally based on the Weber–Fechner law, from which it can be deduced that differences of 2 % in reflectance (with moderate illumination) are imperceptible to the human eye [1]. Actually, this level of contrast, though slight, is definitely visible.

THE ROLE OF PIGMENTS IN HP

Binders and Pigments

A typical paint binder, by itself, forms a transparent and virtually colorless film that neither absorbs nor scatters light to any appreciable degree and therefore makes no contribution to the HP of the coating of which it is a part. This task resides entirely in the pigment constituent of the paint. Pigments are fine-particle-size, insoluble, and usually crystalline solids that when dispersed in paint vehicles contribute to the various properties of the mixture, among which are the optical properties of color and HP. Pigments that absorb light strongly over the entire visible spectrum are black; those that are optically selective, absorbing strongly in parts of the visible spectrum and poorly in other parts, are colored, viz. blue, red, yellow, etc., corresponding to the spectral region of nonabsorption. Those that absorb poorly over the entire visible spectrum are white.

White Pigments

When dispersed in a paint binder, some white pigments scatter light strongly and thereby contribute to hiding, while others scatter very poorly and make little, if any, contribution. On that basis, white pigments are classified as *hiding pigments* or as *extenders*. White hiding pigments in a paint formulation are sometimes called "prime pigments" as distinguished from the nonhiding "extender" types. The latter are also referred to as "inerts" in view of their apparent passivity with regard to both light absorption and scattering. The difference in scattering behavior between hiding and extender pigments is a function of their refractive indices.

Refractive Index

Most pigments are crystalline in nature. If a single crystal of white pigment were grown sufficiently large, it would be perceived as shiny and transparent like glass, and objects observed through it would look bent and distorted as when observed through a glass prism. This is due to the change in direction, referred to as refraction, that occurs when light passes between media in which it has different velocities, as illustrated in Fig. 1. The relationship between the angles in this figure is expressed by Snell's law of refraction

$$n = \sin i / \sin r \tag{18}$$

in which i and r are the angles of incidence and refraction, respectively, and n is a constant referred to as the refractive index, which is the ratio of the velocity of light in the incident to that in the refraction medium. If the large pigment crystal postulated previously is pulverized and dispersed in a paint film, each small particle will refract incident light in the same way as described for the large one. Light will also be partially reflected at the surface, and both refractions and reflections will occur within the pigment particle itself. This activity, endlessly repeated with a multitude of pigment particles as illustrated in Fig. 2 (Ref. [2], p. 1), results in the scattering of the original incident light with concomitant film opacity and paint HP. The greater the difference between the refractive indices of the pigment and the surrounding medium, the greater the amount of light scattering that will occur. Refractive indices are reported in Tables 1 and 2 with respect to a vacuum as the medium of incidence. Values with respect to air are practically the

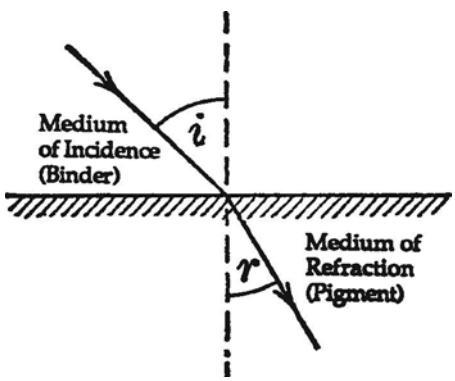

Fig. 1—Bending of a light ray by refraction toward the normal as it enters a medium of lower light velocity (higher refractive index).

[8] It has been proposed to use ΔE of a uniform color space as the HP endpoint instead of CR. This is a valid and feasible concept, although to the writer's knowledge it has not yet been employed in a published test method.

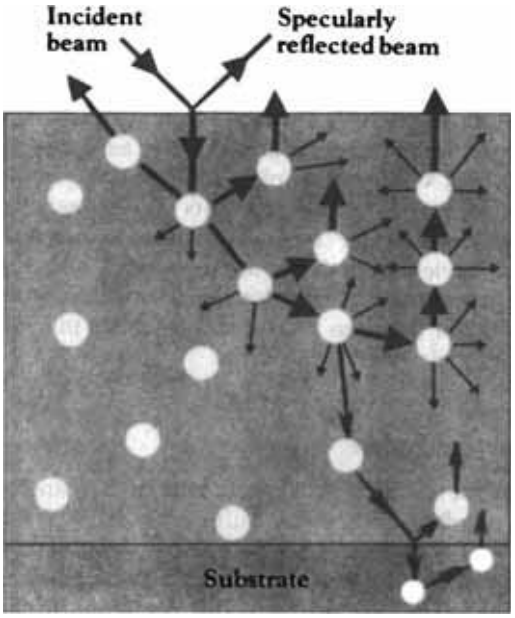

Fig. 2—Light-scattering behavior of a pigmented film.

same. Since white pigments are crystalline in nature, they usually possess different refractive indices along the different crystal axes. Their indices also vary somewhat with the wavelength of the light, generally being higher at the blue (short wavelength) end of the spectrum than at the red (long wavelength) end. Tables 1 and 2 give average values [1,3].

White Hiding Pigments

A rough indication of the relative HP of a white pigment can be calculated from its refractive index using the Fresnell equation of reflectivity (Ref. [2], p. 1)

$$F\ \% = \frac{(n - n_m)^2}{(n + n_m)^2} \times 100 \qquad (19)$$

where F is the Fresnell reflectivity, n is the refractive index of the pigment, and n_m is the refractive index of the medium

TABLE 1—Refractive index and relative HP of some white hiding pigments

Pigment	Refractive Index	Relative HP F %[a]
Titanium dioxide (rutile)	2.76	8.8
Titanium dioxide (anatase)	2.55	6.7
Zirconium oxide	2.40	5.3
Zinc sulfide	2.37	5.0
Antimony oxide	2.19	3.5
Zinc oxide	2.02	2.2
White lead carbonate	2.01	2.1
White lead sulfate	1.93	1.6
Lithopone	1.84	1.0

[a] Calculated from Eq (20).

TABLE 2—Refractive index and relative HP of some extender pigments

Pigment	Refractive Index	Relative HP F %[a]
Barium sulfate	1.64	0.20
Calcium sulfate	1.59	0.08
Calcium carbonate	1.57	0.05
Magnesium silicate	1.57	0.05
Aluminum silicate	1.55	0.03
Silica	1.55	0.03

[a] Calculated from Eq (20).

in which it is dispersed. Since the refractive index of a paint binder is, in general, very close to 1.5, Eq (19) can be rewritten as

$$F\ \% = \frac{(n - 1.5)^2}{(n + 1.5)^2} \times 100 \qquad (20)$$

Tables 1 and 2 illustrate the use of this equation and the general principle that the higher the refractive index of a pigment the greater its HP. The relative HP values shown therein indicate the magnitude of variation related to index of refraction. Other factors can also affect HP substantially, as discussed in "Factors Affecting White HP."

Extender Pigments

Pigments in this category have low refractive indices in the neighborhood of 1.5. In the form of a powder, with the surrounding medium being air with a refractive index of 1.0, the difference in the two indices produces substantial light scattering, so that extender pigments look white. But dispersed in paint binders, which like themselves typically have a value of about 1.5, they scatter light very poorly and are virtually transparent. This is indicated by the low HP values listed for them in Table 2 as compared with the white hiding pigments in Table 1. Although extender pigments are also referred to as inerts, the latter term is somewhat of a misnomer. They have an indirect but strong influence on light scattering and HP through phenomena referred to as "crowding" and "dry hiding." They also have important effects on other physical properties of paints such as consistency and gloss.

Colored Pigments

If a pigment absorbs some wavelengths of light more strongly than others, it reflects back a higher proportion of the weakly absorbed wavelengths and is perceived as having the color of the latter (e.g., red, blue, yellow, etc.). Light absorption of this nature is referred to as selective. Colored pigments can vary greatly in HP depending on their light absorption and light-scattering abilities. With regard to light scattering, as with white pigments this is a function of the refractive index or, more specifically, the difference in refractive index between the pigment and surrounding medium. Refractive indices of colored pigments vary widely with wavelength, ranging from 1.3 to 2.7. These variations cause such phenomena as bronzing, dichroism, color

change with film thickness, and differences in undertone upon dilution with white pigments (Ref. [4], p. 22).

EARLY VISUAL HP METHODS

Brushouts

The earliest methods for determining HP employed the practical procedure of brushing the paint uniformly onto combination black-and-white test substrates, increasing the amount of paint in small increments until reaching the point of essentially complete hiding at which the amount of visual contrast was considered negligible. The quantity of paint was determined by weighing the container and brush in grams before and after painting. The corresponding SR is the HP by definition and was calculated from the equation

$$\mathrm{SR}(\mathrm{ft}^2/\mathrm{gal}) = \frac{\text{test area}(\mathrm{ft}^2) \times \text{paint density}(\mathrm{lb/gal}) \times 454}{\text{weight of paint (g)}} \tag{21}$$

For single-pigment paints, the value calculated from Eq-(21) can be converted to pigment HP using the equation

$$\mathrm{SR}_{\text{pigment}}(\mathrm{ft}^2/\mathrm{lb}) = \frac{\mathrm{SR}_{\text{pigment}}(\mathrm{ft}^2/\mathrm{gal})}{\text{pigment concentration}(\mathrm{lb/gal})} \tag{22}$$

Variants of these equations provide for the use of metric instead of U.S., units.

Early Test Substrates

Originally in the study of HP, test surfaces were prepared in individual laboratories by painting black stripes on white-painted panels. In response to the need for standardized test surfaces, studies were made on oil cloth and linoleum having printed checkerboard-type designs [5]. The Gardner Contrast HP Board was a two-square-foot area glass checkerboard with black and white squares painted on the underside of a thin piece of glass (Fig. 3). The first formalized ASTM method used a linoleum checkerboard surface in the brushout test procedure described in "Brushouts." The Gardner glass board was used in the same way. Since the "complete hiding" end point in those early methods was determined when the paint was freshly applied and still wet, the resultant HP value pertained only to the wet HP of the paint, not to the dry. This was not a problem in the earliest days of HP measurement, when typical paints contained relatively little volatile constituent and the opacity of the film therefore did not change markedly while drying. But, with the advent of modern paint formulations containing substantial amounts of volatiles, the composition and with it the opacity of the dry paint film could be substantially different than that of the initially applied film. The need to measure dry HP therefore became of paramount importance. As a practical problem in this connection, expensive linoleum and glass test surfaces had to be cleaned for reuse after each test, which made it very difficult to use them for the study of *dry* HP. This problem was partly overcome with the introduction of paper test charts circa 1931 that were printed in various designs such as checkerboard, concentric diamond-shaped bands, spirals, crescents, etc., and with various degrees of contrast such as black-white, black-gray, gray-white, and a graded series of stripes from black to white. After printing, a coat of nitrocellulose lacquer or other suitable clear sealer was applied. Many of those chart types became and continue to be commercially available.

Contrast Design and Visual Sensitivity

Kraemer and Schupp [6] evaluated contrast surfaces in a variety of designs prepared on glossy photographic paper. These included the customary checkerboard design, a design of narrow 15-mm-wide bands, another with much broader bands, and one with dark half circles on a light background. The results seemed to favor a narrow band design subsequently employed by the Krebs Pigment Co. in preparing the diamond stripe gray-and-white contrast charts illustrated in Fig. 4. The test area of that chart was 1 ft^2 (0.0929 m^2). The use of a gray-and-white contrast

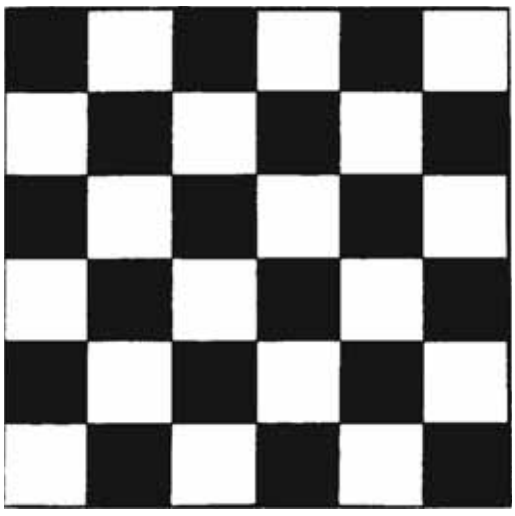

Fig. 3—Gardner contrast HP board.

Fig. 4—Krebs diamond-stripe HP chart.

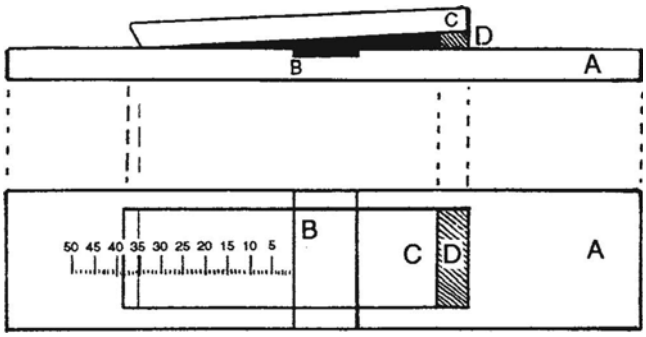

Fig. 5—Diagram of early model of Pfund cryptometer.

combination was based on the idea that this is more representative than black and white of the degree of contrast encountered by paints in actual use.

Relative Dry HP—Krebs Method

Although the introduction of paper test charts as replacements for linoleum or glass made dry HP measurements easier, they were still not easy enough. The problem was that it required the preparation of a considerable number of paint-outs at various SRs to obtain one that after drying could be identified with confidence as representing the "complete hiding" end-point. One solution to this problem was to determine comparative or relative dry HP. In the Krebs Pigment Co. method, their square-foot gray-and-white diamond stripe chart was used for that purpose in the following manner: A partial hiding ladder of six to eight brushout standards is made by applying a standard paint at SRs ranging from 400 to 800 ft²/gal (10 to 20 m²/L) and allowing the brushouts to dry. The SRs are precontrolled approximately by syringing specified volumes of paint onto each chart and then determined accurately by weight measurements and calculation as described in "Brushouts." A single test paint panel is likewise prepared at an intermediate SR. After drying, that panel is compared with the standard panels to determine the two that bracket it in contrast. Then, by visual interpolation, a fairly precise estimate is made of the SR of the standard paint required to match the contrast of the test paint panel. The relative dry HP of the test paint is the percent ratio of its SR to that of the standard paint at equal visual contrast, thus

$$\% \text{ Relative Hiding Power} = \frac{SR_{\text{Test Paint}}}{SR_{\text{Std. Paint}}} \times 100 \quad (23)$$

TABLE 3—HP (m²/kg) of some colored pigments measured with a Pfund cryptometer[a] (Nelson and Norris)

	Black Glass	White Glass
Lampblack	. . .	105
Carbon black	. . .	41
Chromic oxide	29	. . .
Prussian blue	72	. . .
Chinese blue	106	. . .
Blue toner	51	. . .
Light green	129	. . .
Medium green	187	. . .
Deep green	88	. . .
Light green	101	. . .
Medium green	167	. . .
Deep green	181	. . .
Light green	62	. . .
Medium green	98	. . .
Light green	154	. . .
Medium green	202	. . .
Deep green	150	. . .
Green toner	91	. . .
Green toner dark	130	. . .
Chrome yellow	23	27
Hansa yellow	31	34
Lt. chrome orange	44	56
Med. chrome orange	17	20
Dk. chrome orange	29	. . .
Lithol toner	66	. . .
Lithol toner	75	. . .
Maroon toner	65	. . .
Madder lake	36	. . .
Toluidine toner	137	. . .
Light para toner	224	. . .
Deep para toner	160	. . .
Light para toner	41	. . .
Deep para toner	35	. . .

[a] Multiply by 4.9 to obtain HP in ft²/lb.

Pfund Cryptometers

ALL BLACK

Introduced in 1919, this was one of the first laboratory instruments made for determining HP [7]. Referring to Fig. 5, A is a plate of black glass whose upper surface is optically flat; B is a transverse groove 10 mm wide and about 2 mm deep. Beginning at the left edge of the groove is a millimeter scale etched in the upper surface of Plate A. C is a plate of clear glass whose lower surface is optically flat. D is a steel shim cemented to C so that a wedge of paint may be formed between the plates. This wedge abruptly becomes infinitely thick at B, and so long as hiding is not complete, the line of demarcation is visible. Sliding the wedge to the left eventually causes the line to disappear. The WFT at the point of complete hiding is determined from the scale reading at the toe of the wedge and the thickness of the shim at the heel, from which the HP in ft²/gal or m²/L can be calculated using Eq (3) or Eq (7). Dark-colored paints cannot be measured using this instrument because of the lack of contrast with the black glass background. Nelson and Norris of the New Jersey Zinc Co. used this cryptometer to determine HP of colored pigments with results as shown in Table 3. The pastes were prepared by rubbing the colors in No. 0000 lithograph varnish. The rubbing was regulated to represent the maximum development usually obtained in practice. In addition to the regular black glass instrument,

they used one specially made with white glass for several measurements.

BLACK AND WHITE

Pfund [8] introduced the black-and-white cryptometer in 1930. It eliminated the well, making cleaning easier, and worked for use with paints of any color because of the black-and-white instead of all-black background. Referring to 6, the black glass B and the white glass W are fused along line LM. Longitudinal grooves catch the overflow of paint. The wedge is moved to the right to make the line disappear, then to the left to make it reappear. The position of the plate is reversed and the observations repeated. From the mean of all readings, the hiding is calculated as with the all-black cryptometer (see "All Black"). Comparison of results for white paints shows that the two cryptometer types (all-black and black-and-white) yield the same values within experimental error (Ref. [4], p. 22).

ROTARY TYPE

The rotary cryptometer was a short-lived device designed to overcome the jerky movement of the top plate of the regular cryptometer [9]. The wedge of the cryptometers of Fig. 5 and 6 was replaced with a circular glass plate mounted in a metal frame (Fig. 7). The thickness of the film was read on a scale located on the bottom plate. While the movement of the plate was much smoother with this instrument, it was found that bubbles often obscured the end-point.

ASSESSMENT OF CRYPTOMETERS (REF. [4], P. 25)

The cryptometer is a simple instrument requiring only small quantities of paint, and determinations are quickly made. However, reading the end-point is difficult, and the mean of a number of determinations is therefore advisable.

Most users can repeat their own results, but agreement among different users is not satisfactory although it is improved by the use of a standard paint [10]. Another major disadvantage of cryptometers is that they measure only wet HP. One study [11] reported that cryptometers were satisfactory with low-opacity but not high-opacity paints. Consideration of its advantages and disadvantages suggests that the cryptometer is better suited for control work than for specification requirements. The cryptometers shown in Fig. 5 and 6 continue to be commercially available.

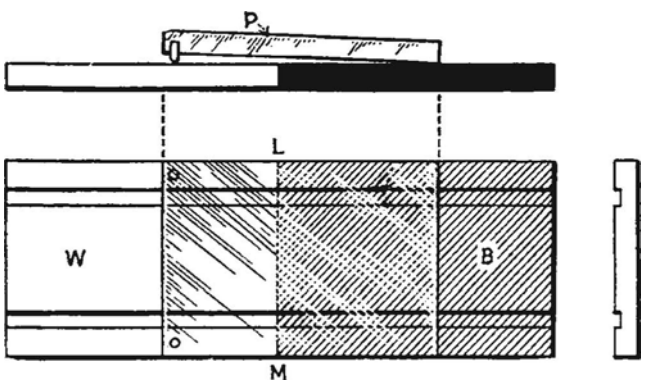

Fig. 6—Pfund black-and-white cryptometer.

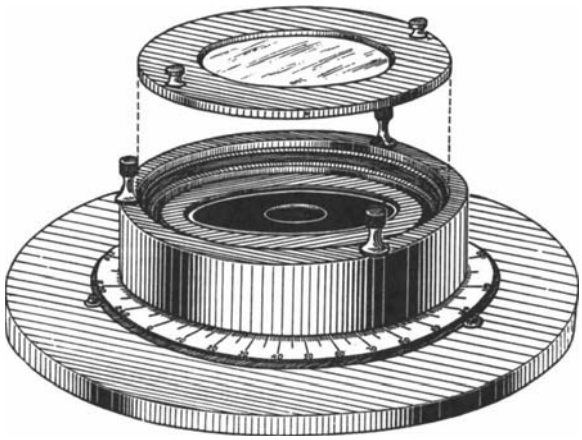

Fig. 7—Rotary cryptometer.

Hallet Hidimeter

Along with the Pfund cryptometer, the Hallet hidimeter [12] was one of the very early devices for evaluating HP. The objective of a regular microscope is replaced by a long tube fitted with a plain ground glass objective; the eyepiece is replaced with a small hole. The principle of the device is the light-diffusing property of ground glass. If a contrast substrate is viewed through a plate of ground glass, the contrast boundaries become more blurred as the distance between plate and substrate increases. If a liquid paint sample is sandwiched between them, it blurs the boundary further, and the distance required to make the boundary disappear decreases. Since that distance is the thickness of the intervening paint film, it is a measure of the HP of the paint. This measurement is essentially comparative because it cannot be translated into regular HP units.

EARLY PHOTOMETRIC HP METHODS

Pfund Precision Cryptometer

In this device (Fig. 8) a photoelectric cell is used to measure the reflectance of paint contained in a wedge-shaped layer [13]. The base plate consists of black-and-white areas B and W, whose boundary is parallel to the length of the plate instead of perpendicular as with the visual cryptometer. The photoelectric device is shifted until a position is found where the reflectance of the paint over the black area is 98 % of that over the white area. The film thickness and HP

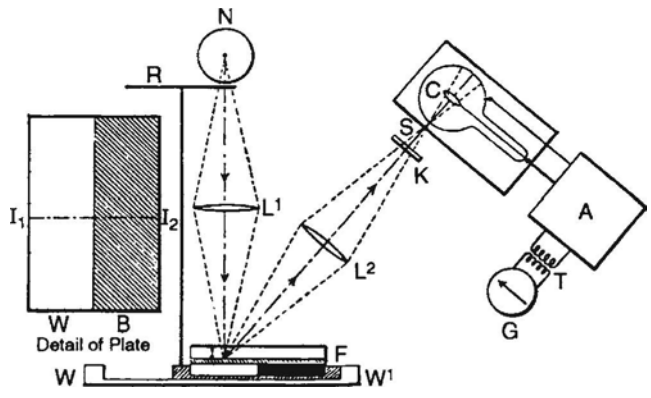

Fig. 8—Pfund precision cryptometer. Uses a photoelectric cell instead of the eye to measure reflectance.

calculations are the same as with the visual cryptometers described in "Pfund Cryptometers."

This cryptometer eliminates the uncertainties of the visual type, as there is no sliding of the top plate over the base plate and no need to estimate visually the appearance and disappearance of an indistinct line. However, it retains the disadvantage of permitting only wet hiding measurements and has therefore been superseded by other photometric devices and methods that permit the measurement of dry HP.

Hanstock Method

Hanstock [14] studied the relationship of light transmission through free paint films to opacity and HP on a black-and-white substrate. For his transmission work, he employed a flicker photometer and found that paint films were perfectly diffusing and that films having the same degree of light transmission had approximately equal opacity. He further showed the correspondence between refractive index, the Fresnel relationship, and HP.

The problem with the transmission concept is that modern paints have so much opacity it is difficult to accurately measure the transmission of films of commercial thickness. Moreover, HP is concerned in practice with paint in intimate contact with opaque surfaces and not as a free film. Consequently, measurement of light transmission through paint films is done today only for very specialized research.

Use of the Fell Equation

An empirical relationship between SR and CR was found by Fell and reported by Sawyer [15] in the following form

$$\log(\text{CR} \times 10) = m \times \text{SR} + b \tag{24}$$

where m and b are experimental constants.

Since the graph for this equation is a straight line, it is a simple matter after determining m and b from measurements at two CR levels to find the SR required for any desired CR. This procedure was adapted by Marchese and Zimmerman to determine the HP of paints at a CR of 0.98, and the method was used for many years by the Titanium Pigment Co. (Ref. [4], p. 24). Experience has shown that reasonably satisfactory results can be obtained if the equation is used for interpolation between points close to the desired CR. But, as pointed out by Switzer [16], extrapolation of results can lead to serious errors. He further pointed out that the Fell equation method allows only a single estimate of HP from at least two test applications, thus requiring a considerable effort to obtain an estimate of intralaboratory precision.

New York Paint Club (NYPC) Method

This method employed doctor blades to apply films at several thicknesses on black-and-white cardboard HP charts. After the films had dried, reflectance, weight, and area measurements were made from which CRs and corresponding WFT were calculated. CR values (rather than log 10 CR as in the Fell equation) were plotted against reciprocal film thickness and the HP calculated from the WFT at 0.98 CR. If the white area of the chart deviated appreciably from the standard reflectance of 0.80, the CR was corrected using Eq (1) or Eq (2). The Club reported that most of the effort in this method was to determine film thicknesses. To minimize that effort they modified the method by casting films on black and white glass plates and determined thicknesses with an interchemical WFT gage in accordance with ASTM Test Methods for Measurement of Wet Film Thickness of Organic Coatings (D1212). Any error in film thickness, of course, carries over to the HP value. According to Mitton, the revised method sacrifices accuracy and precision for speed [17]. In addition, graphical averaging makes it burdensome to estimate the precision with which the HP has been determined for the same reason pointed out in "Use of the Fell Equation" in connection with the Fell equation method.

Van Eyken–Anderson Method

The method proposed by Van Eyken and Anderson [18] uses CRs and film thicknesses in the same way as the NYPC method described in New York Paint Club (NYPC) Method Section, except that films of different thicknesses are applied in a single operation by using a doctor blade having seven clearances. A die is used to prepare uniform area punch-outs of the paper charts to determine SR by the basic weight-area-density-NVW calculation (see Eq (26)). The defects of this method are that the small areas used for reflectance and weighing make the achievement of good precision difficult (Ref. [4], p. 31), and there is no provision for correcting CR if the white substrate reflectance differs from 0.80.

Federal Test Method for Dry Opacity

This is Method 4121 of U.S. Federal Test Method Standard No. 141. It is a pass–fail test calling for a minimum dry film CR at a specified WFT. Black-and-white HP charts are used as the test substrate. For routine testing, the paint may be applied either by brush or doctor blade. For referee tests, application is by doctor blade only. The density and the nonvolatile content of the paint are also required. Several drawdowns are made to bracket the specified WFT. The weight of dry paint film is determined for a measured area on each drawdown and the WFT is then calculated from the equation

$$\text{WFT(mils)} = \frac{61M(\text{g})}{A(\text{in.})^2 \times N \times D(\text{g/mL})} \tag{25}$$

where

M = the dry film weight,
N = the fractional nonvolatile content of paint by weight,
A = the film area, and
D = the density of the paint.

The CR of each chart is measured and plotted against the corresponding WFT. From a smooth curve drawn through the points, the CR at the specified WFT is obtained. If this is equal to or greater than the specified CR, then the requirement for dry opacity has been met.

GENERAL HP METHODOLOGY

Film Application

The objective is to determine the SR at a specified level of dry film opacity, which is usually full hiding as perceived visually or corresponding to the CR: $C = R_0/R_{0.80} = 0.98$. The basic experimental procedure is to apply a uniform film on

a suitable test substrate, to observe its opacity either visually or photometrically, and to determine its SR. Since it is not possible to apply a film with precision at a predetermined dry opacity, several such applications need to be made over a range of SRs and their results plotted graphically or otherwise interpolated to the desired HP end-point. This laborious procedure is exemplified in the visual methods discussed in "Brushouts" and "Relative Dry HP–Krebs Method" and in the CR (CR) methods discussed in "Van Eyken–Anderson Method" and "Federal Test Method for Dry Opacity." The Fell equation and NYPC methods ("Use of the Fell Equation" and "New York Paint Club (NYPC) Method") attempt to reduce the workload to only two SR determinations by plotting SR against CR or log CR and finding the hiding end-point graphically on the basis of perceived empirical straight-line relationships. Kubelka-Munk (K-M) theory (see "K-M Two-Constant Theory") shows how the end-point can be calculated with just one SR determination.

SR (or Film Thickness) Determination

In both visual and photometric HP methods, the procedures for observing film opacity are well-defined and can be performed with dispatch. The experimental task most demanding on the operator's time and ingenuity is to determine the SR or film thickness of the applied coating with good precision. Although gages are available to measure WFT and DFT directly and quickly, the most accurate procedure, by far, is to determine the weight of applied paint film on a measured test area and then to calculate the SR or film thickness as described in "Brushouts" and "Federal Test Method for Dry Opacity." The equations in both of those methods contain mixed metric and common units. When the units are all metric, the equations are simpler. Letting M = dry film weight and A = the film area and using the symbolism in SR and Film Thickness Relationships:

$$H(\mathrm{m}^2/\mathrm{L}) = \frac{A(\mathrm{cm})^2 \cdot N \cdot D(\mathrm{kg/L})}{10M(\mathrm{g})} \tag{26}$$

$$T(\mu\mathrm{m}) = \frac{10^4 M(\mathrm{g})}{A(\mathrm{cm})^2 \cdot N \cdot D(\mathrm{kg/L})} \tag{27}$$

See "Metric Units" for equations interrelating SR, WFT, and DFT. See "U.S.—Metric Unit Conversion" for conversions between metric and U.S. units.

If the volatiles have a relatively low evaporation rate as with most architectural coatings, the film might be weighed rapidly before appreciable loss of volatiles, in which case Eqs (26) and (27) would still apply but with M as the wet film weight and N as unity. The disadvantage of this procedure is that it demands very skillful and speedy manipulation to minimize loss of volatiles before weighing. For that same reason, it is not applicable at all to coatings containing fast-evaporating solvents.

With powder coatings, for which the SR is normally expressed on a weight basis, Eq (26) becomes

$$H(\mathrm{m}^2/\mathrm{kg}) = \frac{A(\mathrm{cm})^2 \cdot N}{10M(\mathrm{g})} \tag{28}$$

Assuming negligible volatile content, the value of N in this equation can be taken as unity.

Photometric Measurements

The CIE-Y reflectance is measured because this function defines the human eye's quantitative response to the luminous character of light across the visual spectrum. This is valid for chromatic, as well as achromatic colors, as reported by Tough [19], who found good correlation in a large series of colored paints between visual HP measurements and CR values based on CIE-Y measurements with a spectrophotometer. The end-point of 0.98 CR is effective with colors, although it appears that other end-points, for example CIELAB color difference: ΔE = 1.5, would make some difference in the relative HP of various colored paints [20]. However, the simplicity of the 0.98 end-point and its history of validity and general agreement among various workers make it the best choice regardless of color (Ref. [4], p. 31). CIE-Y measurements can be made with the green filter of a tristimulus colorimeter or with a spectrophotometer. When properly standardized, results with the two instrument types should be the same. As a precaution, there should be coordination between correspondent laboratories with regard to instrumentation. In all cases, reflectance measurements must be made excluding surface reflection, which is implicit for instruments designed with 0°/45° geometry and optional with most other instrument types.

CURRENTLY USED TEST SUBSTRATES

The substrate is generally the major factor affecting the specific experimental details of a test procedure. It is selected or specified on the basis of its adaptability to the type of coating being tested and for its perceived advantages in the required or preferred test procedure.

Paperboard Charts

Substrates of this type are described in "Relative Dry HP—Krebs Method." Their employment with baking finishes is limited because of distortion and discoloration at high temperatures, but they are used widely with air-dried coatings for general HP observations. Black-and-white charts can be used for precision photometric HP measurements by taking appropriate steps to allow for weight variations in the substrate due to humidity and inherent random variations in the area weight of paper. These steps include the use of unpainted control charts and the averaging of multiple test results. Charts with combinations of gray and black, gray and white, and gradations of gray on a white background are used in visual HP tests to obtain what are considered to be more practical HP measurements.

Clear Plastic Film

Polyester is the preferred chemical type. Because of heat distortion, its use is generally confined to air-dried coatings. After the film has dried, a square of convenient size is cut and the area measured. Values of R_0 and R_w are read by placing the painted plastic film alternately on a black and a white background with the underside moistened with a suitable liquid (e.g., mineral spirits or dibutyl phthalate) to remove the air interface and establish good optical contact. The dry film weight is determined as the difference in the weight of the painted and unpainted substrate by stripping off the paint film with a strong solvent.

Glass Panels

Individual black and white glass panels are used to take advantage of the superior levelness of glass for casting of uniform films and because the hard, smooth surface permits rapid WFT measurements with an ASTM-type of WFT gage (New York Paint Club (NYPC) Method). The same information is obtained less rapidly, but with much better precision by scraping off and weighing a defined area of dry film and calculating as described in SR (or Film Thickness) Determination. In some tests, CRs are calculated on the questionable assumption that separate film applications on black and white glass panels are identical in film thickness.

Painted Metal Panels

Panels of this type are generally used with coatings that are applied by spraying and cured by baking. The weight of the applied film is determined by weighing the panel before the coating is applied and again after drying. The SR or film thickness is then calculated as described in SR (or Film Thickness) Determination. If desired, the DFT can be determined without weighing, though with considerably less precision, by direct measurement with a magnetic or an eddy current thickness gage. Black-and-white panels are used for CR measurements or for visual observation of opacity. Mitton has described the use of all-black panels for measuring the HP of baking enamels [21].

K-M TWO-CONSTANT THEORY

Introduction

The light that enters a paint film is subjected to scattering and absorption as described in "The Role of Pigments in HP," and whatever is not absorbed by the film or substrate eventually re-emerges as reflected light. In 1931 Kubelka and Munk [22] published equations defining the optical behavior of a translucent material in terms of two constants referred to as coefficients of scattering and absorption. Steele [23] in 1935 showed how these equations were adaptable to the measuring of paper opacity, and Judd et al. [24] in 1937 did the same in connection with coatings. Kubelka [25] in 1948 rearranged the original equations into new and simplified forms from which Switzer [26] in 1952 developed equations designed specifically for the study of HP by expressing the film thickness (or SR) as a function of the CR. Using these equations and their derivatives, the CR of a coating can be calculated for any SR (or vice versa) from measurements made at only one and its photometric HP thereby determined by a single test application. This is in contrast with the more laborious procedure of obtaining CR values at two or more SRs for interpolation or extrapolation to the HP end-point. The calculations appear formidable, but are readily accomplished with a suitably programmed computer. Graphs and tables are also available for this purpose, although not as convenient and accurate as a computer. The experimental steps are straightforward, and, as with most HP methods, the most difficult and time-consuming operation is to determine the experimental SR (or film thickness) with sufficient precision. How that is accomplished is the essential difference between various K-M-based methods.

Equation Symbols

The symbols used here are based on ASTM Test Method for HP of Paints by Reflectometry (D2805-2003) as follows:

G = the substrate luminous reflectance (CIE-Y)
For a white substrate $G = W$.
For a standard white substrate $G = W = 0.80$.
For a black substrate $G = B$.
For a standard black substrate $G = B \leq 1 \approx 0$.

R_G = the luminous reflectance of a film applied over a substrate of reflectance G.

R = *reflectivity*—a property of the paint—the limiting reflectance of the paint film as it is increased in thickness. Also defined as the reflectance at complete hiding as evidenced by $R_0 = R_w$ over a black-and-white substrate of uniform film thickness.

C_w = the CR of a film applied at uniform thickness over a black-and-white substrate; thus, $C_w = R_0/R_w$,

$C_{0.80}$ = the CR over a standard black-and-white substrate, thus $C_{0.80} = R_0/R_{0.80}$.

C = abbreviation for $C_{0.80}$; the two are used interchangeably, thus $C = C_{0.80} = R_0/R_{0.80}$.

T = the film thickness in any stated unit, e.g., μm, mils.

H = the SR in any stated unit, e.g., m^2/L, ft^2/gal, m^2/kg, ft^2/lb, cm^2/g.

S = the scattering coefficient, a measure of the ability of the paint to scatter light, expressed in units reciprocal to T or the same as H.

K = the absorption coefficient—a measure of the ability of the paint to absorb light, expressed in the same unit(s) as S.

e = 2.718 28… the exponential base for natural logarithms.

P = scattering power—a measure of the ability of a film to scatter light. A unitless film constant defined mathematically by the relationships: $P = ST$ or $P = S/H$.

Subscripts

x = an experimentally determined value, e.g., T_x, H_x, P_x.

c = a value calculated for a specified CR C, e.g., P_c, H_c.

0.98 = a value calculated for $C = 0.98$, e.g., $H_{0.98}$, $T_{0.98}$.

H = indicates a value pertaining to a SR e.g., C_H, P_H, S_H.

T = indicates a value pertaining to a film thickness, e.g., C_T, S_T.

a and b = simplifying functions of R, defined by

$$a = 1/2\ (1/R_\infty + R_\infty) \tag{29}$$

$$b = 1/2\ (1/R_\infty - R_\infty) \tag{30}$$

From these definitions are derived the additional relationships

$$b = (a^2 - 1)^{1/2} \tag{31}$$

$$R_\infty = a - b = a - (a^2 - 1)^{1/2} \tag{32}$$

Note that R_∞, a, and b are three forms of the same constant, so that the determination of any one of them is

equivalent to determining all three. Sometimes they are used together in the same equation.

Additional simplifying functions which can be expressed in exponential-logarithmic form, or using hyperbolic co-tangents are

$$U = f(P, R_\infty) = b\left(\frac{e^{2bp}+1}{e^{2bp}-1}\right) = b \coth bP \qquad (33)$$

and the converse of Eq (31)

$$P = f(U, R_\infty) = \frac{1}{2b}\ln\left(\frac{U+b}{U-b}\right) = \frac{1}{b}\coth^{-1}\left(\frac{U}{b}\right) \qquad (34)$$

in which

ln = designation for natural logarithms, viz., $\log_e x = \ln x$,

coth = designation for hyperbolic co-tangents, defined by coth x

$$= \frac{e^{2x}+1}{e^{2x}-1}$$

and

$\coth^{-1}$ = designation for inverse hyperbolic cotangents, defined by

$$\coth^{-1} x = \frac{1}{2}\ln\frac{x+1}{x-1}$$

Values of natural logarithms and hyperbolic functions are available in published tables and in calculators. Since the tangent function is frequently provided without the cotangent, the relationships between the two are stated here as follows

$$\coth x = 1/\tanh x, \quad \coth^{-1} x = \tanh^{-1} 1/x$$

Original K-M Equations

The original equations are as follows:

For nonopaque films

$$R_G = f(ST, R_\infty, G) = \frac{G/R_\infty - 1 + (1 - GR_\infty)e^{(1/R_\infty - R_\infty)ST}}{G - R_\infty + (1/R_\infty - G)e^{(1/R_\infty - R_\infty)ST}} \qquad (35)$$

For opaque films

$$R_\infty = f(K/S) = 1 + K/S - (K^2/S^2 + 2K/S)^{1/2} \qquad (36)$$

whose converse and more useful form is

$$K/S = f(R_\infty) = (1 - R_\infty)^2/2R_\infty \qquad (37)$$

Functional forms are shown in this discussion along with the corresponding explicit forms for a clearer perception of the variables. Sometimes the functional form will be used by itself for both brevity and clarity.

Eq (35) shows the reflectance of a paint film in terms of two basic optical characteristics of the paint: the scattering coefficient S, and reflectivity R_∞, and two values that are characteristic of the particular application: the reflectance G of the substrate and the thickness T of the film.

Scattering Coefficient and Scattering Power

The product ST in Eq (35) is a unitless film constant referred to by Kubelka [23] and Judd [22] as the scattering power of the film and symbolized here by the letter P. Thus, given that $P = ST$ and employing simplifying forms of R_∞ and the function U of Eq (33), Eq (35) can be rewritten in the much abbreviated form

$$R_G = f(U, R_\infty, G) = f(P, R_\infty, G) = \frac{1 - G(a - U)}{a + U - G} \qquad (38)$$

Since film thickness T and SR H are reciprocally interdependent (see Eqs (6) and (7)), it follows that $P = S_T T = S_H/H$, with the scattering coefficient (S_T or S_H) being expressed in a unit reciprocal to that of T (e.g., mil^{-1}, μm^{-1}) or in the same SR units as H (e.g., ft^2/gal, m^2/L, ft^2/lb, m^2/kg, cm^2/g). A clarifying concept in which SR units are mandatory is to consider scattering as an entity quantifiable in area units, with the scattering coefficient as the amount of scattering per unit quantity of coating or coating ingredient, and scattering power as the amount of scattering per unit area of film. SR units have the further advantage over film thickness and reciprocal film thickness of being directly relatable to gravimetric, as well as volumetric quantities. Thus, for understandability, convenience, and standardization, it is preferable to use SR units for scattering coefficients and HP and more specifically the metric SR units m^2/L and m^2/kg. These are translatable into film thicknesses and U.S. units using the conversion equations in "U.S.—Metric Unit Conversions." Equations for the numerical conversion of scattering coefficients expressed in various units to standardized metric SR units are given in Table 4.

General K-M HP Method

The experimental procedure, in brief, is to determine the reflectivity R_∞ of the paint and R_0 and H_x of a nonopaque paint film, from which the scattering coefficient S of the paint is calculated. From R_∞ and S is then calculated the SR H_c at any specified CR C or vice versa, or more specifically the SR $H_{0.98}$ when $C = 0.98$, which by definition is the HP of the paint. The K-M equations used in these calculations are derived from Eq (38) (the simplified form of Eq (35)) and can be programmed for quick computer solutions.

DETERMINATION OF REFLECTIVITY R_∞

A paint film is applied uniformly over a black-and-white substrate at normal SR (or film thickness) and dried in the manner usual for the particular coating. After drying, the

TABLE 4—Unit conversion equations for scattering coefficients.

$S(m^2/L) = S(ft^2/gal) \div 40.746$
$S(m^2/L) = S(mil^{-1}) \times 39.37$
$S(m^2/L) = S(\mu m^{-1}) \times 1000$
$S(m^2/L) = S(mm^{-1}) \times 1$
$S(m^2/kg) = S(ft^2/lb) \div 4.888$
$S(m^2/kg) = S(cm^2/g) \div 10$
$S(m^2/L) = S(m^2/kg) \times D(kg/L)$

reflectance values R_0, R_w, and W are measured. If the CR C_w=R_0/R_w is less than 0.96, the application is repeated as a second coat or at a somewhat higher film thickness. A porous film should not be recoated, nor an impractically high film thickness applied in a single coat, due to the possible effect on R_∞. If the original or recoated film hides completely, then $R_0 = R_w = R_\infty$. If not, calculate

$$a = f(R_0, R_w, W) = \frac{1}{2}\left(Rw + \frac{R_0 + W - R_w}{WR_0}\right) \quad (39)$$

and from Eq (32)

$$R_\infty = a - \left(a^2 - 1\right)^{1/2}$$

The preceding two equations may be programmed sequentially to give

$$R = f\left(R_0, R_w, W\right) \quad (40)$$

DETERMINATION OF R_0 AND H_x

This requires the application of a uniform film at a SR (or film thickness) such that the CR C_w is within the range of 0.96 to 0.985. These limits are established because too low a CR requires excessive extrapolation to the C = 0.98 endpoint, and higher CR values become increasingly insensitive to SR (or film thickness) variations. If the initial application is outside that range, the application is repeated at a higher or lower film thickness, as required.

The film may be applied on a black-and-white or an all-black substrate. If black-and-white, then the test application can be the same one used for determining R_∞ in Determination of Reflectivity R_∞. If an all-black test surface is employed, the indicated CR range is still required, but since it cannot be measured directly, it is calculated from

$$C_{0.80} = f(R_0, R_\infty) = \frac{R_0(1 - 0.80R_0)}{R_0 + 0.80(1 - 2_a R_0)} \quad (41)$$

Having obtained a film within the specified CR range, R_0 is recorded and H_x is determined by a suitable method. Various techniques for determining the SR are available, but the most precise is a weight-area-density-NVW method as discussed in "SR (or Film Thickness) Determination," using applicable Eqs (26) and (27). The dry film weight M in those equations is usually obtained as the difference in the weight of the test area before and after application of the paint. Sometimes, as with black glass, it is obtained by removing a known area of film and weighing it directly. Such weighings can be performed on an analytical balance with great accuracy. The density D and nonvolatile N of the paint must, of course, also be determined if not already known.

With considerably less precision, the thickness of the dry film can be measured using a caliper or electronic gage on a metal panel, from which the SR can be calculated using one of the following relationships

$$H(\mathrm{m}^2/\mathrm{L}) = \frac{1000ND}{t(\mu\mathrm{m}) \cdot d} \quad (42)$$

or

$$H(\mathrm{m}^2/\mathrm{kg}) = \frac{1000N}{t(\mu\mathrm{m}) \cdot d(\mathrm{kg/L})} \quad (43)$$

where

N = the nonvolatile fraction by weight NVW of the test paint,
D = the density of a liquid paint,
d = the density of the dry or cured film, and
t = the thickness of the dry or cured film.

CALCULATION OF $H_{0.98}$

Having determined R_∞ of the paint and R_0 and H_x of the testfilm, $H_{0.98}$ is obtained by the following sequence of calculations:

(a) The scattering power, P_x of the test film is calculated from

$$P_x = f(R_0, R) = \frac{1}{b}\coth^{-1}\left(\frac{1 - aR_0}{bR_0}\right) = \frac{1}{2b}\ln\left(\frac{1 - R_0R_\infty}{1 - R_0/R_\infty}\right) \quad (44)$$

(b) The scattering coefficient S of the paint is calculated from $S = P_xH_x$.

(c) The scattering power P_c of a paint film at the CR C = 0.98 is calculated from

$$U_0 = f(C, R_\infty) = \left[\left(a + \frac{1 - C}{1.60C}\right)^2 - \frac{1}{C}\right]^{1/2} + \frac{1 - C}{1.60C} \quad (45)$$

and Eq (34)

$$P = f(U, R_\infty)$$

which are solved sequentially to give

$$P_c = f(C, R_\infty) \quad (45)$$

(d) The HP $H_{0.98}$ is then calculated from $H_c = S/P_c$ where C = 0.98.

CR AT A SPECIFIED SR

Although this is not HP as such, it is frequently used as an alternative HP criterion. After Step (b) of Calculation of $H_{0.98}$, calculate the scattering power P at the specified SR H from: $P_H = S/H$, then calculate the CR C_H from Eq (33)

$$U_H = f(P_H, R_\infty) \quad (46)$$

and

$$C_H = f(U_H, R_\infty) = \frac{a + U - 0.80}{(a + U)[1 - 0.80(a - U)]} \quad (47)$$

which together give

$$C_H = f(PH, R_\infty) \quad (48)$$

Judd Graph (Information Included for Historical Purposes)

Prior to the availability of modern computers, K-M equations were much too complex for a practicable HP test method. Judd [24], therefore, laboriously worked out a general solution to Eq (35) in the form of a graph repro-

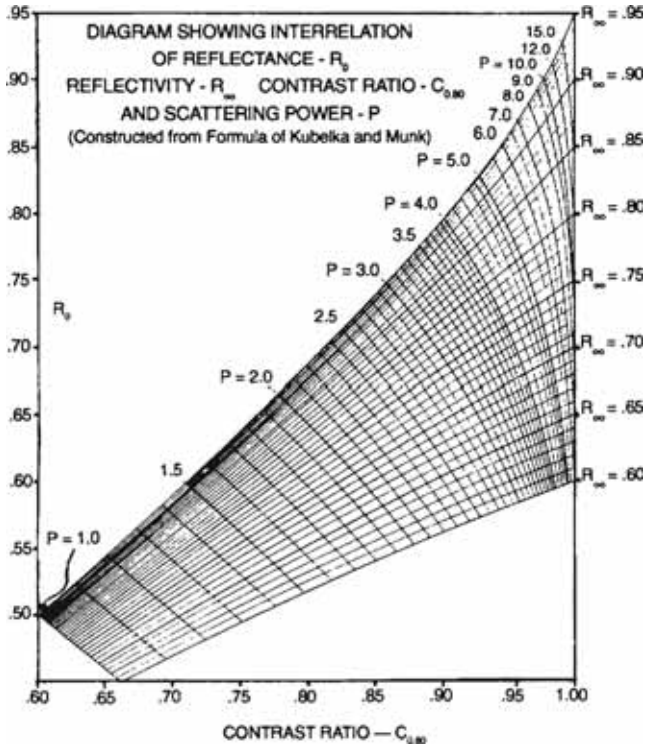

Fig. 9—Judd graph derived from Kubelka–Munk Eq (35).

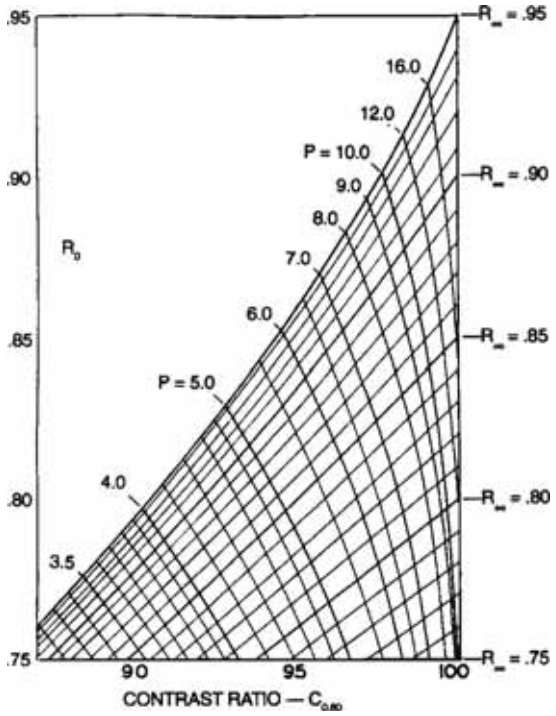

Fig. 10—Judd graph derived from Kubelka–Munk Eq (35)—a portion of Fig. 9 enlarged.

duced in Fig. 9. The graph relates the four variables R_0, $C_{0.80}$, R_∞, and P so that from any two of them the other two can be determined. It consists of two families of curves for constant values of R_∞ and P, plotted on the coordinates R_0 and $C_{0.80}$. The P curves were referred to in the original Judd graph as curves of SX (or ST). The portion pertinent to white paints ($R_\infty \geq 0.75$) has been enlarged and is shown in Fig. 10. Experimentally, R_0, R_W, and H_x are determined as in Determination of R_0 and Determination of Reflectivity R_∞ for a film applied uniformly on a black-and-white test substrate. If W deviates from 0.80 by more than 0.01, $C_{0.80}$ is calculated using correction Eqs (1) and (2). P_x and R_∞ are determined at the graph point corresponding to $C_{0.80}$ and R_0, and the scattering coefficient of the paint calculated from $S = P_x H_x$. The value of $P_{0.98}$ is located at the intersection of the R_∞ curve with the vertical line for $C = 0.98$. The HP is then calculated from $H_{0.98} = S/P_{0.98}$. If desired, the SR can be determined for CRs other than 0.98 in the same way. Conversely, C_H may be determined for any specified value of H by first calculating: $P_H = S/H$, then finding the desired value of C_H at the intersection of the curves for the determined P_H and R_∞.

The Judd graph is also useful for depicting the basic optical properties of paints. It shows that paints with high S values are lighter over black backgrounds than paints of the same reflectivity with low S values. Also, if their S values and film thicknesses are the same, paints with high reflectivity are poorer in hiding than paints of low reflectivity. The latter fact may be demonstrated as follows: Suppose a portion of paint for which $R_\infty = 0.85$ is tinted with a black colorant to an R_∞ value of 0.78 and the untinted and tinted paints are applied at the same thickness such that $P = 5.0$. From Fig. 9, or more accurately from Fig. 10, it can be determined that the colorant addition has increased the CR to 0.965 from its original value of 0.945, representing a considerable increase in visual film opacity. To determine what this amounts to in terms of photometric HP, the P values of the untinted and tinted paints at the intersection of their R_∞ curves with the vertical line $C = 0.98$ are found to be 7.5 and 6.0, respectively. Since S is unaffected by tinting, the SR change at $C = 0.98$ is calculated as

$$\frac{H_{\text{tinted}}}{H_{\text{untinted}}} = \frac{P_{\text{untinted}}}{P_{\text{tinted}}} = \frac{7.5}{6.0} = 1.25$$

representing an increase of 25 % in HP by tinting to a lower R_∞ value. This hiding increase was obtained at negligible monetary cost but at a sacrifice in paint quality in regard to brightness of appearance. For that reason, in evaluating a series of paints experimentally, a fair comparison requires that all R_∞ values be adjusted by tinting to that of its lowest reflectivity member. Examination of the Judd graph shows that, after adjustment to the same R_∞ value, films of the different paints applied at the CR $C = 0.98$ all have the same $P_{0.98}$ value and, since $H_{0.98} = S/P_{0.98}$, their HPs will be directly proportional to their scattering coefficients. Thus the scattering coefficient alone can be an adequate HP comparator, without actually tinting the individual paints.

Mitton Graph and Table [27] (Information Included for Historical Purposes)

As with the Judd graph, these provide precalculated solutions to K-M equations, but with much greater precision. They were designed for the experimental procedure described in "General K-M HP Method," in which R_0 and H_x are determined for a film applied on an all-black test surface, and R_∞ is determined in a separate test application. The test surface of choice is black float glass because the

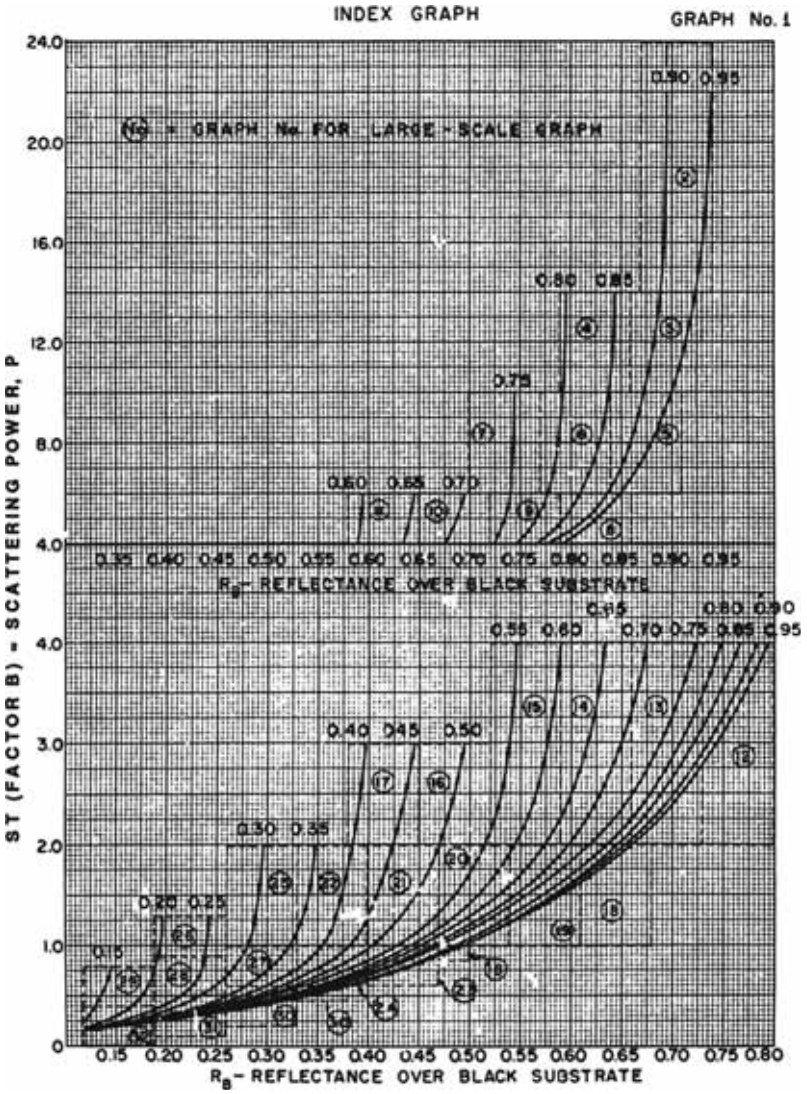

Fig. 11—Mitton graph of Kubelka–Munk Eq (44).

extremely level nature of the surface permits the application of very uniform films with a doctor blade. Mitton also describes the use of all-black metal panels to test spraying/baking-type finishes [21]. The graph is derived from Eq (44): $P = f(R_0, R_\infty)$ and is plotted as a family of curves at constant R_∞ on coordinates of scattering power P and reflectance R_0. The ordinate is indicated as ST (Factor B), which is the same as P, and the abscissa as R_B, which is usually, and in this case necessarily, the same as R_0. It consists of a small-scale index graph (Fig. 11) divided into 31 sections, each then expanded to a much larger scale on a separate sheet. Fig. 12 shows one of the expanded sections.

Associated with the Mitton graph is a table of factor A values derived from Eq (46): $P_c = f(C, R_\infty)$, in which factor $A_c = 1604.2/P_c$. Values of factor A_c are given in this table for C = 0.98, 0.95, and 0.93, for all values of R_∞ from 0.08 to 0.98 (8 to 98 %). The C value of most interest for HP calculations is 0.98, representing full photometric hiding as defined in Section Photometric HP End-Point. If desired, P_c is easily calculated from factor A_c.

The graph and table are typically used as follows: After determining R_∞ and R_0 experimentally, the index graph is consulted in order to select the appropriate expanded graph on which the scattering power P_x of the experimental paint film is to be found. Factor $A_{0.98}$ is determined from the table for the measured value of R_∞. At this point either the film thickness T_x, or SR H_x of the test film associated with R_0 is determined. If, as Mitton intended, T_x is determined in mils, then the scattering coefficient S is calculated in reciprocal mils from $S = P_x/T_x$, and the HP is calculated from the equation

$$H_{0.98}\left(\text{ft}^2/\text{gal}\right) = \text{S}\left(\text{mil}^{-1}\right) \cdot A_{0.98}$$

The preceding simple relationship holds when S is expressed in reciprocal mils and HP is expressed in ft²/gal. If the SR in m²/L is determined instead of the film thickness, then after determining P_x and R_∞, the scattering coefficient is calculated as: S (m²/L) $= P_x \cdot H_x$(m²/L) and the HP calculated from

$$H_{0.98}(\text{m}^2/\text{L}) = \frac{S(\text{m}^2/\text{L}) \cdot A_{0.98}}{1604.2} = \frac{S(\text{m}^2/\text{L})}{P_{0.98}}$$

At a later date, Mitton commented that graphical and tabular aids for K-M calculations had become unnecessary

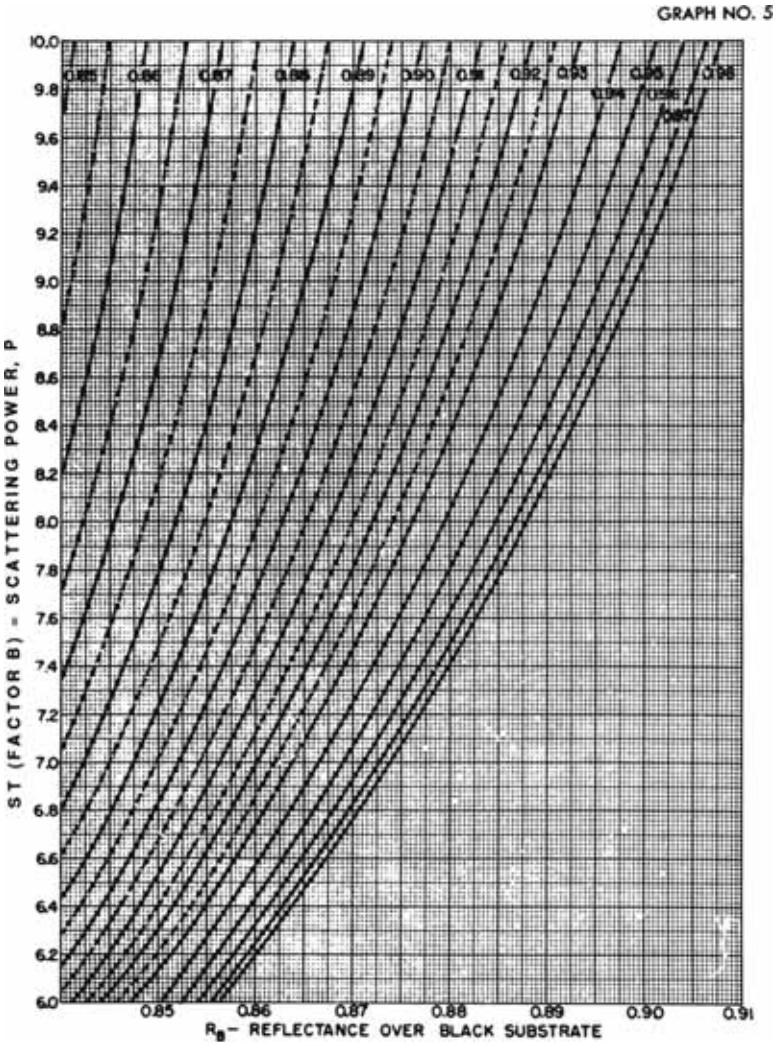

Fig. 12—Mitton graph—expansion of Sector 5 in Fig. 11.

with the advent of inexpensive programmable calculators [28]. Nevertheless, the Mitton graph and table continue to be used in a number of important test methods, and both the Judd and Mitton graphs are useful for instructional purposes. Currently, software is available with color-measuring instruments, and it can be used to carry out these calculations. For this reason, the graphical techniques are seldom used today.

Typical K-M HP Results

Tables 5 and 6 are based on the testing of various commercial paints and pigments. They are intended to illustrate magnitudes of HP and scattering coefficient values encountered in K-M HP measurements. The scattering coefficient values are intended to supplement and clarify, by specific examples, the relationships shown in Table 4. With regard to pigments are (Table 6), it is of course dispersions that are actually measured and the values for the pigments then calculated from their concentrations in the dispersions. For example

$$\frac{H_{\text{pigment}}(\text{m}^2/\text{kg})}{H_{\text{coating}}(\text{m}^2/\text{L})} = \frac{\text{S}_{\text{pigment}}(\text{m}^2/\text{kg})}{\text{S}_{\text{coating}}(\text{m}^2/\text{L})} = \frac{1}{\text{Pigment Conc.(kg/L)}}$$

The values in Table 6 should be considered as comparative because the scattering coefficient of a pigment can vary widely depending on the conditions of measurement (Ref. [4],

TABLE 5—Powder coatings—Representative HP and scattering coefficient data.

	White	Light Gray	Orange
R_∞	0.8234	0.6860	0.4389
$P_{0.98}$ (unitless)	7.011	4.655	2.449
Metric Units			
$H_{0.98}$ (m²/kg)	18.09	20.22	0.26
Density (kg/L)	1.60	1.66	1.41
$T_{0.98}$ (μm)	34.55	29.79	69.12
S (m²/kg)	126.8	94.13	25.13
U.S. Units			
$H_{0.98}$ (ft²/lb)	88.3	98.7	50.1
Density (lb/gal)	13.35	13.85	11.77
$T_{0.98}$ (mils)	1.36	1.17	2.72
S (ft²/lb)	619.2	459.5	122.7

NOTE: Derived from test results obtained by ASTM Subcommittee D01.51 on Powder Coatings.

TABLE 6—White pigments—HP and scattering coefficient values[a]					
	Lead Carbonate	**Zinc Oxide**	**Zinc Sulfide**	**Anatase TiO_2**	**Rutile TiO_2**
R_∞ (estimated)	0.91	. . .	. . .	. . .	. . .
$P_{0.98}$ (unitless)	9.5	. . .	. . .	. . .	. . .
Metric Units					
$H_{0.98}$ (m^2/kg)	3.1	4.1	11.9	23.5	30
S (m^2/L)	29	39	113	223	285
U.S. Units					
$H_{0.98}$ (ft^2/gal)	15	20	58	115	147
S (ft^2/lb)	140	190	550	1090	1390
[a]Based on reported hiding power values at a pigment volume concentration (PVC) of 28 % [30,31].					

p. 34), being affected by pigment volume concentration (PVC), effectiveness of dispersion, the presence of other pigments in the same dispersion, and the nature of the vehicle. Even within a specific chemical class it can vary considerably depending upon the particular method of manufacture employed. Nevertheless, it is frequently useful to determine pigment HP values for a comparison of their efficiency under specified conditions.

Theoretical Problems and Practical Considerations

The validity and usefulness of the K-M equations in HP calculations are predicted on the constancy of the scattering coefficient *S* over a suitably wide film thickness range. Judd [24] studied this question in connection with water-borne paints and vitreous white enamels and concluded that at practical film thicknesses *S* is constant within experimental error. The author has experimentally obtained essentially constant *S* values within a WFT range of 50 to 100 μm (2 to 4 mils), equivalent to a SR of 10 to 20 m^2/L (400–800 ft^2, /gal), with white alkyd gloss, latex gloss, and latex flat paints. Moreover, the effect of any variation of S with film thickness that might occur is minimized in experimental practice by casting films with CRs fairly close to the 0.98 CR hiding endpoint, as called for in Determination of R_0 and H_x. This is not difficult to do.

Refractive indices and resultant scattering coefficients vary with the wavelength of light. Thus, the effective scattering coefficient of a paint is actually an average for all of the encountered wavelengths. With achromatic paint films, the wavelength composition of the light flux remains constant and, therefore, so does the scattering coefficient upon which constancy the validity of K-M equations is predicated. Chromatic paint films, however, absorb light selectively and therefore change the composition of broadband illuminants with a resultant change in the effective scattering coefficient as the light passes through the film. This would, in theory, appear to disqualify chromatic paints from K-M HP calculations. In practice, however, the equations are used successfully for that purpose (Ref. [29]; Ref [4], p. 31), which is undoubtedly related to the previously noted fact that the experimental measurements are made fairly close to the HP end-point (C = 0.98), so that the K-M extrapolation and thus any associated error is relatively small.

As discussed by Mitton (Ref. [4], p. 27), the use of K-M theory for HP calculations has been questioned because it is phenomenological rather than based on fundamental theoretical considerations, and the measurements and equations omit needed corrections for surface reflection that are theoretically substantial. However, in experimental practice the errors are generally small despite the theoretical defects. Simpson took note of this in his comment that when uncorrected values of *S* and *K* are inserted back into the uncorrected K-M equations, "it would appear that an approximately correct answer is obtained" (Ref. [2], p. 111).

Calculation of HP from Tinting Data

Initially, the *S* and R_∞ values of a standard white paint are determined in accordance with the procedure described in "General K-M HP Method." The *K* value of the paint can then be calculated from Eq (37): $K/S = (1 - R_\infty)^2/2R_\infty$.

From Scattering Coefficient and Scattering Power, *S* and *K* can be considered as concentrations of "scattering" and "absorption" per unit weight or volume. The *K* value of a black tinter is determined by adding a measured ratio to the standard paint sufficient to reduce the reflectivity to about 0.40. The *K* value of the tinted paint is its initial *K* value plus the tinter contribution, thus

$$K_2 = K_1 + XK_t \tag{49a}$$

from which

$$XK_t = K_2 - K_1 \tag{49b}$$

and dividing through (b) by the common value of *S*

$$XK_t/S = K_2/S - K_1/S \tag{49c}$$

in which

K_t = the absorption coefficient of the tinter,
X = the ratio of tinter to paint,
K_1 = the initial K value of the paint,
K_2 = the K value of the paint after tinting, and
S = the scattering coefficinet of the paint.

The ratios K_2/S and K_1/S are calculated from measured values of R_∞ for the tinted and untinted paints using Eq (37): $K/S = (1 - R_\infty)^2/2R$). If the standard paint is an untinted white with a reflectivity no lower than 0.93, then its absorp-

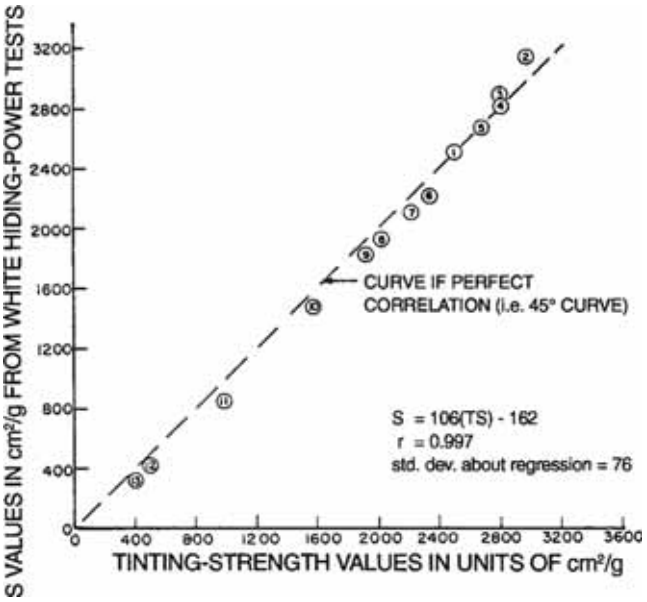

Fig. 13—Scattering coefficients determined by tinting and by HP tests.

tion contribution K1 is considered negligible compared with that of the tinter, in which case K_1/S is dropped from Eq (49c) to give

$$XK_t/S = K_2/S \tag{49d}$$

The absorption coefficient K_t of the tinter can be calculated from Eqs (49c) or (49d) since all other terms in these equations are known [30,31].

Having determined K_t, the *S*-value of a test paint can be determined using the same tinting procedure and equations as before, but this time calculating unknown *S* from known K_t, instead of vice versa. With the values *S* and R_∞ of the test paint having thus been determined, its HP $H_{0.98}$ can be calculated as in Calculation of $H_{0.98}$ (c) and (d) without the tedious requirement of measuring the SR.

Experimental evidence for the validity of this procedure is given by Mitton and Jacobsen [32], who, equating the tinting strength of a white pigment with its scattering coefficient, measured *S* (cm²/g) for a number of white pigments by direct HP measurement and by the tinting procedure. As shown in Fig. 13, the correlation between the two methods is very close. If this simplified method is to work, the *K* value of the black tinter must be the same in any paint being tested. Also, the tinter must not change the degree of dispersion of the white pigment so as to cause a change in its *S* value. These conditions are not always met, so that it is safest to apply the method only under favorable circumstances, when interaction of tinter and paint are known to be negligible.

Determination of Relative HP of Untinted White Paints from Tinting Data

For this purpose there is no need to determine the *K* value of the tinter as in "Calculation of HP from Tinting Data." An equal ratio of black tinter is added to comparison paints A and B, sufficient to reduce their R_∞ values to about 0.40. The R_∞ values of paints A and B are measured before and after tinting and the four corresponding *K*/*S* values calculated from Eq (30). Then, as in Eq. (49c) of "Calculation of HP from Tinting Data," for paint A:

$$XK_t/S_A = K_{A2}/S_A - K_{A1}/S_A \tag{50a}$$

for paint B

$$XK_t/S_B = K_{B2}/S_B - K_{B1}/S_B \tag{50b}$$

Next, dividing Eq (49b) into Eq (49a), *X* and K_t cancel to give

$$S_B/S_A = (K_{A2}/S_A - K_{A1}/S_A) \div (K_{B2}/S_B - K_{B1}/S_B) \tag{50c}$$

If the comparison paints are both untinted high reflectance whites then, as pointed out in "Calculation of HP from Tinting Data," the untinted *K*-values can be considered negligible and Eq (49c) becomes

$$S_B/S_A = K_{A2}/S_A \div K_{B2}/S_B \tag{50d}$$

As stated at the end of Judd Graph, at the same reflectivity R_∞, the HP values of paints A and B will be in the same ratio as their scattering coefficients.

K-M EQUATIONS FOR CORRECTING REFLECTANCE AND CR MEASUREMENTS TO A STANDARD WHITE SUBSTRATE REFLECTANCE

The reflectances of applied paint films, and hence their CRs, vary with the substrate reflectance. In practice, black substrates are effectively zero and constant, but white substrates can vary appreciably. Normalization equations that correct for this variation, derived from Eq (39) of "Original K-M Equations," are as follows:

$$R_G = f(R_w, R_0, W, G) = R_w - \frac{(W-G)(R_w - R\ )}{W(1-GR_\infty} \tag{51a}$$

$$C_G = f(R_w, R_0, W, G) = \frac{WR_0(1-GR_0)}{R_0(W-G)+GR_w(1-WR_0)} \tag{51b}$$

$$C_G = f(C_w, R_0, W, G) = \frac{WC_w(1-GR_0)}{C_w(W-G\ )+G(1-WR_0)} \tag{51c}$$

TABLE 7—Scattering coefficient of a 20 % PVC TiO_2-alkyd paint film versus crystal size of pigment.

S, μm^{-1}	Mean Crystal Size, μm
0.76	0.24
0.73	0.20
0.64	0.16

where

R_0 = reflectance of the coating over the black area
W = measured white substrate reflectance
R_w = measured reflectance of the coating over the white substrate
C_w = measured CR
G = standard white substrate reflectance Nominal:0.80
R_G = normalize reflectance of the coating over the white substrate
C_G = normalized CR

FACTORS AFFECTING WHITE HP

As shown in Table 1 and Table 6, rutile titanium dioxide is by far the most effective of the white hiding pigments in producing light scattering and HP, which is true on a cost as well as a weight basis. This fact has effectively eliminated the use of other white hiding pigments except for special properties or considerations. The important variables that determine the scattering and hiding efficiency of a titanium dioxide pigment in a paint are: (1) its mean crystal and particle size, (2) the state of pigment dispersion, (3) its concentration in the paint film, and (4) film porosity.

Crystal and Particle Size

By decreasing the particle size of the pigment, the number of particles and surfaces for light reflection and refraction increase, and the light-scattering ability of a given quantity of pigment will, therefore, tend to be enhanced. However, if the particle size is too small in relation to the wavelength of light, the wave front passes around rather than through it, so there is no light scattering, and the dispersion is transparent. Obviously, there is some intermediate optimum size related to the wavelength of light at which maximum scattering efficiency is obtained. The wavelength of the visible spectrum ranges from approximately 0.4 to 0.7 μm, peaking in luminosity at 0.55 μm. The mean crystal size for maximum opacity ranges from approximately 0.20 to 0.30 μm depending on both the PVC and the fraction of the pigment consisting of single crystals. Commercial grades of titanium dioxide developed for high-gloss finishes exhibit a single-crystal content of about 20 % and have a mean crystal size between 0.22 and 0.24 μm. The adverse effect of a lesser crystal size in such formulations is shown in Table 7 [33].

Pigment Dispersion

The process of obtaining a satisfactory dispersion involves the wetting of the pigment by the dispersion medium to displace air, breakdown of larger particles by milling, and stabilization after the dispersion has been obtained. With alkyd media, standard grades of titanium dioxide disperse easily and develop full hiding with very little milling. Thus, the main reason for milling alkyd dispersions is to reduce or eliminate oversize particles that affect the appearance of the film. With latex paints, milling can have an important effect on opacity depending on the grade of pigment employed [33], but the appearance factor is also an important consideration, particularly with semigloss and gloss finishes.

A major factor affecting the efficiency of TiO_2 in the completed formulation is the phenomenon referred to as flocculation, which is the formation of large particle groups or floccules due to weak forces of cohesion. Floccules are easily broken down but can spontaneously and quickly recur in the wet paint or drying paint film. Despite their weak bonding, floccules have the optical effect of increasing the mean particle size, thereby decreasing the scattering efficiency of the pigment. An auxiliary phenomenon related to increased particle size is the preferential scattering of longer wavelengths. Balfour and Hird took advantage of this phenomenon to quantify pigment flocculation by measuring backscattered infrared radiation (wavelength 25 μm) from a dried paint film to obtain what they refer to as a "flocculation gradient" [34,35].

Pigment Concentration

In "Refractive Index," it was pointed out that a very large single crystal of a white hiding pigment is actually transparent. Without undertaking a theoretical analysis, it is to be expected that as the concentration of pigment increases and its particles become more crowded, they approach the optical condition of a very large particle with resultant loss of scattering efficiency and HP. The crowding effect was studied by Stieg [36–38], whose results were used by Mitton (Ref. [4], pp. 34–35) to draw curves of HP $H_{0.98}$ versus PVC for pure rutile and anatase titanium dioxide in alkyd enamels. These are shown in Fig. 14, in which HP is expressed in ft²/lb of nonvolatile matter. If the paint is formulated at 50 % nonvolatile by volume, the HP results would be half that shown in Fig. 14, but the shape of the curves would be unchanged. Note the maximums in the curves at 25 to 30 % PVC, above which HP actually begins to decrease with increasing concentration of pigment. When calculated in terms of ft²/lb of pigment, the results appear as shown in Fig. 15, clearly indicating the drastic decrease in TiO_2 efficiency due to crowding.

Stieg [36] found empirically that the relationship between TiO_2 HP and PVC, as shown in Fig. 15, could be expressed by the equations

$$\text{rutile:} H_{0.98}(\text{ft}^2/\text{lb}) = 370 - 410(\text{PVC})^{1/3} \quad (52)$$

$$\text{anatase:} H_{0.98}(\text{ft}^2/\text{lb}) = 290 - 330(\text{PVC})^{1/3} \quad (53)$$

The PVC values in these equations are decimal fractions. Expressed in metric units, the equations become:

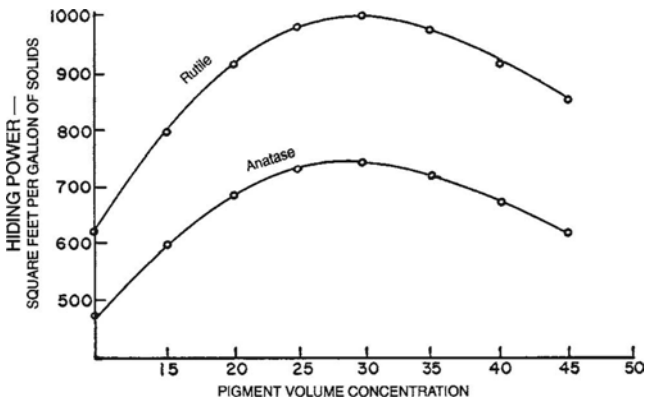

Fig. 14—HP $H_{0.98}$ (ft² /gal) of solids at various PVC levels.

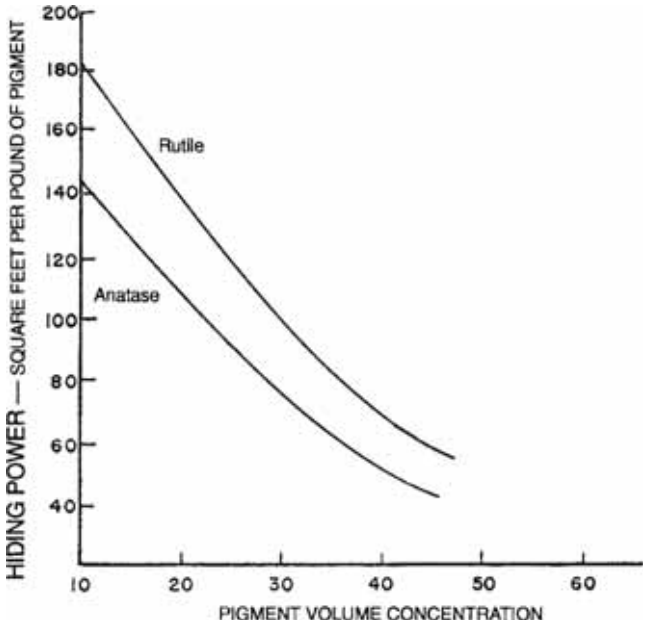

Fig. 15—HP $H_{0.98}$ (ft²/lb) of pigment at various PVC levels.

$$\text{rutile: } H_{0.98}(\text{m}^2/\text{kg}) = 75.7 - 839(\text{PVC})^{1/3} \quad (54)$$

$$\text{anatase: } H_{0.98}(\text{m}^2/\text{kg}) = 59.3 - 67.5(\text{PVC})^{1/3} \quad (55)$$

The question has been studied [36,39] of whether extenders added to a gloss or semigloss paint film might tend to increase the spacing of the TiO_2 pigment and thereby its scattering efficiency. The physical picture that emerges is of large particle-size extenders acting as massive intrusions having no effect on the original TiO_2 spacing, and of fine particle-size extenders dispersing uniformly so as to increase TiO_2 spacing, but no differently in this respect than an equal volume of binder. Consequently, when binder is replaced by an equal volume of large particle-size extender, TiO_2 efficiency decreases, whereas with small particle-size extenders, TiO_2 efficiency has been found to remain essentially the same and in no case improved.

Film Porosity

The preceding relationships pertain to pigment concentrations at which there is sufficient binder to wet the pigment completely and form a continuous phase, which means below the critical pigment volume concentration (CPVC). Above the CPVC, the dried film becomes porous, containing entrapped air that increases pigment-scattering efficiency by effectively lowering the refractive index of the surrounding medium. The air itself, as particulate matter in contact with the higher refractive index binder, contributes to light scattering. Thus, if the curves of Fig. 14 were extended to a sufficiently high PVC, the HP of the film would begin to rise again due to the opacification effect of film porosity. Obviously this is an extremely impractical use of expensive titanium dioxide with no relation to actual formulation practice. However, porosity does in practice make a major contribution to HP in the important interior flat wall paint sector. In paints of that type, inexpensive inert white pigments are included in the formulation, along with titanium dioxide for the esthetic purpose of producing a flat finish and to contribute HP by means of porosity. Stieg and Ensminger [38] showed that with paints over the CPVC that contain both TiO_2 and extender, HP is in a straight-line relationship with the Porosity Index (P.I.), with the slope of the line depending on the percentage of prime pigment and the nature of the extender. The P.I. is calculated from the equation

$$\text{P.I.} = 1\frac{\text{CPVC}(1 - \text{PVC})}{\text{PVC}(1 - \text{CPVC})} \quad (56)$$

The low-cost HP obtained from porosity is unfortunately accompanied by a deterioration in the quality of the film as manifested by poor scrub, soil, and stain resistance. This is due to an insufficiency of binder, resulting in an air phase continuum that gives ready capillary access to staining materials.

MICROVOIDS FOR WHITE HP

Through the use of encapsulated preformed microvoids, it has been found possible to obtain some of the HP benefit of entrapped air while avoiding or minimizing the deleterious effect of film porosity. The microvoids are supplied as a water dispersion of hollow beads having a plastic outer shell and water-filled core. Incorporated into a latex paint, the water in the core evaporates during the drying of the film and is replaced by air that functions as light-scattering particulates shielded from staining penetrants by the surrounding plastic shell. Because the microvoids alone are not able to produce the desired level of opacity in a film of normal thickness, the inclusion of titanium dioxide pigments in the paint formulation along with microvoids is essential. One widely used microvoid bead product is referred to as "opaque polymer" and employs a shell of thermoplastic polystyrene. Another type is a vesiculated bead in which titanium dioxide and water-filled "vesicles" are associated in a cross-linked polyester/styrene matrix. By using such products to partially replace titanium dioxide pigment, raw-material cost savings have been demonstrated with no loss in film integrity or HP [35,40].

FORMAL HP METHODS

ASTM Methods

ASTM D344: TEST METHOD FOR RELATIVE HIDING POWER OF PAINTS BY THE VISUAL EVALUATION OF BRUSHOUTS

This is essentially the same as the Krebs Method described in "Relative Dry HP—Krebs Method," differing only in requiring black-and-white instead of gray-and-white charts and in permitting checkerboard or other suitable contrast designs as well as the diamond-stripe pattern. Modern charts are 0.1 m² in area (1.076 ft²) instead of 1 ft² as specified originally. Provision is made for reporting results in m²/L as well as ft²/gal.

ASTM D2805: TEST METHOD FOR HIDING POWER OF PAINTS BY REFLECTOMETRY

This was adopted in 1969 and is actually a combination of two earlier methods, ASTM D1738 and ASTM D2614, that differed only in technique. It conforms with the general K-M method described in "General K-M HP Method" but is

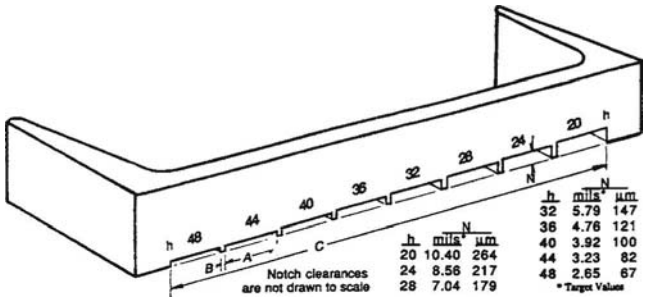

Fig. 16—Multi-notch applicator for ASTM D5007.

designed specifically for air-dried coatings. Originally it provided for the use of either black glass or charts for determining H_x and R_0. In later versions, black glass is mandatory. R_∞ is determined by a separate application as described in "Determination of R_0 and H_x." The need for two test applications does not represent a significant extra effort since only the application on black glass requires the time-consuming SR determination. The latter is accomplished by placing a template of predetermined area on the dry film, scraping off and discarding the film outside the confines of the template, then carefully scraping off the remaining film in the defined test area and weighing it on an analytical balance. The SR is then calculated from the density and nonvolatile content of the paint using Eq (26). Having obtained the experimental values R_0, H_x, and R_∞, the scattering coefficients and HP $H_{0.98}$ of the paint are calculated from these values using the K-M sequence shown in Calculation of $H_{0.98}$, thus: $P_x = f(R_0,R_\infty)$, $S = P_x H_x$, $P_c = f(C;R_\infty)$, $H_c = P_c/S$ for $C = 0.98$.

Earlier versions of ASTM D2805 and its predecessor standards included or referenced the Mitton tables and graphs described in Mitton Graph and Table [27], for solving the K-M equations. The method can be adjusted by appropriate experimental modifications to the measurement of baked enamels on black-painted metal panels as discussed in "Painted Metal Panels," or to other types of coatings and test substrates.

ASTM D5007: TEST METHOD FOR WET-TO-DRY HIDING CHANGE

This test method is concerned with determination of the change in hading power of an architectural coating during drying by visual evaluation of the wet and dry coating films. It is a rapid visual test designed to measure percent change in HP during drying. The paint is drawn down on a black-and-white test chart using a special multinotch applicator (Fig. 16) having eight notches with clearances in geometric progression ranging from 67 to 264 μm (2.65 to 10.4 mils). The clearance corresponding to an agreed visual endpoint (Visual HP End-Point) is estimated immediately after application and again after drying. The ratio of the two clearances multiplied by 100 gives the percentage change in HP:

$$\frac{\text{CLEARANCE}_{\text{WET ENDPOINT}}}{\text{CLEARANCE}_{\text{DRY ENDPOINT}}} = \frac{\text{WFT}_{\text{WET ENDPOINT}}}{\text{WFT}_{\text{DRY ENDPOINT}}}$$

$$= \frac{\text{SPREADING RATE}_{\text{DRY ENDPOINT}}}{\text{SPREADING RATE}_{\text{WET ENDPOINT}}} \qquad (57)$$

The equation assumes that, for any one drawdown, the ratio of clearance to WFT for the several notches does not deviate appreciably. On that basis, WFT variations due to application technique or paint rheology would not affect the final test result. This is not a precision test, but provides significant information of a practical nature with minimal effort.

ASTM D5150: TEST METHOD FOR HIDING POWER OF ARCHITECTURAL PAINTS APPLIED BY ROLLER

This is a visual comparison method designed for use with interior wall finishes and intended to provide practical information from tests performed on a convenient laboratory scale. The test substrate is a large, sealed paper test chart (Fig. 17), with a series of stripes numbered 1 through 6 on a white background. The stripes range in shade from very light gray to black and were selected so that the color difference ΔE^*_{ab} between each successive stripe and the white surround is in a geometric progression from 2 to 64 CIELAB units. The dimensions of the test area are 24 by 36 in. = 6 ft^2 (610 by 914 mm = 5575 cm^2), sufficiently large to simulate practical application of paints with a roller. The paint is applied at a specified, controlled SR, and the HP is reported as the stripe number of the darkest stripe perceived as being completely obscured. The concept of this test is that in practical applications the levelness of the paint film and, hence, its effective opacity are affected by the rheological properties of the paint. Thus, in practice paints tend to have lower HP than indicated by more customary test methods in which films are applied with maximum uniformity using a blade-type applicator. Relative practical HP among paints can be influenced for that same reason.

ASTM D6441: TEST METHOD FOR MEASURING THE HIDING POWER OF POWDER COATINGS

This standard conforms with the power coating industry practice of reporting HP in terms of film thickness rather than SR. A "wedge" shape film providing a range of film thicknesses is applied by electrostatic spraying on black and white painted metal panels. After curing, film thicknesses are measured with an electronic film thickness gage and reluctances measured with a small aperture (e.g. 4 mm)

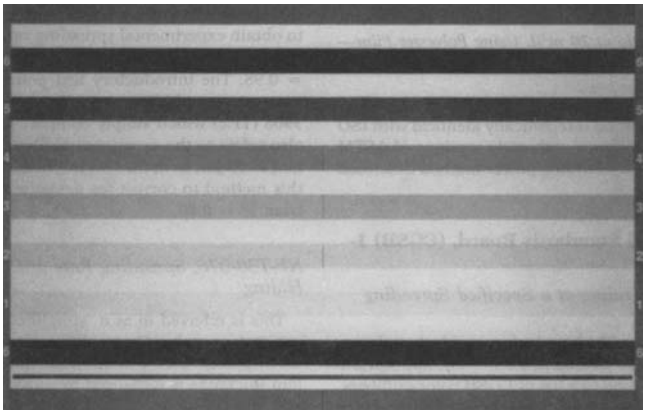

Fig. 17—Large gray scale chart (6 ft^2, 5575 cm^2) for roller application tests per ASTM D5150.

spectrophotometer. Method A reports the CR at a specified film thickness, and Method B the film thickness at a specified CR.

Federal Test Method Std. 141

METHOD 4121, CR AT A SPECIFIED SR

This pass–fail test was previously described in some detail in "Federal Test Method for Dry Opacity." Paint films are applied on black-and-white charts by brush or drawdown, and SRs are determined by a typical weight-area-density procedure, discussed in "SR (or Film Thickness) Determination." CR values are plotted at several SRs to obtain graphically the CR at a specified SR. For the test paint to pass, the CR at the specified SR must have a specified minimum value.

ISO (International Standardization Organization) Methods

ISO 2814, CR (CR) AT A NOMINAL SR (SR) OF 20 m^2/L ON BLACK-AND-WHITE CHARTS OR POLYESTER FILM

A paint film is applied with a 100-μm clearance applicator to give a nominal WFT of 50 μm, corresponding to a SR of 20 m^2/L. Black and white substrate reflectance are measured and the CR calculated without a determination of actual SR. Films cast on clear polyester film are measured, as described in Clear Plastic Film, by placing the film alternately on black and white glass. Because different paints and application techniques with the same applicator give films differing significantly in thickness, the method is satisfactory only as a rough guide for paints of the same type and color evaluated by one operator.

ISO 6504-1, KUBELKA-MUNK METHOD FOR WHITE AND LIGHT-COLORED PAINTS

This is in accordance with the general K-M HP method described in "General K-M HP Method" section. It calls for an all-black substrate, which can be glass or polyester film over black glass. The Mitton graph and table described in Mitton Graph and Table [27] are included, which makes it very similar to early versions of ASTM D2805.

ISO 6504-3, DETERMINATION OF CR (OPACITY) OF LIGHT-COLORED PAINTS AT A FIXED SR

This method is analogous to ISO 2814, but the SR is determined precisely by a weight-area-density procedure at several film thicknesses. Substrates are clear polyester film in Method A and black and white charts in Method B. The CRs and SRs are plotted graphically and the CR at 210 m^2/L is reported. The CIE-Y reflectance of the white substrate is specified to be 80 ± 2 %.

British Standards Institute, BSI 3900

Part D4. Comparison of CR of Paints of the Same Type and Color—This method is technically identical with ISO 2814 (11.c).

Part D6. CR at 20 m^2/L *Using Polyester Film*—This method is technically identical with ISO 3906-1980 (11.c).

Part D7. True HP (*SR at C* = 0.98) *by the Kubelka-Munk Method*—This method is technically identical with ISO 6504-1 (11.c) and in accordance with early versions of ASTM D2805 and the general K-M HP method described in "General K-M-HP Method" section.

Canadian General Standards Board, (CGSB) 1-GP-71

METHOD 14.1, VISUAL HIDING AT A SPECIFIED SR

The test substrates are black-and-white or black-and-gray checkerboard charts with an area of 0.1 m^2. The appropriate chart is specified according to a list of CGSB color numbers, with black-and-gray being used for lighter colors. The paint is applied by brush or drawdown. In brush application the SR is controlled accurately by weighing container and brush before and after application, with a specified volume being delivered to the chart surface by syringe. With drawdowns, presumably identical applications are made on glass and charts and the WFT determined on glass by means of an Interchemical (ASTM D1212) WFT gage. For the test paint to pass, the dry paint film is required to completely obscure the contrast pattern of the chart.

METHOD 14.2, SR DETERMINED AT FULL VISUAL HIDING (FOR QUICK-DRYING COATINGS)

Successive thin coats are applied by spraying onto black-and-gray or black-and-white charts until visual hiding of the dry film is complete. The SR is calculated from the difference in weight of the coated and uncoated chart. This can be expressed in m^2/kg of dry film or m^2/L of the original liquid coating.

METHOD 14.7, CR ON BLACK AND WHITE GLASS PANELS AT A GIVEN SR OR DRY FILM THICKNESS

This is modeled after the NYPC method described in "New York Paint Club (NYPC) Method." WFT is determined with an interchemical gage or DFT with a micrometer. The target film thickness is bracketed experimentally to obtain two points on a CR versus reciprocal film thickness graph and the CR at the target thickness determined by interpolation. The experimental CR values are corrected for $W = 0.80$ before plotting the graph.

French Standards Association (AFNOR)

NF-T30-075, SR AT A CR (CR) OF 0.98

Paint films are cast on clear polyester at several thicknesses and CR values are determined after drying by measuring reflectance over a black-and-white substrate. Dry films just below and above 0.98 in CR are measured by weight or micrometer to obtain experimental SRs in m^2/kg or m^2/L and results interpolated to obtain the SR at exactly CR = 0.98. The introductory text points out that this method measures true HP in preference to ISO methods that simply compare CR values at 20 m^2/L. It also refers to the experimental film thickness not being limited to 50 μm as in ISO methods. No provision is made in this method to correct for deviations of the white substrate from $W = 0.80$.

NF-T30-076, SR AT COMPLETE VISUAL HIDING

This is referred to as a "simplified" method. Several films are cast on polyester to obtain one that shows full hiding when placed over a black-and-white background. The DFT is measured by difference with a micrometer and the HP calculated in m^2/L. Potential users should consider whether this method, though simple in concept, might be excessively burdensome in execution.

German Standards Institute (DIN)

DIN 53162, HP OF AIR DRYING NONCHROMATIC PAINTS

This is a K-M method that is essentially the same as ISO 6504-1, but includes auxiliary test procedures for measuring paint density and nonvolatile content. The Mitton nomograph and table Mitton Graph and Table [27] are employed.

DIN 53164, RELATIVE SCATTERING POWER OF WHITE *(TiO_2)* PIGMENTS

This method measures the K-M scattering coefficient S of a TiO_2 pigment and reports its value as a percentage of the scattering coefficient of a reference pigment measured in the same way. The determination of S is based on the solution of Eq 44: $P = f(R_0, R_x)$ using the Mitton monograph. The method calls for the test pigment to be dispersed in an alkyd or a plasticized polyvinyl chloride vehicle. R_∞ is measured from a thick, full hiding film of the dispersion and R_0 from a nonopaque film applied on a black plastic substrate. The SR H_x of the pigment is determined in a unique way, by igniting a known area of film on plastic and weighing the residue. This method is basically the same as DIN 53162 and other K-M methods (General K-M HP Method), with the difference that only relative values are reported. There is no attempt to report actual scattering coefficients or to calculate HP in physical units, although this could easily be done on the basis of the accumulated data.

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Mass Color and Tinting Strength of Pigments

Joseph V. Koleske[1]

PREFACE

IN PREPARATION OF THIS CHAPTER, THE CON-tents of the Fourteenth Edition of this manual were drawn upon. The author acknowledges the author of the chapter in the Fourteenth Edition, Julio I. Aviles. The current edition will review and update the topics as addressed by the previous author, introduce new technology, and include up-to-date references.

INTRODUCTION

Color is a common but complex subject that can be described by perspective and in mathematical terms. As early as 1666, when he was 23, Isaac Newton developed his famous and useful "Newton color circle" that provided an understanding about additive color mixing and complementary colors. His experiments with prisms demonstrated that ordinary sunlight is made up of all wavelengths in the visible spectrum and thus all colors. Thomas Young,[2] an English physicist, in the early 1800s suggested that color perception is three-fold in nature, and he speculated that there were three kinds of nerve fibers or receptors in the eye's retina—something that was experimentally proven in 1959. These eye receptors are for long, middle, and short wavelengths that correspond to the primary colors of red, green, and blue (the RGB primaries) that had been useful in matching many visual colors by additive mixing. Later Hermann von Helmholtz put the qualitative analysis on a quantitative basis wherein three parameters are used to describe a color sensation—the well-known tristimulus values.

While James Maxwell was examining usage of the three primary colors in the 1860s, he found that no additive combination would cover the entire range of hues perceivable to the eye. It was found that the set of primary colors was not unique and that more widely wavelength-separated spectral primaries would produce a more complete range of perceived hues. In addition, with some subtractive combinations, the entire range of perceived colors could be included. Maxwell also demonstrated that the hue and saturation or chromaticity of a colored surface is in effect insensitive to brightness. His studies are considered the basis of modern colorimetry.

In the 1920s and early 1930s, experimental efforts by W. David Wright and John Guild pointed out that all colors within a particular range could be matched with the additive RGB primaries but not all spectral colors could be matched. The lack of matching was particularly true in the green portion of the range. However, if an amount of red wavelength light were added to the color being matched, all colors were possible. These quantitative studies were expressed in the modern terms of tristimulus values for the RGB primaries, but negative values had to be imposed for the red values so that all colors could be matched.

In 1931 the International Commission on Illuminations (CIE)[3] defined a color system in which all tristimulus values were positive and all visible colors could be represented by two color coordinates, x and y, that specify the color point on a chromaticity diagram. The third or Y parameter used in the CIE system for defining colors is a luminance parameter. This CIE system has some difficulties associated with it, and a new system was introduced in 1976. While the 1976 CIE standard removes the difficulties, it has not gained acceptance, and currently the 1931 CIE standard is the basis for almost all quantitative color measurements.

Basic tristimulus color measurement is usually carried out with either a colorimeter or a spectrophotometer. Tristimulus colorimeters are a combination of an illumination source, an array of filters, and a photoelectric output instrument. Measurements are comparative with the device standardized by using ceramic or glass standards that have colors similar to those of the materials to be measured. If precise measurements are needed, spectrophotometers that measure reflectance at each wavelength are used to determine the tristimulus values.

This brief passage into the history of color merely scratches the surface of color technology. Color and its management in paint and coatings are important from both an aesthetic and a practical or economic standpoint. It plays a role in our everyday lives and it affects our emotions and moods as we react to the colors around us. From an economic standpoint, it was well pointed out by Rich [1], who stated, "Getting the customer's color right the first time, whether it involves paint, coatings, or ink, is often the first and most crucial test of quality."

The tinting strength of pigments is often used as a guide for estimating relative hiding power of a pigment or paint to completely obliterate the background to which it has been applied. It may seem as if one is stating the

[1] *1513 Brentwood Road, Charleston, WV 25314.*

[2] Young is also the investigator who devised the concept of a modulus of elasticity that is known in mechanical properties as Young's modulus.

[3] The abbreviation CIE is taken from the French title for the commission, *Commission Internationale de l'Eclairage*. The address for the commission, which is an independent organization that was conceived in 1913, is International Commission on Illuminations, CIE Central Bureau, Kegelgasse 27, A-1030 Wien, Austria.

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obvious, but when light falls on a painted substrate, some of the light is reflected from the surface and the remainder enters the paint or coating film. The light that enters the film either emerges from the various faces, including the top face, or is absorbed. If all or most of the light is absorbed, the film appears dark in color or black, the coating effectively hides the substrate, and the pigment involved is said to have good tinting strength. The factors that have an effect on tinting strength and mass color include pigment refractive index, particle size, concentration, degree of dispersion, and inherent light-absorbing characteristics. Applied coating thickness also has an effect on this characteristic. It has been suggested to the author that most industrial colorists consider tinting strength as a "quality control measurement comparing a batch to a standard of the identical materials." The ASTM definitions of tinting strength are given in a following section dealing with definitions.

For both mass color and tinting strength, it is the final appearance or reflectivity (R_∞-value) of the opaque film that is of importance. In turn, reflectivity depends on pigment light-scattering and light-absorption characteristics and particularly with variation of these properties with wavelength(s) of the impinging light. In the case of mass color, the R_∞-value depends primarily on the relative quantity of each characteristic and secondarily on the absorption property of the vehicle. For tinting strength, reflectivity depends on the amount of each characteristic as related to the amount found in a standard paint or pigment.

Historical information about these parameters and early studies related to their development can be found in the literature, and they have been summarized by Mitton [2] and in a follow-up publication by Aviles [3]. A fairly recent publication by Völz [4] deals with color testing and includes chapters that deal with determination of tinting strength and related hiding power. An easy-to-read handbook concerned with color can be found on the Internet [5].

DEFINITIONS

Mass color is the color, when viewed by reflected light, of a pigment-vehicle mixture of such thickness as to obscure completely the background. Sometimes mass color is referred to as over-tone or mass-tone [6]. In a different ASTM publication [7], mass color is not listed, but mass-tone (note, no hyphen) is defined as "in paint technology, a pigment-vehicle mixture containing a single colorant only," but the discussion points out that "at times colorants are developed that contain more than one pigment, but are tested and used as if they contained only a single pigment. This definition is meant to include such colorants."

Mass color is produced by the reflected light, R_∞, of an opaque coating, and it depends on the pigment concentration, degree of dispersion, coating thickness, and the light absorption, K, and scattering, S, of pigments and binders. Mass color is applicable to both chromatic and achromatic pigments.

Tinting strength is a "measure of the effectiveness with which a unit quantity of a colorant alters the color of a material. For scattering and absorbing colorants, both scattering and absorption tinting strength must be specified" [7]. ASTM D16 [6] defines tinting strength as "the power of coloring a standard paint or pigment." ASTM E284 defines tinting strength as a "measure of the effectiveness with which unit quantity of a colorant alters the color of a material."

Other definitions that are of interest include the following [7]. The listing is by no means complete and it is given to help guide a reader/user to the terms used in the technology. In certain cases, designation symbols are listed to again provide guidance.

- Absorption is the transformation of radiant energy to a different form of energy by interaction with matter.
- Absorption tinting strength is the relative change in the absorption properties of a standard white material when a specified amount of an absorbing colorant, black or chromatic, is added to it.
- Achromatic (1) *for primary color sources,* the computed chromaticity of the equal-energy spectrum; (2) *for surface colors,* the color of a whitish light, serving as the illuminant, to which adaptation has taken place in the visual system of the observer; (3) the perception of having no hue, that is, as white, gray, or black.
- Brightness (1) is an aspect of visual perception whereby an area appears to emit more or less light or (2) brightness of an object is the combination of lightness and saturation. Different definitions of brightness are used in the textile industry, the paper industry, and by dyers.
- Chroma is an attribute of color used to indicate the degree of departure of the color from a neutral color of the same lightness. Munsell chroma is an attribute of color used in the Munsell color-order system to indicate the degree of departure of a color from a gray to the same Munsell value, in steps that are visually approximately equal in magnitude.
- Chromatic describes the perception of something having a hue; not white, gray, or black.
- Chromaticity Diagram is a plane diagram in which points specified by chromaticity coordinates represent the chromaticities of lights (color stimuli).
- CIE is an abbreviation for the French title of the International Commission on Illumination, *Commissione Internationale de l'Eclairage.*
- CIE 1931 standard colorimetric system is a system for determining the tristimulus values of any spectral power distribution using the set of reference color stimuli X, Y, Z and the three CIE color-matching functions $x(\lambda)$, $y(\lambda)$, and $z(\lambda)$ adopted by the CIE in 1931.
- Colour Index International is a listing of colors by name and number by the Society of Dyers and Colourists and American Association of Textile Chemists and Colorists [8].
- Hue is the attribute of color perception by means of which a color is judged to be red, orange, yellow, green, blue, purple, or intermediate between adjacent pairs of these, considered in a closed ring (red and purple being an adjacent pair). Neutral colors are judged to have no "hue." Munsell hue is an attribute of color used in the Munsell color-order system to indicate the hue of a specimen viewed in daylight.
- Lightness is (1) the attribute of color perception by which a non-self-luminous body is judged to reflect more or less light; (2) the attribute by which a perceived color is judged to be equivalent to one of a series of grays ranging from black to white.
- Luminance is the luminous flux in a beam, emanating from a surface, or falling on a surface, in a given

direction, per unit of projected area of the surface as viewed from that direction, per unit solid angle.

- Munsell Color System was developed just before the end of the nineteenth century by A. Munsell, an American artist. The system is depicted as a globe with a band of colors running equatorially and an axis of gray values wherein white is the North Pole and black is the South Pole. At each gray value, there is a change in color that gradually ranges from full saturation to neutral gray, and in this manner a myriad of colors could be described by their hue, chroma, and value.
- Saturation is the attribute of a visual sensation that permits a judgment to be made of the proportion of pure chromatic color in the total sensation.
- Scattering is the process by which light or other electromagnetic radiant flux passing through matter is redirected over a range of angles.
- Scattering tinting strength is the relative change in the scattering properties of a standard black material (with no scattering colorant present) when a specified amount of a white or chromatic scattering colorant is added to it.
- Shade is (1) a color produced by a dye or pigment mixture including black dye or pigment; (2) an expression of color difference from a reference dyeing such that another dye must be added to produce a match; and (3) a color slightly different from a reference color. Shade is related to "tint."
- Tint is a color produced by the mixture of white pigment or paint with a chromatic pigment or paint. When used as a verb, "tint" means to adjust the color of a test specimen to be a closer color match to the standard. Also see "Shade" above.
- Tristimulus values are the amount of three specified stimuli required to match a color. In the CIE system, these three stimuli are assigned the symbols X, Y, and Z.

TINTING STRENGTH

As mentioned above, tinting strength is a measure of the effectiveness with which a unit quantity of a colorant changes the color of a material. One may think of it as a pigment's "coloring power." For colorants that both absorb and scatter light, scattering and absorption tinting strengths must be specified. Scattering tinting strength is the relative change in scattering properties of a standard black material that has no scattering colorant present when a specified amount of white or chromatic scattering colorant is added to it. Absorption tinting strength is the relative change in absorption properties of a standard white material when a specified amount of an absorbing colorant, black or chromatic, is added to it.

Since pigment concentration is important to coating strength and cost, tinting strength is an important economic factor when selecting one paint over another. There is no particular value of tinting strength that can be stated as desirable unless an end use is stated. In certain cases, a high value is desirable and in other cases a low value is required to achieve a desired color/strength effect. Pigments each have a different ability to vary the color of a mixture. When economy is a factor in paint formulation, stronger tinting strength is desirable. Some colors, such as phthalocyanine blue, are very strong in their tinting strength whereas other colorants can be relatively weak. Tinting strength increases as pigment particle size decreases with synthetic organic pigments generally having greater tinting strength than mineral pigments.

In a general sense, tinting strength is determined by dilution of a test paint and a reference paint with a standard "mixing white paint" in the case of chromatic paints or a standard "tinting color" in the case of white paints. These diluted pastes are then drawn down on a suitable substrate, and then either instrumentally measuring tristimulus values or visually comparing the specimens. As would be expected, the visual comparison technique has lower precision than the instrumental method. Details for preparation of standard white paints are described [9] or a commercial titanium dioxide-white artists' paint may be used as the standard. It should be understood that the mixing white paint must be made with the same vehicle chemical type—acrylic, alkyd, or oil—as the paint to be tested.

When color tints are considered, differences in gloss and haze can be mistaken for a lighter tint or lower tinting strength than really exists. In grays, these factors may be interpreted as higher white pigment strength than exists. Instruments cannot compensate for specular gloss or haze differences between a sample and a standard, and this can result in erroneous tint strengths. It is possible to equalize gloss differences between specimens by top coating them with a clear coating. Evaluation through the clear coating reveals the true tinting strength differences between sample and standard.

Tinting strength results can also be affected if the lightness, chroma, and saturation of the sample differ significantly from those of the standard, since the measurements involve matching two color variables—either lightness and chroma or lightness and saturation—by adjusting only the amount of pigment used [10,11].

Chromatic Paints

ASTM D4838 [12] is a method used for determining the absorption tinting strength of a chromatic test paint relative to that of a standard or reference paint of the same chemical type. The procedures in this method are based on dilution of paints with a standard mixing white paint followed by instrumental measurement and calculation. Provision is made for correcting the results for small differences in hue or chroma (or both) between the test and reference chromatic paints. The method is meant for comparison of paints that contain the same chemical type vehicle (acrylic, alkyd, or oil) and single-pigment colorants of the same Colour Index name and number. It is unnecessary to have information about the amounts of pigments or other components in the paint.

The color-measuring instrument can be either a spectrophotometer that provides 1931 CIE tristimulus values, X, Y, and Z for CIE standard illuminant C or a tristimulus colorimeter providing either such tristimulus values or colorimeter readings R, G, and B. Other test methods or practices useful in following the results of this test method can be found in the literature [13–15]. ASTM E1347 [16] deals with a test method for the use of a tristimulus colorimeter to evaluate specimens and provide color coordinate and color difference values. The device is also known as a tristimulus filter colorimeter or a color-difference meter.

ASTM D387 is used to compare the color and strength of a pigment that is being tested with a reference standard of the same type and grade [17]. The method specifically points out that it does not apply to white pigments. The pigments are dispersed in a suitable vehicle with a mechanical muller. Opaque drawdowns are made on white paper charts that have a black band and a surface that is impervious to paint liquids. These drawdowns are compared either visually or instrumentally for color and strength differences. ASTM D3022 is similar to this method, but it utilizes a miniature sandmill rather than a mechanical muller to disperse the color pigment [18].

ASTM D2066 is a related test method that is applicable to the relative tinting strength of paste-type printing ink dispersions [19] and is similar in nature to other referenced ASTM test methods [12, 17]. The strength may be determined by instrumental or visual observation of manually or automated mixed tints. The methods are applicable to paste-type printing inks, flushed pigments, and other pigment dispersions that are essentially nonvolatile under ordinary room conditions and for which there is a wet reference standard of the same pigmentation and consistency. If the proper choice of tinting base is used, the methods are applicable to dispersions of any color, including black and white.

White Paints

ASTM D2745 is a standard method for determination of the relative tinting strength of white pigments by reflectance measurements made on black tints [20]. It is only applicable for comparing the test pigment with a reference standard of the same type and grade. The method is carried out by dispersing the pigment in an agreed-on, solvent-free vehicle and then letting it down with additional vehicle that has been tinted with a lampblack that has been predispersed in a vehicle similar in nature to the test vehicle. Refined or low-bodied linseed oil should not be used with this procedure. Both dispersion and let-down are done with an automatic, mechanical muller. Tristimulus values are determined with a colorimeter.

ASTM D332 is a test method for determination of the relative tinting strength of white pigments by visual assessment of blue tints [21]. It is only applicable for comparing a test pigment with a reference standard of the same type and grade. The test is conducted by dispersing specified amounts of a white pigment and a blue tinting pigment that conforms to specifications [22] in a refined linseed oil with an acid number of about 4 using a glass, hand muller, or an automatic muller. The pastes are drawn down on a specified panel and visually evaluated for tinting strength. A numerical rating of tinting strength is obtained by preparing dispersions with the standard white pigment and more or less of the tinting pigment. These are compared until the lightness of the test paste is matched. The weight of the tinting pigment is used to calculate the relative tinting strength.

PIGMENT DISPERSION

Tinting strength and mass color require that pigments be well dispersed in the binder to achieve maximum tinting strength. Ideally, it would be desirable to break down pigment agglomerates into the smallest possible individual particles, i.e., to an ultimate dispersion state. The smaller the particle size the greater the surface area of a given weight or mass of pigment. This then results in more intense color production in the same volume of liquid. However, an ultimate dispersion state is impractical and effectively impossible to achieve. Therefore, pigments under investigation for these properties must be processed in the same manner and receive the same level of mechanical work. Mechanical mullers, which are instruments that have two circular, usually ground-glass grinding surfaces that contain the pigment and vehicle, are used to disperse the two components. A variety of these devices are commercially available. Development of tinting strength is dependent on the force applied to the glass plates, the number of revolutions used, and the mass of pigment and vehicle used. If muller conditions, pigment, and vehicle have not been agreed on by purchaser and seller, the mandatory dispersing conditions given in the Annex of ASTM 387 should be used to attain a consistent level of tinting strength [17]. These conditions include:

- Determination of the appropriate ratio of color pigment to dispersing vehicle for the standard and test pigments.
- Determination of appropriate masses of pigment and vehicle to use.
- Preparation of a standard tint by application of 100 lbf (N) to the muller plates, introducing the appropriate mass of pigment/vehicle, and mulling the paste for 100 revolutions in two stages of 50 revolutions each. This is then repeated on three more specimens of the standard mixture except the mulling is carried out for 200, 300, and 400 revolutions in stages of 50 revolutions.
- Each of the four specimens is compared one to the other for tinting strength and the minimum number of revolutions needed to develop maximum or full tinting strength is ascertained.

The parameters and dispersing conditions used for three pigments that were investigated in an interlaboratory test to determine the precision of this standard method are given in Table 1.

TABLE 1—Interlaboratory pigment dispersing parameters and specific conditions obtained for maximum tinting strength [17]

	Pigment Type		
Parameter	**Yellow Iron Oxide**	**BON Red**	**Phthalocyanine Green**
Force applied, lbf (N)	100 (440)	100 (440)	100 (440)
Total No. revolutions	100 (2 × 50)	200 (4 × 50)	400 (8 × 50)
Mass of color pigment, g	1.0	0.6	0.75
Mass of dispersing vehicle, g	1.7	1.4	1.8

PIGMENT DISPERSION TECHNIQUES

It should be kept in mind that the techniques described in this chapter pertain to preparing specimens for determination of tinting strength and mass color, and they are not meant for pigment dispersion in general. The general topic of pigment dispersion is discussed elsewhere in this manual as well as in a variety of references [23–31]. There is a vast amount of literature that deals with the surface treatment of organic pigments to improve ease of dispersibility, and interested readers are encouraged to seek such information in the classic work of Hayes [32], the above listed references, and others [33–35]. Detail regarding the surface treatment of inorganic pigments is also in the literature [36–38].

Spatula and Hand Mullers

Grinding pigment/vehicle combinations can be carried out with a spatula or a hand muller[4] by rubbing or mulling the materials over a 3 × 12 in. (8 × 30 cm) strip area on a glass plate. The rubbing is done by pushing the muller up one side and pulling it down the other side of the strip area so that all color particles receive the same amount of rubbing. One rub is one up and down course on the strip area. Early studies by Ayers [39] indicated that the muller gave more reliable results than a spatula and that the rubbing surface may vary a great deal without affecting the results. Stutz's [40] results during investigation of the tinting strength of white pigments also found a muller was superior to a spatula. It was also found that a weighted or un-weighted muller could be used without affecting the results.

Automatic Mullers

Automatic[5] or mechanical mullers have two circular glass grinding surfaces that contain the pigment/vehicle mixture. The grinding surfaces are usually constructed of ground glass with one surface stationary and weighted to exert a pressure of 100 psi (440 N) and the other surface rotary with rotation effected with a motor. Because rotation is about the diskcenters, paste located at the center can receive less mulling than paste located near the edges. To compensate for this effect, it has been found helpful to spread the paste in a ring approximately halfway between the edge and the center. The revolutions per mulling cycle can be adjusted in increments of 1 to 999. Mechanical muller advantages include very good development of tinting strength, the possibility to rapidly mull small quantities of materials, and efficient processing of a large number of samples. The specific way to operate a mechanical muller when determining tinting strength or mass color can be found in the annex to Ref. [17].

LABORATORY MINIATURE MEDIA MILLS

Commercial horizontal or vertical laboratory media mills that can process up to one quart of millbase are available. In a general sense, media can be nonferrous or ferrous as, for example, flint pebbles, sand, ceramic alumina, porcelain, stainless steel, high carbon steel spheres, etc. but for test grinds, specified media must be used. For small grinds, a media mill can be simulated with a laboratory dispenser equipped with a fiber or Telfon 1 5/8 in. disk, a 200 mL tall-form beaker, and media. Equal volumes of millbase to media are used. Grinds may be 60.0 g for carbon black and some organic pigments to 160.0 g for inorganic pigments. The millbase must be carefully prepared to eliminate gross and oversized agglomerates. Peripheral impeller speed should be 2000 feet (610 m) per minute, and the mixture should be ground for a set time or to a set dispersion level such as a Hegman value of 7.0+. Advantages of media mills include development of the highest tinting strength and mass color, simulation of actual factory grinding conditions, and low cost.

LABORATORY ROLLER MILL

Small, three-roller mills have been found useful for grinding small, laboratory-size batches of paint. Rolls of such mills are about 4 in. (10.16 cm) in diameter and 8 in. (20.82 cm) in length. Batches as small as 5 g have been prepared in such mills.

PALL GLASS MILL

Small quantities of metal-free pigment paste can be prepared with the Pall Glass Mill [41]. The mill is a heavy ground-glass stopper in a heavy glass joint. The mixed, un-ground materials (1–8 g) are placed in the joint and the stopper/plunger is inserted. The stopper is rotated with a small motor at about 150 rpm. In this mill grinding pressure ranges from 20 to 30 psi. The Pall Glass Mill is said to be an improvement over hand mulling because it saves time and because it results in greater development of tinting strength.

PIGMENT CONCENTRATION

Paste viscosity has an effect on grinding efficiency, and it is a property that determines the level of tinting strength and mass color that is developed. Ayers [39] investigated iron oxides, and his results indicated that color developed faster as paste viscosity increased. A low-viscosity paste had a reflectance of 26 % at a wavelength of 700 nm, whereas a high-viscosity paste was darker and redder with a reflectance of 23 %. It should be pointed out that there is a point above which viscosity has no effect on grinding efficiency.

MIXING TIME OF LIQUID COLORS

An important property of oil or universal liquid colorants is the ease with which they can be incorporated into white paints. A method for testing the speed of incorporation of such colorants has been described by Paul and Diehlman [42]. Their method involves use of a mechanical rotating bottle that contains a white paint, the liquid colorant, and a grinding media. When the test was first developed, No. 11 lead shot was used as the media; however, today glass beads, zirconia grinding media, and steel shot are among the media used to avoid lead contamination of the paint.

The test is conducted by charging the bottle with 550 g of grinding media, 2 mL of the liquid colorant, and 75 mL of white paint. The bottle is then closed with a cork that is concave on the inner end to match the glass end of the bottle and placed in the holder of the rotating device. The

[4] Hand mullers are implements made of a hard substance such as glass, stone, or similar material and used as a pestle to grind pigment/vehicle (i.e., paint) combinations. These are seldom, if at all, used today.

[5] Automatic in this area of technology means "motor driven."

TABLE 2—Related ASTM Documents

ASTM Designation	Title
D282	Methods of Test for Mass Color and Tinting Strength of Pigments (withdrawn[a])
D2244	Practice for Calculation of Color Tolerances and Color Differences from Instrumentally Measured Color Coordinates
D3265	Standard Test Method for Carbon Black-Tint Strength
D5326	Standard Test Method for Color Development in Tinted Latex Paints
D6531	Standard Test Method for Relative Tinting Strength of Aqueous Ink Systems by Instrumental Measurement
E179	Guide for Selection of Geometric Conditions for Measurement of Reflection and Transmission Properties of Materials
E284	Terminology of Appearance
E805	Standard Practice for Identification of Instrumental Methods of Color or Color-Difference Measurement of Materials
E1164	Practice for Obtaining Spectrometric Data for Object Color Evaluation
E1345	Practice for Reducing the Effect of Variability of Color Measurement by Use of Multiple Measurements
E1347	Standard Test Method for Color and Color Difference Measurement by Tristimulus Colorimetry

[a] This particular method was withdrawn in 1929 and has not been replaced. It will not be found in ASTM's listing of standards. It is included for historical purposes.

bottle is then tilted and rotated slightly by hand to wet the container walls.

This is followed by mechanical rotation of the bottle until the paint is homogeneous in that no streaking of the color is seen. The time in seconds for mixing is determined and recorded.

OTHER RELATED TEST PROCEDURES

While the various test procedures cited above each contain reference to a number of ASTM documents, it is worthwhile to list some of these. Table 2 is a partial listing of such potentially useful documents.

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Part 11: Physical and Mechanical Properties

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Adhesion

Gordon L. Nelson[1]

PREFACE

IN PREPARATION OF THIS CHAPTER, THE CONTENTS of the fourteenth edition were drawn upon. The current edition will review and update the topics as previously addressed, introduce new technology that has been developed, and include additional references.

INTRODUCTION

Organic coatings are applied to a variety of substrate materials (woods, metals, plastics, ceramics) for decorative, protective, and functional applications. In each case, it is imperative that the coating adheres well to the substrate. Accordingly, adhesion assessments should be an integral part of the coating development. This may seem a straightforward task, but coating adhesion is, in fact, extremely complex and often poorly understood. The growing use of plastics to replace metals and other "traditional" materials renders the issue even more complex [1,2].

The objectives of this chapter are to briefly review salient concepts of the adhesion process and to discuss currently accepted standard test methods.

FUNDAMENTAL CONCEPTS

While the very definition of "adhesion" is of some controversy [1], adhesion may be loosely defined as the attraction between dissimilar bodies for one another. ASTM D907 on Terminology of Adhesives defines adhesion as "the state in which two surfaces are held together by interfacial forces which may consist of valence forces or interlocking action or both." In discussing adhesion assessment, one may consider the issue from two different aspects: *basic* adhesion and *practical* adhesion. Basic adhesion signifies the summation of all interfacial, intermolecular forces, whereas practical adhesion is used to represent the forces or work required to disrupt the adhering system [3]. The next section will be devoted to theories and concepts of basic adhesion and will out of necessity be brief. The perspective will be from that of a polymeric coating on a plastic substrate [2]. Metal and metal oxide substrates will be discussed where appropriate. The reader is referred to Refs. [4–7] for a more thorough discussion.

BASIC ADHESION

Work of Adhesion

Bonding between polymeric coatings and substrates may be viewed as the union of two contiguous polymer phases, one a solid and the other a liquid that solidifies to form a thin film. The reversible separation of the two phases may be expressed by the work of adhesion

$$W_a = Y_1 + Y_2 - Y_{12} \tag{1}$$

where W_a is the work of adhesion, and Y_1 and Y_2 are the surface tensions of the two phases. The maximum force per unit area, σ^2, to effect this process is the ideal adhesive strength [8]

$$\sigma^2 = [16 / 9(3)^{12}](W_a / Z_0) \tag{2}$$

where Z_0 is the equilibrium separation between the two phases, usually about 5 Å. The average value W_a for polymers is typically 50 ergs/cm^2, yielding a theoretical value for σ^2 of 15 000 psi (103 mPa). For practical purposes this value is never attained, primarily due to the fact that perfect inter-molecular contact is most unlikely. In fact, this is at least an order of magnitude higher than the practical adhesive strength usually observed. This deviation from ideality has led to the promulgation of several theories of adhesion, none of which are universally recognized [9]. This is not unexpected, since most theories deal exclusively with the mechanisms of bond formation and disregard the fact that bond strength is ultimately a function of both the degree of bond formation, the nature of the bond (chemical and physical), and the rheological properties of the bonding phases. The strength of an adhesive bond is, in fact, a function of all of these factors. Summary paragraphs about basic theories of adhesion follow below.

Fracture Theory

The area of interfacial bonding between coating and substrate will, in most instances, contain voids or defects. The result is deviation between the ideal adhesive strength and the practical limit.

Good [10] and Williams [11] have applied the theory of cohesive fracture to coating fracture. The concept that fracture propagates from the weakest point, a defect, is fundamental to fracture mechanics. The strength of a bond, in terms of the energy required to induce fracture, is described as a function of the defect size and the energy dissipated by irreversible processes (plastic deformation, light emission, and electric discharge). The general equation given is

$$f = k(EF/d)^{1/2} \tag{3}$$

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where f is the fracture stress, $k = (4/\pi)^{1/2}$, E the elastic modulus of the material, d the defect length, and F the fracture energy or total work per unit area of fracture surface, which is dissipated. Accordingly, the fracture energy

$$f = W_a + W_i \tag{4}$$

where W_a is the work of adhesion and W_i is the total work for the irreversible processes. For all practical purposes W_i is much greater than W_a therefore [12,13]

$$f = W_i \tag{5}$$

Weak Boundary Layer Theory

Proposed by several workers [14–16], the weak boundary layer theory maintains that true interfacial fracture does not occur, and that fracture usually occurs *cohesively* in a weak boundary layer, which may be near the interface between coating and substrate. Experimental evidence has perhaps disproved the first point [10], that true interfacial failure can occur, but it has been shown that the second is valid in some instances [17,18].

Of practical importance to WBL investigations is the locus of fracture, which can occur in one or more of the zones in Fig. 1. For a strong bond, the boundary layer (layers) must be rheologically sound and chemically durable. The zone of failure may, of course, be studied by scanning electron microscopy (SEM), transmission electron microscopy, and Fourier transform-infrared [19]. In fact, thin layers of coating have been noted where interfacial failure was only thought to occur on visual examination.

Wetting-Contact Theory

The wetting-contact theory states that van der Waals attractive forces alone provide sufficient coating/substrate bond strength given perfect molecular contact, and that the extent of contact and resulting bond strength are functions of wetting energetics [20–28]. No one denies the importance of wetting in adhesion, i.e., the lower the contact angles, the more the interfacial area of contact, which generally yields improved adhesion (Fig. 2).

However, thermodynamic wetting is a necessary but not sufficient condition for the establishment of coating film adhesion. Wetting is a kinetic phenomenon as well. Furthermore, this model does not consider the effects of weak boundary layers or the effects of defects or fracture mechanics. What is the effect of surface contamination on the contact angle?

For guidance on the measurement of contact angle, see ASTM D7334 (WK11928) Standard Practice for Surface Wettability of Coatings, Substrates and Pigments by Advancing Contact Angle Management.

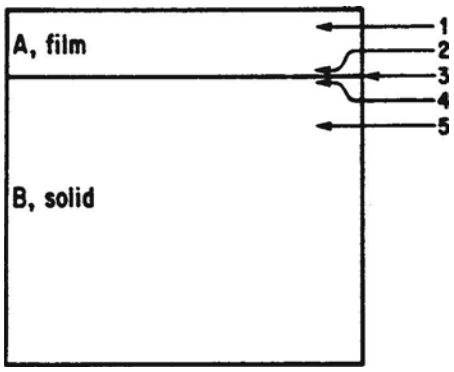

Fig. 1—Weak boundary layer theory. Possible zones of failure (after Good [19]).

Diffusion Theory

Voyutskii and others [29–33] have proposed that coating adhesion between high polymers arises from interdiffusion. This has been validated somewhat by the observation that adhesive strength is a function of polymer molecular weight, structure, and contact time.

Key to this theory is the concept that no clear-cut inter-facial boundary exists, but rather that an interphase exists which consists of polymer chain segments from both contiguous phases. The theory has been criticized for giving insufficient weight to the contribution of van der Waals attractive forces. Nevertheless, for the case of solvent-borne organic coatings applied to plastic substrates, this phenomenon is intuitively appealing.

Interdiffusion of coating and substrate polymer molecular segments is a function of polymer-polymer compatibility. An interphase forms as a result of the blending of the two phases. Although polymer pairs are generally incompatible, Helfand and others [34–38] have utilized statistical thermodynamics to predict that interdiffusion also occurs as a result of the tendency for free energy at the interface to minimize. A useful equation that describes interfacial thickness as a function of the Flory–Huggins interaction parameter as derived from Hansen solubility parameters is [36,38]

$$a_i = 2(m/\mathrm{x})^{1/2} \tag{6}$$

where a_i is the interfacial thickness expressed as the cross-sectional area of a lattice cell, m is a lattice constant directly proportional to nearest-neighbor contacts, and x is the Flory–Huggins interaction parameter. By this equation, interfacial thickness increases by interdiffusion as the solubility parameter difference between the two phases decreases. Although experimental verification is scarce, adhesive strength has been shown to decrease with increasing disparity in the solubility parameters of the two phases [39].

It is important to note that diffusion should occur in the latter stage of bond formation, the first stage being wetting to establish contact. Additional support for the theory comes from the observation that adhesive strength between certain high polymers increases with time [30]. This theory, however, cannot be applicable to systems involving one or more hard solids (metals, glass, or metal oxides).

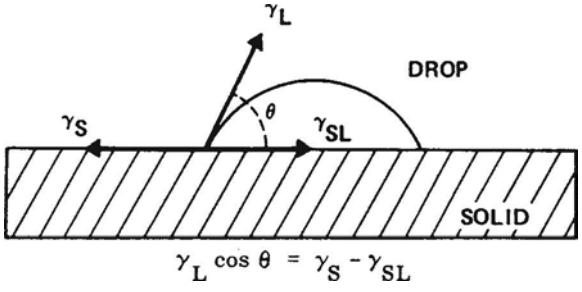

Fig. 2—Contact angle.

Chemical Adhesion

The bond strength of covalent bonds is 1 to 2 orders of magnitude greater than van der Waals attractive forces. There have been numerous applications where interfacial chemical bonds have been employed to promote adhesion. Dramatic increases in bond strength have been reported [40].

Coupling agents such as chrome complexes [41], silanes [42], and titanates [43] have been used effectively, Organic functionalities, including isoeyanates, carboxyls, amides, amines, hydroxyls, and epoxides [43,44], have been reacted interfacially to enhance adhesion.

Adhesive strength has been shown to increase with functional group concentration as expressed by

$$f = kC^n \tag{7}$$

where f is the adhesive strength, C the functional group concentration, and k and n are positive constants [45]. There, however, appears to be an upper limit for functional group concentration above which adhesion may tend to decrease [46,47].

Mechanical Adhesion

In mechanical adhesion substrate roughness is thought to provide a mechanical locking of the coating to the substrate. However, if there is not intimate contact between the coating and the substrate, then increased roughness should lead to a *decrease* in adhesion by producing uncoated voids. In the practical application of electroless metals on polymer substrates, etchants are used that create deep channels, increasing adhesion. Other examples are anchor coats for polytetra fluoroethylene, adhesion to porous anodic films on aluminum, and hot melt polyolefin coatings on metals. Mechanical adhesion is also important for porous substrates such as wood, cloth, and paper. Since good adhesion can be obtained on smooth surfaces such as glass, questions can be raised about the general validity of the mechanical adhesion mechanism. It should also be noted that mechanical abrasive treatment of a solid surface may also yield macroradicals and active secondary chemical products, which if they do not come into contact with atmospheric oxygen, may interact with components of the coating. This has been shown for certain adhesives. Active radicals or functionality would yield adhesion, better described as mechanico-chemical adhesion than just mechanical [7,48,49].

Electrostatic Adhesion

In the theory of electrostatic adhesion, when two dissimilar materials are brought into contact, a charge transfer takes place, which results in the formation of an electrical double layer, much like a capacitor. Work would then be required to separate the two charged layers. This is thought to be particularly applicable to metal-polymer bonds. Indeed, ionizing discharge has been shown to affect a copper to acrylic bond but not copper on salt (NaCl) or glass. This theory would not be applicable to two nonpolymer systems [49,50].

Acid-Base Adhesion

In the acid-base adhesion theory, it is said that the strength of the adhesive bonds is increased significantly by acid base interactions between coating and substrate. Appropriate modification of surface acidity or basicity of the substrate should increase adhesion. Modification of surface acidity or basicity of inorganic solids can increase mechanical properties (modulus, extension to break, and toughness) of coatings on these substrates. It has also been claimed that the reverse is true, however [51,52].

Combination of Phenomena

The preceding theories interpret adhesion in terms of single phenomena, each of which undoubtedly plays some role in interfacial bonding between coating and substrate. One should be cautioned, however, against exclusive use of a single theory to explain the adhesion of a given system. A more logical approach has been proposed by Allen [53].

$$\psi = a\psi_A + b\psi_B + c\psi_C + \ldots \tag{8}$$

which suggests that a combination of phenomena is more realistic, that is, that basic adhesion is the summation of all interatomic or intermolecular interactions at the interface. One would think that systematic studies could be made to assess the contribution of a given variable to the adhesion process, with the others being held constant. This would reveal useful information as to factors critical to coating adhesion for a particular system. Unfortunately, being able to accomplish that task is questionable given that adhesion assessment not only involves factors of basic adhesion but variation in application of the applied external stress (tensile, shear, or peel) and many other factors.

It can be concluded that adhesion is an interfacial phenomenon in which both physical and chemical forces operate when surfaces develop to form an interface. Adhesive strength is a measure of the degree to which the two surfaces are attracted. This is a function of wettability, relative surface energetics of both phases, and of the kinetics of wetting. For integrity of a bond at the interface between a coating and a substrate, one needs to consider the following factors:

1. Thermodynamics and kinetics of the formation of the bond.
2. The forces acting near the interface in both the coating and the substrate.
3. The cohesive forces within the coating layer.
4. Internal stresses in the coating layer.
5. The behavior of the coating layer under stress.

To understand basic adhesion one must understand the surface chemistry, surface physics, surface architecture, coating polymer chemistry and physics, polymer rheology, coating internal stresses, fracture mechanics, and effects of changes in the environment. In fact, it has been noted that spontaneous loss of adhesion can occur due solely to internal strain of the coating [54–56].

Effects of Substrates

ADDITIONAL CHEMISTRY

The adhesion of organic coatings to metals is at a high level of development in the practical sense. The contribution of surface energy, chemical functionality, surface irregularities, and contaminants (oxides, adsorbed water, etc.) have been identified.

On the other hand, coating adhesion to plastic substrates has presented additional complexities. Polymer

surfaces are often more difficult to wet and bond because of low surface energy, incompatibility, chemical inertness, or the presence of contaminants (oils, lubricants, plasticizers, etc.), and weak boundary layers. Surface modification techniques have been developed to enhance adhesion. In the absence of surface preparation, coating adhesion is felt to be a function primarily of van der Waals and/or polar-dipolar attractive forces, mechanical adhesion (from surface irregularities), and interdiffusion. This latter contribution to adhesion has been studied using SEM. In Fig. 3 is presented a scanning electron micrograph of a thermoplastic acrylic coating applied to modified polyphenylene oxide (a blend of PPO and polystyrene), an important engineering thermoplastic. The first coating contains 60 % of the recommended amount of solvent. The interface formed is sharp and well-defined. In this instance, adhesion appears to be due largely to mechanical and attractive forces. Fig. 4 shows the same substrate and coating, which in this case contains 100 % of the recommended amount of solvent. The sharp interface seen in Fig. 3 is no longer present, an intermediate zone or interphase having formed in its place. Diffuse interface formation of this magnitude is undoubtedly unique to coatings applied to plastics. Bond strength will be a function of formulation, solvent content, and drying time [2].

Organic coatings are complex formulations, thus, the polymer chemistry at the developing coating substrate interface will clearly be impacted by the solid surface, whether plastic, metal, or inorganic, that is, the polymer interface may be somewhat different than the bulk coating (i.e., a boundary layer). Fully developed coatings may also be porous or permeable, thus aging and weathering may impact adhesion, as water, oxygen, and other agents penetrate to the polymer coating solid interface [7,57]. Indeed, some coatings that have acceptable adhesion while dry may fail badly when tested under high humidity or after immersion in water for several hours.

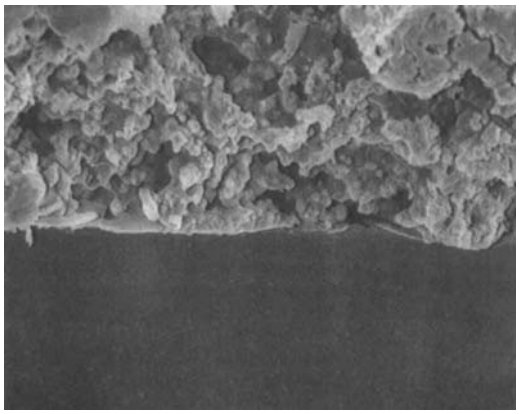

Fig. 3—SEM of sharp interface.

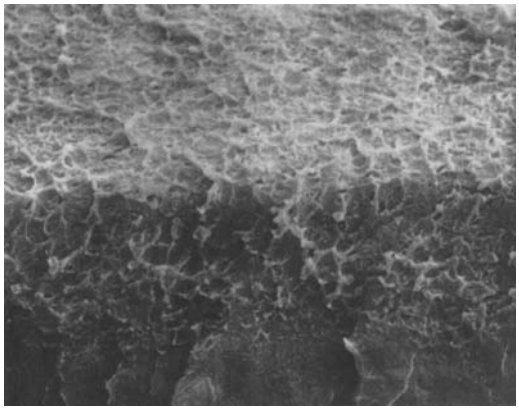

Fig. 4—SEM of diffuse interface.

It has been shown for polyolefin-metal adhesion that oxidation of the polymer attached to the surface occurs through action of oxygen absorbed by the metal and the polymer. The appearance of oxygen-containing groups in the otherwise inert polymer should promote an increase in the extent of interaction with the metal. Adhesion in this case would also be increased by oxygen donor fillers [7,57].

All metals (except gold) are known to exist with an oxide film on their surfaces. The volume of oxide formed may be smaller than the metal reacted, and consequently the oxide film is porous and nonprotective (alkali and alkaline earth metals) or the volume may be larger and therefore protective (transition metals and aluminum). However, in the latter case, migration of metal cations from the surface leaves vacancies, which aggregate to form cavities. Treatment of a metal before coating to produce a preferred or controlled bonding surface is therefore common [7,57]. From the above discussion, it is clear that chemical interaction between coating and solid can occur even when not recognized or anticipated.

Finally, a change in substrate may impact adhesion. Weathering failures such as blistering and scab corrosion are often regarded as adhesion failures by coatings development chemists. Delamination of coatings in the absence of substrate corrosion can also be produced by weathering. A common problem involves the interfacial chalking of an epoxy primer and a topcoat that has a high UV light transmission. In the presence of UV light, moisture, and oxygen, the epoxy primer is degraded at the interface between the primer and topcoat, leading to delamination of the topcoat from the primer.

Delamination of clear or semitransparent exterior wood coatings can also occur by UV, water, and oxygen attacking the wood substrate. Delamination of the intact coating results when the wood substrate coating interface is destroyed. The solution to this problem is to add organic and inorganic UV absorbers to the coating to protect the wood substrate from degradation.

PRACTICAL ADHESION

Given the complexities of the adhesion process, can adhesion be measured? As Mittal [3] has pointed out, the answer is both "yes" and "no." It is reasonable to state that at the present time no test exists that can precisely assess the actual physical strength of an adhesive bond. But it can also be said that it is possible to obtain an indication of relative adhesion performance.

Practical adhesion test methods are generally of two types: *implied* and *direct*. Implied type tests include indentation or scribe techniques, rub testing, and wear testing. Criticism of these tests arises when they are used to quantify the strength of adhesive bonding. But this, in fact, is not their purpose. An implied test should be used to assess coating performance under actual service conditions. Direct measurements, on the other hand, are intended expressly

to measure adhesion. Peel, lap-shear, and direct tensile are common examples. Meaningful tests of this type are highly sought after, primarily because the results are expressed by a single discrete quantity, the force required to fracture the coating/substrate bond under prescribed conditions [2].

Test Methods

In practice, a battery of tests is used to evaluate adhesion by inducing bond rupture by different modes. Criteria deemed essential for a test to warrant large-scale acceptance are: use of a straightforward and unambiguous procedure, relevance to its intended application, reproducibility, and quantifiability, including a meaningful rating scale for assessing performance. Test methods used for coatings on metals are peel adhesion or "tape testing," Gardner impact flexibility testing, and adhesive joint testing including shear (lap joint) and direct tensile (butt joint) testing. These tests do not, in fact, strictly meet the criteria listed, but an appealing aspect of the above tests is that in most cases the equipment/instrumentation is readily available or can be obtained at reasonable cost [2].

A wide diversity of test methods has been developed over the years. In this chapter only selected test methods developed through the consensus process will be discussed in detail. The reader should recognize, however, that numerous test methods have been developed that measure aspects of adhesion [7,58–61] and that there generally is difficulty in relating these to basic adhesion phenomena (Fig. 4).

The Tape Test

By far the most used test to access coating "adhesion" is the peel test. In use since the 1930s, in its simplest version, a piece of adhesive tape is pressed against the paint film. The test consists of observing whether the film is peeled off when the tape is removed. The method can be refined to measure the force required for film removal. In other tests, crosses or a cross-hatched pattern are cut into the coating, a tape applied and removed, and the coating removal assessed against an established rating scale. The current widely used version was first published in 1974 as ASTM D3359, Standard Test Methods for Measuring Adhesion by Tape Test. Two test methods are covered. This is one of the top-selling ASTM test methods, regardless of field.

These test methods cover procedures for assessing the adhesion of coating films to metallic substrates only, by applying and removing pressure-sensitive tape over cuts made in the film. Method A is primarily intended for use at job sites, while Method B is more suitable for use in the laboratory. The cross-hatch test, Method B, is not considered suitable for films thicker than 5 mils (125 μm). Both test methods are used to establish whether or not the adhesion of a coating to a substrate is at a generally adequate level. They do not distinguish between higher levels of adhesion for which more sophisticated methods of measurement are required. In multicoat systems, adhesion failure may occur between coats so that the adhesion of the coating system to the substrate is not determined. In Test Method A an X-cut 1.5 in. (3.8 cm) long is made in the film (to the substrate) with a sharp cutting device. A 1-in. (2.5-cm)-wide pressure sensitive tape is applied over the cut and firmly adhered with a pencil eraser and then removed, and adhesion is assessed qualitatively on a 0 to 5 scale.

In Test Method B, a lattice pattern with either 6 or 11 cuts in each direction is made in the film (to the substrate), pressure-sensitive tape is applied over the lattice and then removed, and adhesion is evaluated by comparison with descriptions and illustrations.

For Test Method A, the following rating scale is used:

5A = No peeling or removal.
4A = Trace peeling or removal along incisions.
3A = Jagged removal along incisions up to 1/16 in. (1.6 mm) on either side.
2A = Jagged removal along most of incisions up to 1/8 in. (3.2 mm) on either side.
1A = Removal from most of the area of the X under the tape.
0A = Removal beyond the area of the X.

For Test Method B, 3/4 in. (1.9 cm) cross-cuts are made.

For coatings having a dry film thickness up to and including 2.0 mils (50 μm), 11 cuts are spaced 1 mm apart.

For coatings having a dry film thickness between 2 mils (50 μm) and 5 mils (125 μm), 6 cuts are spaced 2 mm apart.

For films thicker than 5 mils (125 μm), Method A is used instead of Method B.

For Test Method B, adhesion is rated according to the following scale (as illustrated in Fig. 5):

5B = The edges of the cuts are completely smooth; none of the squares of the lattice is detached.
4B = Small flakes of the coating are detached at intersections; less than 5% of the area is affected.
3B = Small flakes of the coating are detached along edges and at intersections of cuts. The area affected is 5 to 15 % of the lattice.
2B = The coating has flaked along the edges and on parts of the squares. The area affected is 15 to 35 % of the lattice.
1B = The coating has flaked along the edges of cuts in large ribbons, and whole squares have detached. The area affected is 35 to 65 % of the lattice.
0B = Flaking and detachment worse than Grade 1.

Repeatability within one rating unit is generally observed for coatings on metals for both methods, with reproducibility of 1 to 2 units. The method is widely used and is viewed as "simple" as well as low in cost.

Peel Adhesion Testing on Plastic Substrates

ASTM D3359 has drawn fire when used for substrates other than metal, such as plastics. The central issues are that the test may lack reproducibility and does not relate to its intended application. Poor reproducibility is a direct result of several factors intrinsic to the materials employed and the procedure itself. More importantly, in this instance the test is being applied beyond its intended scope. ASTM D3359 was designed for relatively ductile coatings applied to metal substrates, not for coatings (often brittle) applied to soft plastic parts [1].

Nevertheless, the tape test enjoys widespread popularity. The tape test is economical to perform, lends

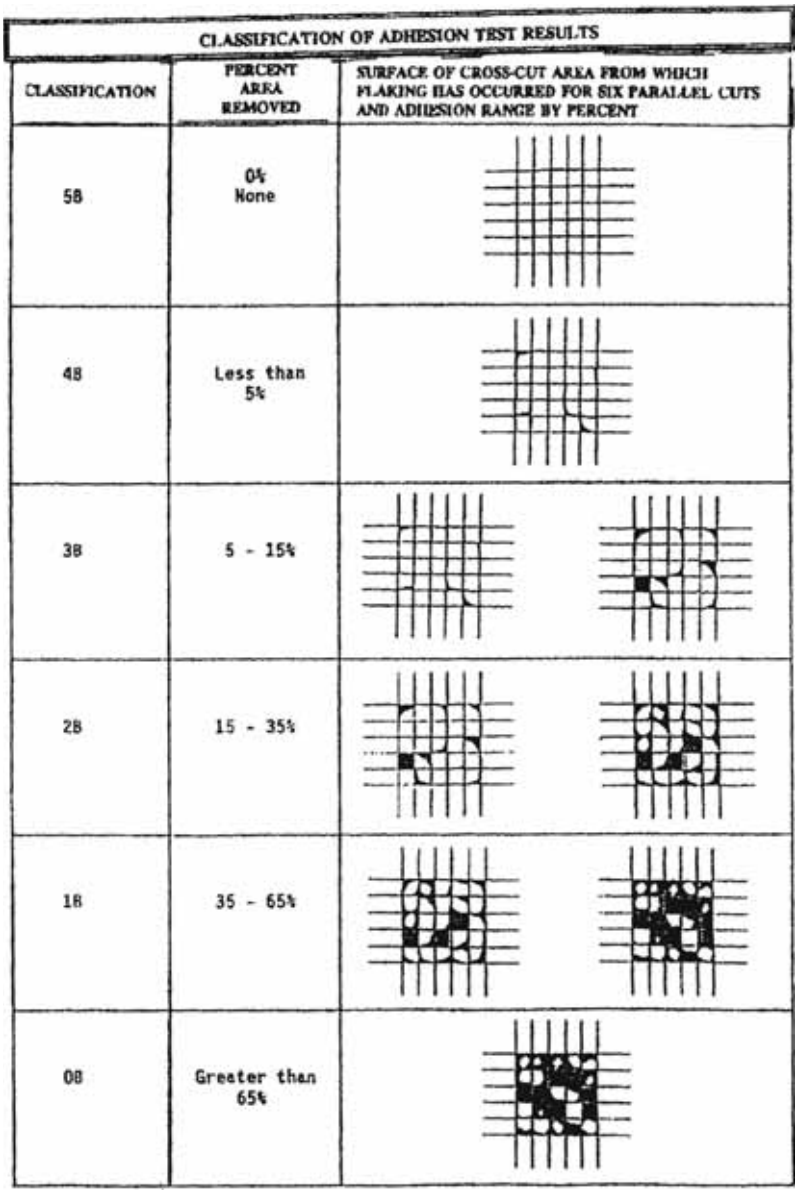

Fig. 5—Classification of adhesion test results. From ASTM D3359.

itself to job site application, and most importantly, after decades of use, people feel comfortable with it [42]. Unfortunately, the often unique functional requirements of coatings on plastic substrates dictate that the tape test as written may not be a satisfactory measure of practical adhesion performance.

When a flexible adhesive tape is applied to a rigid coated substrate surface and then removed, the removal process has been described in terms of the "peel phenomenon," as illustrated in Fig. 6.

Peeling begins at the "toothed" leading edge (at the right) and proceeds along the coating-adhesive interface. It is reasonable to assume that any coating removal is due to a tensile force generated along this interface, which would be a function of the rheological properties of the backing and adhesive layer materials and the strength of the bond between the adhesive layer and the coating surface. Note, however, that in actuality this force is distributed over a discreet distance (0 to A in Fig. 6), which relates directly to

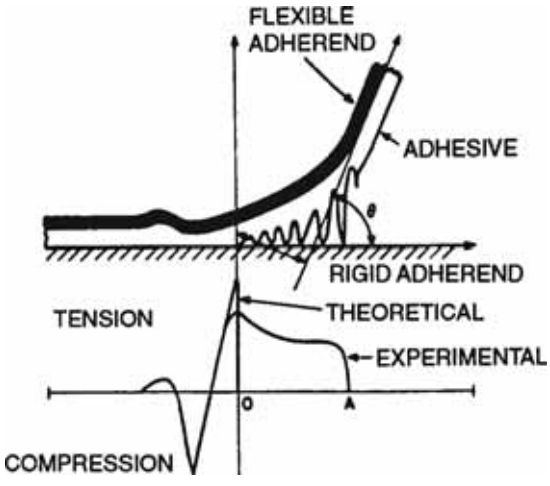

Fig. 6—Peel profile [62].

the properties described [63], not concentrated at a point (0 in Fig. 6) as in the theoretical case, though tensile force is greatest at the origin for both. It is worthwhile to note the significant compressive force which arises from the response of the tape-backing material to being stretched, which precedes the tensile force. Both tensile and compressive forces are involved in tape testing.

Close scrutiny of the tape test with respect to the nature of the tape employed and certain aspects of the procedure itself reveal several factors, each or any combination of which can dramatically affect the results of the test as discussed below.

The Tape Controversy

Beginning in 1991, given the withdrawal of the originally specified tape, 3M-710, ASTM D3359 no longer specified a specific tape. Differences in tapes can lead to different results for reasons noted above since small changes in backing stiffness and adhesive rheology cause large changes in the tension area. It is also important to note that tapes, like most products, are manufactured to meet minimum standards. A given lot may surpass these criteria and be suitable for general market distribution, but a source of serious and unexpected error for tape testing [63]. There was, in fact, a commercially available tape test kit that included a tape with adhesion variations of up to 50 % claimed by the manufacturer [64]. And, of course, tapes age on storage. Bond strengths change over time.

While there are tapes available that would appear to deliver consistent performance, a given tape does not adhere equally well to all coatings. For example, the peel removal force of the tape previously recommended by ASTM (3M-710) was examined with seven coatings. It was found that while peel was indeed consistent for a given coating, it varied by 25 % between the highest and lowest ratings among coatings. This observation could be the result of several factors, notably coating composition and topology, but the bottom line is that no single tape is likely to be suitable for testing all coatings. It is also useful to note the tape test does not give an absolute value for the force required for bond rupture, but serves only as an indicator that some minimum value for bond strength was met or exceeded [1,2].

Procedural Problems

The tape test is operator intensive. By design it was made as simple as possible to perform and requires a minimum of specialized equipment and materials that must meet certain specifications. Therefore, the burden of accuracy and reproducibility relies largely upon the skill of the operator and his/her ability to perform the test in a consistent manner. Key steps that directly reflect the importance of operator skill include the angle and rate of tape removal and the visual assessment of the tested sample. It is not unexpected that different operators might obtain different results [1,2].

PEEL ANGLE AND RATE

The standard requires that the free end of the tape be removed rapidly at as close to a 180° angle as possible. But if peel angle and rate vary, the force required to remove the tape can change dramatically. Nearly linear increases were observed in peel force approaching 100 % as peel angle was changed from 135 to 180°, and similar large differences can be expected in peel force as peel rate varies. These effects are related in that they both reflect certain rheological properties of the backing and adhesive, which are molecular in origin, but the most useful conclusion is that these phenomena can make large contributions and must be minimized to assure reproducibility [65].

VISUAL ASSESSMENT

The final step in the test is visual assessment of coating removed from the specimen, and this can be subjective in nature. This assessment can vary among individuals evaluating the same specimen [65].

Performance in the tape test is based on the amount of coating removed compared to a relative scale. But it was found that the exposure of substrate can be due to factors other than coating adhesion, arising from the requirement that the coating be cut (hence the synonym "cross-hatch adhesion test"). Justification for the cutting step is reasonable; cutting provides a free edge from which peeling can begin without having to overcome the cohesive strength of the coating layer. This might be suitable for coatings applied to metal substrates, but for coatings applied to plastics, the cutting process can lead to false indications of poor adhesion. This is due to the unique interfacial zone mentioned earlier. For coatings on soft plastics, how deep should this cut penetrate? Is it possible to cut only to the interface?

If microscopic examination of panels is included, in several instances it is clearly evident that coating removal results from substrate failure at or below the interface, not from adhesive failure between coating and substrate. At the same time, it is also observed that cohesive failure within the coating layer is a frequent occurrence. The latter observation is significant in that the tape test assessment criteria make no provision for it [1,2].

Mechanized Tape Test

A mechanized tape test was published by ASTM Committee B 8 in 2000. The scope of ASTM B905, Test Methods for Assessing the Adhesion of Metallic and Inorganic Coatings by the Mechanized Tape Test, includes the assessment of adhesion of metallic and inorganic coatings and other thin films to metallic and nonmetallic substrates. A pressure-sensitive tape is applied to the coated surface and then a mechanized device is utilized to remove the tape at a regulated, uniform rate and constant angle while the removal force is simultaneously recorded (Fig. 7). Four methods are described: A1 and A2, which do not involve cuts made to the coating (for use on parts), and B1 and B2, which use a cross-hatch pattern of six lines (plus six at 90°) for laboratory use. Methods 1 and 2 refer to peel angles of 90° and 180°, respectively. Methods B1 and B2 are not recommended for polymeric substrates. For Method A coating detachment (failure) or no coating detachment (pass) are reported versus the maximum registered peel force. For Methods B a classification similar to ASTM D3359 is reported versus the maximum registered peel force. The spacing of cuts, however, is 4 mm versus 1 or 2 mm in D3359. In B 905 a 90° peel angle is preferred "due to the stress strain behavior of the tape," versus the 180° peel angle of D3359.

An interlaboratory study during the development of the test method revealed that the maximum peel force of the tape depends significantly on the type of coating, the type of tape, the peel rate, and the peel angle. The pressure used

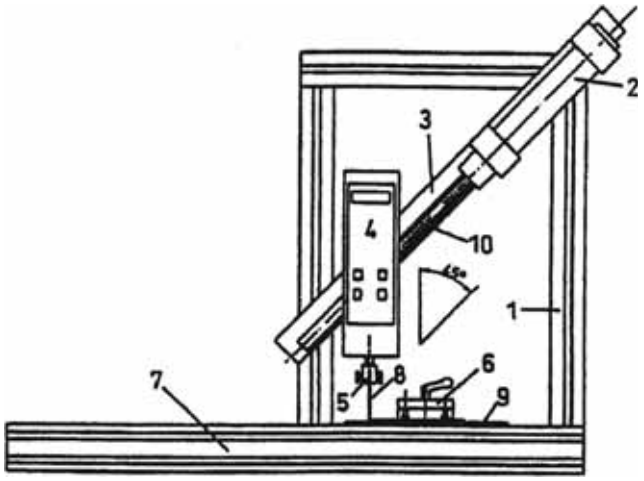

Fig. 7—Mechanized tape tester.

for adhering the tape (a roller is used) was not significant. Results for the four test methods should not be compared. While the methods provide a regulated uniform peel rate and constant angle of test, and most importantly provide a way of measuring peel force, the other underlying issues in tape testing are not overcome. If two different coatings have different peel forces despite a single tape, peel rate, and angle of peel, then the adhesion rating/results are still not directly comparable.

Other Peel Tests

The corresponding test in the International Standards Organization to ASTM D3359 is ISO 2409. The cross-hatch test is used in ISO 2409 up to a coating thickness of 10 mils (250 μm). A single crosscut test is used above 10 mils, versus 5 mils (125 μm) for D3359. A 1-mm cross-hatch spacing is used for a coating thickness up to 60 μm for hard substrates, a 2-mm spacing for soft substrates, a 2-mm spacing for coatings 61–120 μm, and a 3-mm spacing above 120 μm. In ISO 2409 six cuts for the 90° cross-hatch are made in each direction. In D3359 a 1-mm spacing is used for coatings up to a thickness of 50 μm (11 cuts in each direction) and a 2-mm spacing for coatings 50–125 μm (6 cuts), with the single crosscut test applied at higher coating thickness. In ISO 2409 the tape is removed at an angle of 120° (angle away from operator) versus 180° in D3359. The classification scheme is 0 to 5 with 0 meaning no coating detachment in ISO 2409. This is the opposite in D3359, with ratings 5B to 0B, with 0B signifying greater than 65% coating removal. Thus ISO 2409 and ASTM 3359, while both being tape peel tests, differ in many significant ways, not the least of which being that the classification schemes signify opposite results.

Numerous tape peel tests exist in the industry. Examples include the General Motors Engineering Standard GM 9071P-Tape Adhesion Test for Paint Finishes, which is similar to ASTM D3359, and Boeing Specification Support Standard (BSS) 7225, which provides more varied cross-hatch patterns than D3359 and provides specific procedures for tape testing after wet immersion.

Direct Tensile Testing

A long-used approach to coating adhesion testing is the direct tensile test, perhaps "conceptually" the simplest of all methods for measuring adhesion. A dolly or stud is bonded to the coating film. The normally applied force that is required to remove the film is measured. If failure occurs at the substrate-film interface, this force is taken to be the "force of adhesion." An obvious limitation is, of course, the strength of the adhesive bond of the stud to the cured coating. Such methods have been available since the 1930s. Many of these test methods have unfortunately suffered from their own lack of reproducibility. This is not unexpected since the forces involved are not quite as simple as appearance would have it [5,66].

It is essential that the force is applied strictly in the direction normal to the sample and that no bending moment is active across the test area. Deviations from symmetry in the test arrangement, poor alignment, deviations from homogeneity and of thickness of the adhesive (coating), and random variations in the strength of the bond between film and substrate affect test results [5,66].

The stress at locations where the adhesive film is thinner will be higher than the average stress and will be transmitted to the film under test. Another factor may be peeling during the test, which is not easily identified or analyzed.

The adhesive used to bond a stud to the coating has the potential to influence the coating film properties by penetration through the film into microcracks and possibly into the substrate [66]. Test adhesive flexibility may also be an issue, as well as the flexibility of the substrate, if the sample is unrestrained.

There exists now within ASTM both laboratory and field versions of direct tension tests for coatings. Test Method for Measuring Adhesion of Organic Coatings to Plastic Substrates by Direct Tensile Testing. ASTM D5179, while limited to organic coatings on plastics, uses a restrained sample and commonly available tensile test apparatus. The second, Method for Pull-Off Strength of Coatings Using Portable Adhesion-Testers, ASTM D4541, defines a class of portable pull-off adhesion testers for field evaluation of coating adhesion. ASTM D5179 is the successor to numerous attempts to develop a reproducible coating tension test and was approved in 1991. It will be discussed first.

ASTM D5179

This test covers the laboratory determination of adhesion of organic coatings to plastic substrates by mounting and removing an aluminum stud from the surface of a coating and measuring the force required to break the coating/substrate bond with a tensile tester. The test method provides an inexpensive test assembly, which can be used with most tensile test machines. The method is used to compare the pull-off strength (commonly referred to as adhesion) of coatings to various plastic substrates, thus allowing for a quantitative comparison of various coating/substrate combinations.

A carefully prepared 2-cm diameter aluminum stud is bonded directly to a coated, cured panel using a cyanoacrylate adhesive. The adhesive is allowed to cure for 2 h at room temperature. Adhesive buildup is removed from around the stud. The specimen is then subjected to test on a tensile tester equipped with an upper coupling adapter and a restraining device (Fig. 8) to provide for sample alignment and minimal substrate flexing. The sample bearing the stud is installed in the restraining device, with only the stud protruding. The tensile machine crosshead is lowered so the upper coupling adaptor can be attached to the specimen.

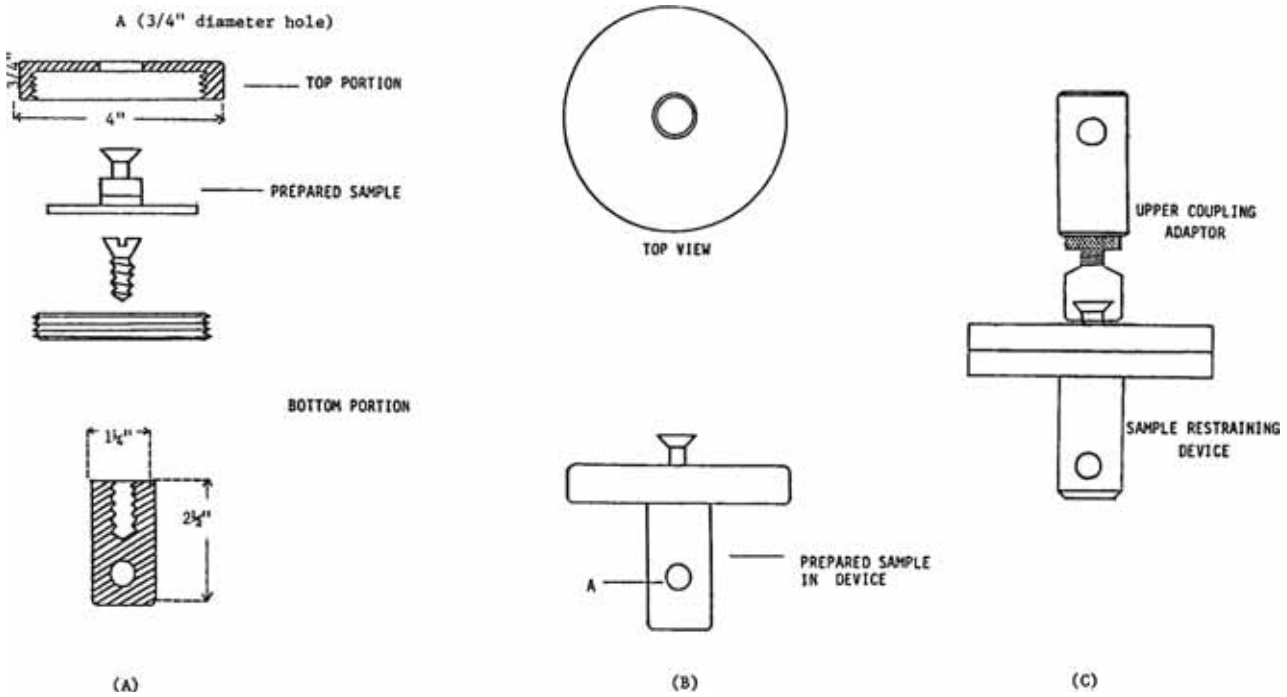

Fig. 8—Direct tensile restraining device. From ASTM D5179.

When testing thin substrates, a piece of plastic is placed in the restraining device behind the specimen to insure a rigid assembly. The tension test is conducted, and pull strength recorded. Each specimen is rated according to type of coating failure, as follows:

A = Adhesive failure of the coating from the substrate.
C = Cohesive failure in the coating.
AC = Combination of adhesive failure at the coating/substrate interface and cohesive failure in the coating.
S = Adhesive failure at the stud.
CS = Combination of adhesive failure at the stud and cohesive failure in the coating.

For multilayer coatings, failure between the layers is noted and labeled as CM. Five specimens of each coated substrate are tested one day and five on a second day. If one specimen differs significantly from the other four tested at the same time, fails because of an uneven (nonplanar) stud, or for another reason performs unlike the other four, a replacement specimen is tested. The stud and specimen are carefully examined. The adhesive should have been applied uniformly to the entire stud surface. Coating should have pulled off uniformly over the *entire* stud surface either with adhesive failure from the substrate (A) or cohesive failure in the coating (C). If failure is less than 90 % A or C (or CM), if the adhesive has failed at the stud, a retest, exercising particular care in the specimen and stud preparation is performed. Pull strength for the ten runs on each coating substrate combination are averaged and reported.

The precision and bias are primarily dependent upon the accuracy of the force measurements, the alignment of the device, and the care exercised in stud and specimen preparation, and in the care in testing. A ten-laboratory round robin on ten samples gave an average standard deviation of 29 % for reproducibility and 22 % for repeatability. A range of pull strengths of 2 orders of magnitude has been observed (Table 1) for diverse coating-plastic combinations.

ASTM D4541

This test method defines a class of portable adhesion testers for measuring the pull-off strength of coatings. The method covers a procedure and apparatus for evaluating pull-off strength by determining either the greatest perpendicular force (in tension) that a surface area can bear before a plug of material is detached or whether the surface remains intact at a prescribed force (pass/fail). Failure will occur along the weakest plane within the system comprised of the test fixture, adhesive, coating system, and substrate and will be exposed by the fracture surface. The method maximizes tensile stress as compared to the shear stress applied by other methods such as scratch or knife adhesion, and results are not comparable. It is recognized that the pull-off strength reflects both material and instrumental parameters and therefore provides a relative, not absolute, measure of adhesion. The pull adhesion testers defined are portable and capable of applying a concentric load and counter load to a single surface so that coatings in the field can be tested even though only one side is accessible. Measurements are limited by the strength of adhesion bonds between the loading fixture and the specimen surface or the cohesive strength of the substrate. The pull-off test is performed by securing a "loading fixture" (dolly or stud) normal (perpendicular) to the surface of the coating with an adhesive. After the adhesive is cured, the testing apparatus is attached to the loading fixture and aligned to apply tension normal to the test surface. The force applied to the loading fixture is then gradually increased (in less than 100 s) and monitored until either

TABLE 1—Representative pull strength for organic coatings on plastics

Sample No.	Coating	Substrate	Failure Mode	Pounds Per Square Inch[a]
1	Lacquer	Polyester/ Polycarbonate	C	58
2	Lacquer	Polycarbonate	A	36
3	Lacquer	ABC	C	82
4	Lacquer	Polycarbonate	A	37
5	Lacquer	ABS	A	93
6	Lacquer	PVC	AC	103
7	Enamel	Polycarbonate	A	308
8	Urethane	ABC	A	639
9	Urethane	ABS	A	476
10	Urethane	Metal	S	666
11	Enamel	Metal	75% A	342
12	Lacquer	PPO/Nylon	C	226
13	Enamel	PPO/Nylon	C	226
14	Enamel	PPO/Nylon	A	242

[a] To convert to metric, multiply by 6.89 kPa.
NOTE: ABC = acrylonitule-butadiene-styrene, PVC = polyvinyl chloride, PPO = polyphenylent ether.

a plug of coating material is detached or a specified value is reached. The nature of the failure is assessed as to the percent of adhesive or cohesive failure, and the actual interfaces and layers involved are identified. The pull-off strength is computed based on the maximum indicated load, the instrument calibration data, and the original surface area stressed (Fig. 9).

This method is general and is applicable to any portable apparatus meeting the standard's basic requirements for determining the pull-off strength of coatings. Five apparatuses are commonly recognized to meet the requirements of the standard.

It is known that the rigidity of the substrate affects pull-off strength results and is not a controllable test variable in field measurements as defined by this standard. For example, steel substrates of less than 1/8 in. (3.2 mm) thickness show reduced pull-off strength results compared to 1/4-in. (6.4-mm) thick panels.

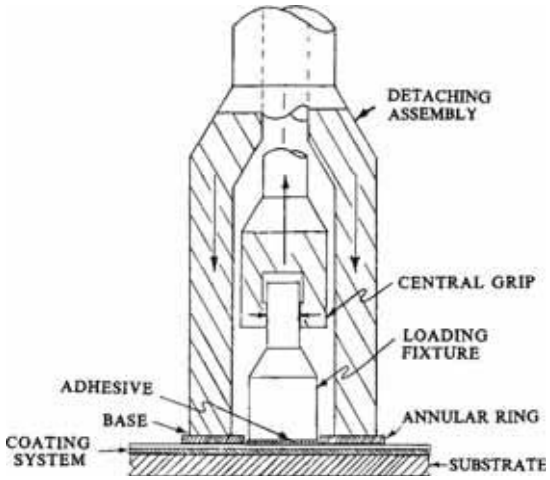

Fig. 9—Portable adhesion tester. From ASTM D4541.

Errors in measurement in this test result from alignment of the apparatus that is not normal to the surface, poor definition of the area stressed due to improper application of the adhesive, poorly defined glue lines and boundaries, holidays in the adhesive caused by voids or inclusions, improperly prepared surfaces, and sliding or twisting of the fixture during the initial adhesive cure. Also, scratched or scored samples may contain stress concentrations leading to premature fractures. Interlaboratory data have been obtained for four commercial test apparatus and are presented in Table 2.

ISO 4624

Similar pull-off test methodology has been approved through the International Standards Organization, and the parameters involved have been carefully studied. ISO 4624, "Pull-off Test for Adhesion," was approved in 1978. ISO 4624 specifies two different tests assemblies (A and B of Fig. 10).

Test Assembly A (Sandwich Method) consists of a substrate painted on one or both sides, with test cylinders (studs) with a specified diameter bonded coaxially to the coated test surface and on the reverse. Test Assembly B consists of a rigid substrate coated on one side, with one test cylinder (stud) applied to that side only. While the latter is the more practical, Test Assembly A on stress analysis shows a smoother stress distribution than B. Test Assembly B shows strong stress peaks at the coating layer periphery. The result is that Test Assembly B shows 20 to 60 % lower breaking strength results than the sandwich method for several organic coatings on metal [67].

TABLE 2—ASTM D 4541 interlaboratory data (psi)[a]

Instrument Loading Fixture Diameter Paint Sample	Patti 13 mm	Elcometer 20 mm	Hate 19 mm (mean of 3 results)	Dyna 50 mm
A	1160	586	1185	201
B	1099	624	1157	185
C	1333	827	1245	190
D	1678	888	1686	297

[a] To convert to metric, multiply by 6.89 kPa.

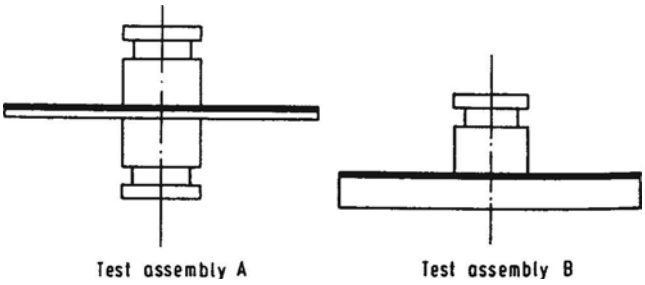

Fig. 10—ISO 4624 test assemblies.

For Test Assembly B, breaking strength values have been shown to be a function of the diameter of test cylinders (studs) as well as their geometry. On the range of 10 to 28 mm diameters, a factor of 2 in breaking strength was seen with a peak at about 14-mm diameter. It was observed that tensile forces only affected the central part of the test area. Even test cylinders of the same diameter, but different shapes, gave different results, up to 45 % lower. It has been noted that while uniform tensile stress can only be approached, the length of the test cylinder (stud) should be no less than half its diameter. When this is done, similar results are achieved regardless of cylinder diameter [67].

Perhaps it is only a coincidence, but it is interesting to note in Table 2 for apparatus meeting ASTM D4541 that the loading fixture diameter and geometry differ significantly and at least partially account for the greater than factor of 4 variation in test results, with the apparatus having a 50-mm loading fixture diameter showing the lowest numerical results.

Substrate thickness (flexibility) has a significant effect upon results. In a study of steel panels in the range of 2 to 30 mm thick, breaking strength increased to a thickness of 15 mm using Test Assembly B. A comparison of results with the sandwich method for substrates above 15-mm thickness, however, still showed breaking strength values about one third higher for Test Assembly A. These observations can be explained in terms of differences in stress distribution. Thinner substrates show increased stress intensity at the periphery, which is distinguishable up to 15-mm thickness [67].

ISO 4624 specifies that tensile stress shall not be increased at a rate greater than 1 MPa/s, so that failure occurs within 90 s of initial stress application. An investigation of the rate of tensile stress increase in the range 0.15 to 1.2 MPa/s yielded indistinguishable results [67].

Sample parameters are important. Coating thickness (and adhesive thickness) is a key factor. The energy stored in a 5-mil (125μm) coating, by virtue of its internal strain, increases as the coating thickness increases and at a particular thickness can be sufficient to overcome the work of adhesion at the interface (spontaneous peeling). The variation is largest at thicknesses below 125 μm (5 mils), which of course is the area of most practical application. It was also observed that at the lowest coating thickness for the coatings studied, cohesive failure occurred in the uppermost parts of the coating, leaving a very thin film of coating on the test cylinder (stud). With thicker coatings, the fracture propagated deeper into the coating. Through study of the locus of failure, one can also study the effects of environmental conditions (aging, solvents, moisture) and of coating resin cure [67].

More recent studies have also looked at instrument and sample parameters. Rocke et al. studied the influence of measured pull-off strength by stud area, adhesive thickness, the thickness of the substrate, as well as coating composition [68]. A comprehensive Norwegian study involved some 1400 pull tests using three different instruments on a three-coat paint system and on thermal arc-sprayed ALMg5 on blast-cleaned steel, with the blast-cleaned steel also assessed as a standard. The parameters investigated included the effect of panel thickness on pull strength (5, 8, and 12 mm), the effect of cure time of the paint system on pull-off strength (8, 15, 28, 37, and 76 days after application of the top coat), the effect of four different brands of cyanoacrylate adhesive on pull-off strength, the effect of different temperatures on adhesive cure or pull-off on pull-off strength (8.5°C, 23°C, and 70°C), the effect of stud diameter on pull-off strength, and the effect of cutting around the edge of the stud on pull-off strength. The data reported were the averages of 10 to 30 runs [69].

Adhesion on blast-cleaned steel using an epoxy adhesive showed a 24–58 % increase in mean pull-off strength in going from 5 to 12 mm thick panels. The increase in pull-off strength for the three-coat paint system increased 30–34 % from 8- to 76-day coating cure time. Four cyanoacrylate adhesives were cured for 1, 2, 5 at 23°C or 8.5°C at 50 % relative humidity on bare blast-cleaned steel. At 23°C (1h) pull-off strength ranged from 25.6 to 35.4 MPa, while at 5 h pull-off strength ranged from 29.1 to 38.2 MPa. Corresponding data at 8.5°C were 21.5 to 27.0 and 22.2 to 30.6, respectively. Testing of arc spray coated samples at different temperatures showed an increase in pull-off strength for one of two cyanoacrylate adhesives and not the other and also a difference in locus of failure was also noted. Some effect of stud size was seen, with higher mean pull-off strength for studs at 1.57 cm^2 versus 3.14 cm^2. Cutting around the stud showed a slight lowering of pull-off strength (under 10 %). A number of experimental factors affect test results. A 5-mm rigid steel panel is not "infinitely thick." Cured coatings may still be undergoing changes over long time periods. Such changes can effect adhesion. Temperatures of cure coatings and adhesives may affect pull-off strength [69].

Clearly, stress distribution changes, as altered by test apparatus and sample parameters, can alter results dramatically. Pull-off strength (breaking strength) is therefore a relative number. Comparisons must be made carefully in concert with an examination of the locus of failure. Practically speaking, while absolute values are only approached, relative values and studies of the locus of failure are sufficient for most purposes.

Scrape Adhesion Testing

Used to a lesser extent than the preceding methods is ASTM D2197, Test Methods for Adhesion of Organic Coatings by Scrape Adhesion.

This test method covers the determination of the adhesion of organic coatings such as paint, varnish, and lacquer when applied to smooth, flat (planar) panel surfaces. The materials under test are applied at uniform thickness to planar panels, usually sheet metal of uniform surface texture. After drying, the adhesion is determined by pushing the panels beneath a rounded stylus or loop loaded in

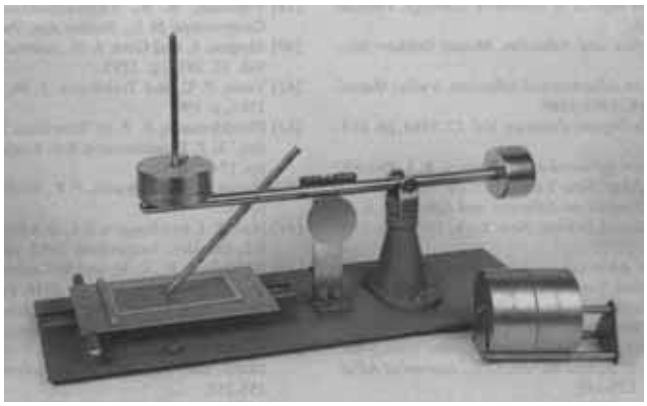

Fig. 11—Balanced-beam scrape adhesion tester.

increasing amounts until the coating is removed from the substrate surface.

The method is most useful in providing relative ratings for a series of coated panels exhibiting significant differences in adhesion. The balanced-beam, scrape-adhesion tester (Fig. 11) consists of a balanced beam to which is secured a platform for supporting weights and a rod at an angle of 45° that holds the scraping loop. The rod is set so that the scraping loop contacts test surfaces directly below the weights. The loop is a 1/16-in. (1.6-mm)-diameter rod bent into a "U" shape with an outside radius of 0.128±0.002 in. (3.25±0.05 mm) hardened to Rockwell HRC 56 to 58 and chromium plated and polished.

At least 1/2 in. (1.3 cm) at the end of a test panel is un-coated. The surface of the substrate must be hard enough so that it is undamaged by the scraping loop. The test procedure is as follows. A test panel on the sliding platform is placed so that it may be moved away from the operator and the uncoated portion is toward the main beam support. Weights are placed on the weight support using an initial amount estimated to be appropriate for the particular coating. The beam is lowered until the loop rests on the uncoated portion of the specimen and the full load is applied; then the sliding platform is slowly pushed away from the operator 1 to 2 s/in. for a distance of at least 3 in. (76 mm). If the coating is removed, the testing is continued using successively smaller loads (0.5-kg increments) until the coating is not removed. If the coating is not removed by the initial scrape, the testing is continued, using successively larger loads (0.5-kg increments) until the coating is removed or until the maximum load of 10 kg has been applied. A new area of the test surface is used each time a scrape is made. When the critical load has been approximately located, the test is repeated five times at each of the three loadings: above, below, and at the load determined in the first trial.

For each applied load, the number of times the coating was removed or adhered is tabulated. The load where the scrape results change from mainly adhering to mainly removed, ignoring the first 1/2 in. (13 mm) of the scratch if the coating was removed, is the adhesion failure end point.

Perhaps the most "practical" approach to paint adhesion is assessment by the use of a paint knife. A test method that provides guidance for such evaluations is ASTM D6677, Test Method for Evaluating Adhesion by Knife.

TORQUE TESTS

While the scope of ASTM D3359 provides for the testing of coatings on metal substrates only, it and other tests discussed previously have been used to assess the adhesion of coatings on wood. Little data have, however, been published with wood as the substrate. Several papers using a torque technique have been published [70–73]. While such methods have not been standardized, it was felt that they might be of interest to readers. In this shear technique, studs are glued on the painted samples using a solvent-free, dual-component epoxy glue. After the glue has dried, a slot is drilled in the paint film around the studs until the wood surface is reached. The studs are removed using a recording torque wrench. The failure load is noted and the locus of failure determined. The shear stress (adhesion value) is calculated using the equation $T = (167I)/(\Pi d3)$ where I is the measured torque (Nm), and d is the diameter of the stud (in this case, 12.5 mm). A minimum of six replicates is used for the calculation of the mean adhesion value. Adhesion values are given in MNm^{-2}. Painted samples have been tested dry and after water immersion [74,75].

UNIFORM DOUBLE-CANTILEVER BEAM TESTS

While not standardized, workers have found success with a uniform double-cantilever beam technique for the testing of the adhesion of coatings on wood [74,75].

Other ASTM Standards

Other ASTM standards that pertain to aspects of adhesion measurements of films and coatings include the following:

ASTM B533 – Standard Test Method for Peel Strength of Metal Electroplated Plastics.

ASTM B571 – Standard Practice for Qualitative Adhesion Testing of Metallic Coatings. (This method includes bend, burnishing, chisel-knife, draw, file, grind-saw, heat-quench impact, peel, push, and scribe-grind tests.)

ASTM C633 – Standard Test Method for Adhesion or Cohesion Strength of Thermal Spray Coatings.

ASTM D3730 – Guide for Testing High-Performance Interior Architectural Wall Coatings. (This guide includes a pull-strength test for adhesion assessment.)

ASTM D4145 – Standard Test Method for Coating Flexibility of Prepainted Sheet. (This method includes a tape pull-off test.)

ASTM D4146 – Standard Test Method for Formability of Zinc-Rich Primer/Chromate Complex Coatings on Steel. (This method is a tape test after dome-shaped deformation.)

ASTM D7234 – Standard Test Method for Pull-Off Adhesion Strength of Coatings on Concrete Using Portable Pull-Off Adhesion Testers.

ASTM D7334 – Standard Practice for Surface Wettability of Coatings, Substrates and Pigments by Advancing Contact Angle Measurement.

ASTM F692 – Standard Test Method for Measuring Adhesion Strength of Solderable Films to Substrates.

ASTM F1044 – Standard Test Method for Shear Testing of Calcium Phosphate Coatings and Metallic Coatings.

ASTM F1147 – Standard Test Method for Tension Testing of Calcium Phosphate and Metal Coatings.

ASTM F1842 – Standard Test Method for Determining Ink or Coating Adhesion on Plastic Substrates for Membrane Switch Applications. (This test is based upon D3359.)

Additional tests exist for electrodeposits, and bending, burnishing, and wrapping tests for coatings on wire. Tests for adhesives have also been applied to coatings as well. Use of reverse impact tests, lap and butt joint tests, and tensile shear tests have been reported [1].

CONCLUSIONS

Basic adhesion is the summation of multiple phenomena. Ideal adhesion is probably neither obtainable nor measurable experimentally. Practical techniques do, however, allow sufficient assessment of relative adhesion for most purposes, if used with care and knowledge. Workers need to understand both basic adhesion concepts and the factors affecting practical adhesion for systems of their interest if they are to make improvements in real world products.

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Abrasion Resistance*

Daniel K. Slawson[1]

PREFACE

IN PREPARATION OF THIS CHAPTER, THE CONTENTS of the fourteenth edition were drawn upon. The author acknowledges the authors of the fourteenth edition. The current edition will review and update the topics as addressed by the previous authors, introduce new technology that has been developed, and include up-to-date references.

The problem of resistance to abrasion exists all around us: on floors, walls, furniture, automobiles, farm implements, construction equipment, military gear, appliances, shoe soles, and so on. Because resistance to abrasion is a basic factor in the durability of a coating, its measurement is of practical importance to both producer and consumer.

Abrasion is caused by mechanical actions such as rubbing, scraping, or erosion from wind and water. It can take two general forms: marring or wearing.

DEFINITIONS

Mar abrasion consists of permanent deformations that have not ruptured the surface of a coating. The resistance of a coating to marring is its ability to withstand scuffing actions that tend to disfigure or change the appearance of its surface. Some examples of potential causes of marring of organic coatings are (a) sliding an object across the surface of furniture; (b) rubbing of a belt buckle, button, zipper, or rough fabric on an automobile finish; (c) sliding a toy across a wall or a refrigerator door, etc.

Wear abrasion is caused by mechanical action that removes material from the surface of a coating. In many cases, the removal is gradual or progressive due to repetitive mechanical action.

RELATIONSHIP TO OTHER PHYSICAL PROPERTIES

Abrasion resistance is not a unique or isolated property of a material but is rather related to other physical characteristics such as hardness, cohesive and tensile strength, elasticity, and toughness. Also, from the standpoint of retaining its protective or decorative function, the thickness of a coating can be an important factor.

Hardness, Elasticity, and Tensile Strength

Abrasion resistance is related to hardness, yet the relationship is not simple. A first thought might be that the harder a coating, the better would be the abrasion resistance; however, this is not always true. Steel is much harder than rubber, for example, but steel "tires" on an automobile, in addition to not giving a smooth ride, would not last long on concrete roads in comparison to the service life of a good rubber tire. The ability of a material, such as a rubber tire, to undergo elastic deformation and recover or "to ride with the blow" is associated with good abrasion resistance.

The energy transferred to an elastic material by an impacting object is largely returned to the object, though redirected, instead of being expended in the destruction (separation and removal of material) of the impacted surface. From a fundamental viewpoint, this is a consequence of the smaller deceleration and hence smaller force generated, since force is equal to the product of mass and acceleration, when the impact is with a material that will deform or "give" with the impacting object. If the deformation caused by the object is not elastic, the material will yield and flow, causing damage. Therefore, soft materials with a low tensile strength are not abrasion resistant.

The fact that elastic materials are often abrasion resistant does not mean that hard materials are not abrasion resistant. Theoretically, however, if one is given two materials of equal tensile strength, the material of lower modulus should have the best abrasion resistance. The deceptive factor here is that a hard material usually has a much higher tensile strength than a soft material. Thus, when a rubber is compared with steel, materials with orders of magnitude difference in tensile strength are being considered. The fact that rubber is abrasion resistant emphasizes that the value of a low modulus of elasticity and adequate tensile strength are factors that play a role in obtaining good abrasion resistance.

In theory, a very hard material that has a hardness and cohesive strength adequate to completely resist any impact force it might encounter would not be dependent on rubberlike elasticity to reduce or dissipate impact stresses. It would be more abrasion resistant than the best elastic but weaker material [1].

CORRELATION WITH END-USE PERFORMANCE

From the discussion above, it is apparent that the measurement of abrasion resistance involves measuring a complex combination of interrelated properties among which there is no direct relationship. The task of devising a test methodology that will correlate with end-use performance is, therefore, complex and difficult but not impossible to

* This chapter is an abridged and modified version of the chapter with the same title, written by Mark P. Morse, found in the previous edition of this manual.

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develop. If the test method subjects the material under test to a composite of destructive forces similar to those met in service, then the test method will correlate—or predict—the service performance of the material in at least a qualitative or relative ranking respect.

When accelerated tests are being considered, even tests that rank materials in the same sequence as actual service tests, a quantitative correspondence with actual service is seldom expected or obtained. Actual end-use tests, while the most reliable in providing an indication of a material's probable long-term durability, suffer from the difficulties of ensuring equivalent usage and measurement, especially when the comparison of different materials is attempted. Because of such difficulties and because service tests are usually very time consuming, a wide variety of test machines have been developed to provide an accelerated indication of the abrasion resistance of coatings and related materials such as laminate flooring, plastics, linoleum, and wall coverings. In a comprehensive review article by Harper [2], there is a list of no less than 49 different abrasion-causing machines. An investigation by the International Study Committee for Wear Tests of Flooring Performance [3], in which seven commercial, organic flooring materials were systematically tested on 21 abrasion machines of 17 different types, indicated that very few of these machines were capable of providing a reliable comparison of the abrasion resistance of widely different materials that could be correlated with end-use performance. In addition, the different machines did not correlate very well with each other.

On the basis of a round robin conducted in 1956 by ASTM with six different clear floor coatings evaluated by six different abrasion test methods [4], only two of the methods were found to correlate with actual end-use performance and to have the reproducibility necessary for acceptance as ASTM standards. These were ASTM Test Method for Abrasion Resistance of Organic Coatings by Falling Abrasive (ASTM D968) and ASTM Test Method for Abrasion Resistance of Organic Coatings by Air Blast Abrasive (ASTM D658, withdrawn in 1996). The jet abrader (ASTM D658, withdrawn in 1996) offers greater speed and precision of measurement [1]. More recent comparative testing (see Comparison of Wear Abrasion Testers) indicates ASTM D658 is superior to ASTM D968 and that ASTM Test Method for Abrasion Resistance of Organic Coatings by the Taber® Abraser (ASTM D4060) is superior to both of these tests regarding precision and sensitivity in differentiating between coatings.

MECHANISM OF ABRASION

The success of the particle impingement types of abrasion testers in correlating with service performance is perhaps not surprising when one considers the abrading mechanism. Whether or not a particular type of abrasion test correlates with end-use performance depends not only on a similarity of abrading mechanisms and the abradants used in both cases, but also on the extent to which that mechanism is maintained during the course of the abrasion test. It is on the latter factor that many methods fail.

Rubbing (friction) and scraping methods obviously wear away the test surface in a different manner than methods in which abrasive particles are contacted with the surface. One aspect of the mechanistic difference lies in the angle of contact with the surface. Abrasive particles striking the surface of a coating at nearly normal incidence tend to compress, scar, and cut into the coating. As a result, minute portions of the coating eventually should be crosscut and displaced. On the other hand, the rubbing and scraping types of abrasion that take place at near grazing incidence would tend to undercut and to shear through very thin layers of the coating in successive, irregular slices that ultimately wear it away. Different devices might incorporate various degrees of these basic processes, depending on the angle and force of particle attack.

Apart from the nature of the above mechanisms, it should be apparent that whatever the mechanism, it is not maintained uniformly in friction methods. Such methods suffer from changes in the abrading conditions as the testing proceeds, either because of heating of the specimen or clogging of the abradant or other.

If an abrasion test using the direct impingement of particles is chosen so the undesirable frictional effects are avoided, there may be doubt about whether the method correlates well with a type of service in which the coating is, for example, walked upon. Yet, the previously mentioned ASTM round robin of abrasion tests carried out with floor coatings clearly established the validity of particle-impingement-type tests for evaluating this type of end-use service life.

Until the mechanism of abrasion is more completely studied and understood, industry must continue to rely to a large extent on experimentation and even intuition when devising abrasion test methods. In addition, properly designed test programs must be employed to determine the extent to which a given method correlates with actual end-use performance [1]. A side variety of useful abrasion testing procedures are described in sections that follow.

ABRADANTS

The most sophisticated and precise abrasion testing instruments are only as good as the contact point between the test specimen and the abradant used to wear the specimen. A consistent abrasive material to evenly wear the specimen is key to accurate abrasion testing. The abradant must be consistent from lot to lot. The Taber Abraser uses a variety of resin (Calibrase®) and vitrified (Calibrade®) abrasion wheels containing a wide range of silicon carbide and aluminum oxide grains. The scrub abrasion testers use black nylon or black hog bristle brushes, sponges, abrasive paper, and stainless steel/nylon balls. The Linear Abraser uses abrasive plugs (Wearasers®) containing the same abrasive material as the Taber Abraser wheels. The Falling Abrasive Test uses Ottawa silica sand and silicon carbide. The oscillating sand tester uses silica or alumina zirconia abrasive.

Falling Abrasive Test

This widely used abrasion test method has both ASTM and federal counterparts. Originally developed at Gardner Laboratory the method has been studied and further developed by others [5]. ASTM D968 employs an apparatus, Fig. 1, that is simple and inexpensive compared with other more complicated instruments, and the test results correlate reasonably well with various types of service [4]. However, the method is laborious and time consuming since large

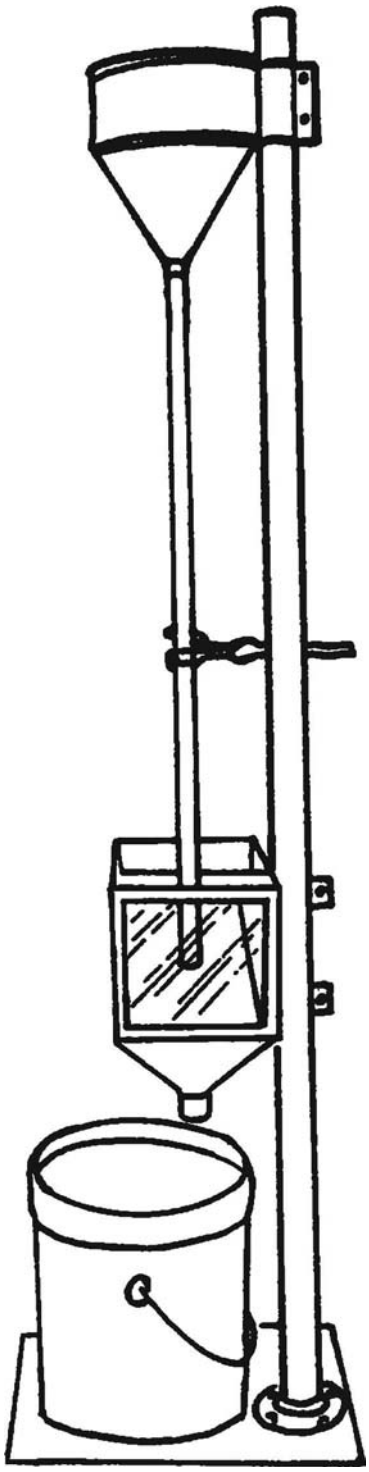

Fig. 1—Falling sand abraser (courtesy of Paul N. Gardner Co.).

quantities of abrasive must be handled due to the slow rate of abrasion, particularly when the material under test is abrasion resistant.

Over the years a variety of abrasives have been used in the basic apparatus. These abrasives include sand, emery, and various grades of silicon carbide. Sand, although having the disadvantage of a slow abrasion rate, is readily available and has given reproducible results at low cost. Therefore, it has been the abrasive of choice in the standard methods. Only sand and silicon carbide are used in ASTM D968, which specifies that a natural silica sand graded to a particular sieve size and known as Ottawa sand is the standard sand abrasive and a silicon carbide of particular sieve size is the other standard abrasive. Abrasion resistance is expressed in terms of the volume of abrasive required to wear through a unit thickness of the coating with the abrasive falling from a specified height through a guide tube. The substrate is supported at a 45° angle to the vertical.

ABRASIVE BLAST METHODS

Air Jet Erosion Tester and Micro-Abrader

These testers shown in Fig. 2 are used to test the erosion resistance of solid materials to a stream of gas containing abrasive particulate. Micro-sized abrasive particles are mixed with pressurized air to generate an abrasive flow. The abrasive flow is propelled and directed through a small nozzle toward the test sample. Material loss, in this case, is achieved via the impingement of small abrasive particles upon the surface of the test sample. Materials such as metals, ceramics, minerals, polymers, composites, abrasives, and coatings can be tested with this instrument. Depending on the test instrument used; the test specimen, temperature, angle of incidence of the jet stream, abrasive particulate speed and flux density, can be varied to best simulate actual conditions.

Fig. 2—Micro-abrader (courtesy of Taber Industries).

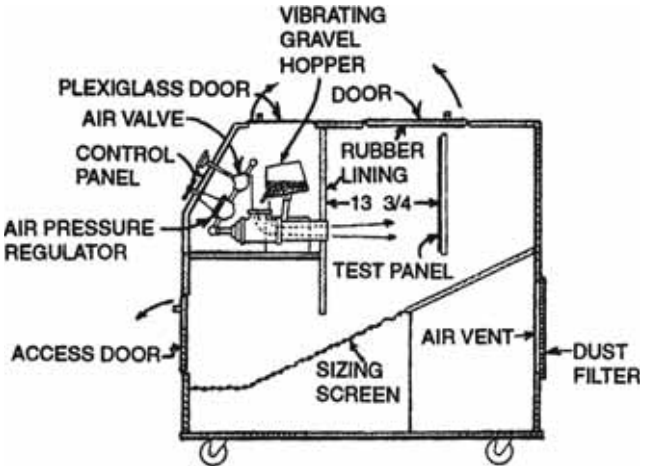

Fig. 3—Interior of a gravelometer (courtesy of the Q-Panel Company).

Gravel Projecting Machine

This machine, which is commonly termed a gravelometer, is a device designed to evaluate the resistance of automotive and railway finishes to abrasion by flying gravel and road ballast. ASTM Test Method for Chip Resistance of Coatings (ASTM D3170) has a description of such a device and provides a procedure for its use. Fig. 3 illustrates the interior components of a device that meets specification given in ASTM D3170. A test chamber is provided in which a coated panel is supported vertically and blasted with a stream of particular gravel. One pint of this gravel is introduced into an air stream having a pressure of 70±2 psi (4.92±0.14 kg/cm^2) over a 10 s period. Tests are usually conducted in a cold room to simulate winter-like driving conditions. At the completion of the test, the coated panel is visually rated for degree of chipping by using a photographic reference standard provided with D3170. SAE Method J400 describes the test procedure used for evaluating the chip resistance of automotive coatings.

METHODS USING ROTATING DISKS

Schiefer Abrasion Testing Machine

(This machine is available from Frazier Precision Instrument Company, Inc., 925 Sweeney Dr., Hagerstown, MD 21740. www.frazierinstrument.com) The machine was designed for measuring wear resistance of textiles such as rugs and fabrics [6–9] but it offers a potentially useful means for evaluating the wear abrasion of organic coatings. It has two unique features: (a) a uniform abrasion pattern and (b) interchangeable steel and Carboloy abradant disks with crosscut and rod patterns that reduce heating and clogging (Fig. 4).

To conduct a wear abrasion test, the specimen is mounted on a motor-driven rotating plate where it is abraded uniformly in all directions by the motion of the offset rotating abradant mounted directly above it. Both specimen and abradant rotate in the same direction with approximately the same angular velocity, 250 rpm, each about its own axis. The axes are spaced 1 in. (2.54 cm) apart and are parallel. The abradant is loaded with a standard weight.

Fig. 4—Schiefer abrasion testing machine (courtesy of Frazier Precision Instrument Company).

METHODS USING ROTATING ABRASIVE WHEELS

Taber® Abraser

(This instrument is available from Taber Industries, 455 Bryant Street, North Tonawanda, New York 14120. www.taber-industries.com) This apparatus, Fig. 5, is widely used for evaluating the wear abrasion resistance of organic coatings. A procedure for its use is given in ASTM Test Method for Abrasion Resistance of Organic Coatings by the Taber Abraser (ASTM D4060), in ISO/DIN Methods 3494 and 4584. ASTM D4060 utilizes a specimen in the form of a 4-in. (10.2-cm)-diameter disk or a 4-in. (10.2-cm)-square mounted on a turntable that is rotated at a fixed speed under a weighted abrading wheel. A wide variety of resin and vitrified abrasion wheels containing a wide range of aluminium oxide and silicon carbide grits create different types of abrasion. An important feature of the Abraser is the wheels traverse a complete circle on the specimen surface. This reveals abrasion resistance at all angles relative to the grain of the specimen. A vacuum pickup is used to remove

Fig. 5—Taber Abraser (courtesy of Taber Industries).

any loose particles generated during actual tests. Wear abrasion resistance is expressed in terms of (a) Wear Index, which is the weight loss per specified number of revolutions (usually 1000) under a specified load (500 or 1000 g), and/or (b) wear cycles per mil, which is the number of cycles required to wear through a 1-mil thickness of coating and is reported as the number of revolutions per mil.

ASTM D6037 Standard Test Methods for Dry Abrasion Mar Resistance of High Gloss Coatings, utilizes two test methods to assess mar resistance by measuring the gloss of abraded and unabraded areas. Mar resistance is directly related to the coating's ability to retain gloss in abraded areas. Test Method A uses a device that contains an abrasive wheel (Taber Calibrase® CS-10 Wheel unless otherwise specified or agreed). Test Method B uses a device that contains a wheel that has been fitted with abrasive paper.

ASTM D1044 Standard Test Method for Resistance of Transparent Plastics to Surface Abrasion describes a procedure for estimating the resistance of transparent plastics to one kind of surface abrasion by measuring the change in optical properties. This test uses Calibrase®, CS-10F Wheels resurfaced on a ST-11 Refacing Stone to create the wear. The abrasive damage is visually judged and numerically quantified by the difference in haze percentage in accordance with Test Method D1003 between abraded and unabraded specimen.

Fig. 6—Taber Grit Feeder Attachment (courtesy of Taber Industries).

Taber® Grit Feeder Attachment

When used with the Taber Abraser, the Grit Feeder, seen in Fig. 6, provides a unique method to evaluate three-body abrasion resistance on a variety of materials. This instrument was originally designed to simulate abrasion caused from grit embedded in leather soled shoes and is typically used to test flooring. Aluminum oxide grit particles are evenly distributed onto the specimen wear path and pass under a pair of leather wheels. This loose grit acts as an abradant and aids in the rolling action that contributes to the physical breakdown of materials. The Abraser Vacuum is attached to the grit feeder, and continuously removes both abraded material and used grit.

In an ASTM round robin, Taber Abraser tests with a series of organic coatings produced abrasion resistance values that exhibited a within-laboratory coefficient of variation of 10 % and an interlaboratory coefficient of variation of 30 %. Another study of the reliability of test results was conducted by Hill and Nick in 1966 [10].

TESTS BASED ON LINEAR MOTION

Straight-Line Reciprocating Machines (Scrub Abrasion Testers)

These machines, as shown in Fig. 7, pull a sled or boat back and forth over the surface of a coated panel. The sled surface can be a brush, a sponge, rubber, or sandpaper. A sled travel of at least 10 in. (25.4 cm) is provided by the machines, and they can provide reciprocating cycles ranging from 35 to 60 per minute.

Both dry and wet surface tests may be performed with these machines. For dry surface tests, wear abrasion resistance is reported as: (a) number of cycles to reach a certain visual end point, (b) degree of abrasion observed after a specified number of cycles, and (c) number of cycles required to abrade through the coating to the substrate.

Procedures for conducting wet adhesion (scrub resistance) tests on interior paints are described in ASTM Test Method for Wet Abrasion Resistance of Interior Paints (ASTM D4213), and ASTM D2486 Standard Test Methods for Scrub Resistance of Wall Paints. Other methods include DIN 52778 and ISO 11998.

In these test procedures, coating films are applied to a plastic substrate and allowed to dry. A sponge surface is mounted on the sled. Both the sled and the coating surface are wet with a soap solution of specified composition. Wet abrasion resistance is reported as: (a) computed rate of

Fig. 7—Scrub Abrasion Tester (courtesy of Byk-Gardner).

Fig. 8—Taber Linear Abraser (courtesy of Taber Industries).

erosion of the wet coating film and (b) number of cycles required to wear through the coating film to the substrate or to produce breaks in the film.

Taber® Linear Abraser

The Taber® Linear Abraser, shown in Fig. 8, utilizes the same abrasive material contained in the Taber Abraser wheels in the form of an abrasive plug (Wearaser®). This instrument is designed to test virtually any size or shape specimen in a wet or dry environment. This instrument can also be modified to evaluate scratch resistance and color transfer. A precision bearing on the spline shaft creates a "free-floating head." As the arm strokes, the abradant follows the contour of the specimen, curved or flat. The user can customize the abradant, stroke length, speed, and weight load. A procedure for its use is given in ASTM Test Method D6279 Test Method for Rub Abrasion Mar Resistance of High Gloss Coatings.

Fig. 9—Taber Large Linear Abraser (courtesy of Taber Industries).

Fig. 10—Taber Reciprocating Abraser (courtesy of Taber Industries).

Taber® Large Linear Abraser

The Large Linear Abraser, shown in Fig. 9, combines a longer test stroke and heavier weight load, than the Taber® Linear Abraser, with a scouring pad to simulate the wear bakeware and cookware receive in extensive home use as it is cleaned.

Taber® Reciprocating Abraser

The Reciprocating Abraser, shown in Fig. 10, referenced in "ISO 1518 Paints and Varnishes—Scratch Test," is used for evaluating resistance to abrasion, scratch, and mar on most flat or slightly contoured objects. A sliding specimen platform moves in a horizontal, reciprocating motion under a stationary tool, generating a linear wear, scratch/mar path.

RCA Abrasion Wear Tester

(This device, is available from Norman Tool and Stamping Co., 15415 Old State Rd., Evansville, IN 47711. www.normantool.com). It is being used for evaluating the abrasion resistance of appliance finishes and of coatings on television set controls. The machine abrades a 2 in. by 2 in. (5.1 cm by 5.1 cm) coated panel surface by passing computer or polyester tape over the surface. A fresh tape surface is presented for each cycle of abrasion. Weights ranging from 55 to 275 g are applied to the tape depending on the nature of the coating under test. Abrasion resistance is reported either as the number of cycles required to produce the onset of visible scuffing or as the number of cycles required to wear through to the substrate.

Oscillating Sand Tester

This testing device, seen in Fig. 11, is used to determine the resistance of transparent plastics and transparent coatings utilized in windows or viewing ports to surface abrasion. The test specimen is mounted in a tray (so that it forms part of the bottom of the tray) and covered with abrasive media to a depth of 12.7 mm. The tray reciprocates in a linear motion at a speed of 300 strokes per minute over a distance of 100 mm. A typical test utilizes a specimen that is 100 nm by 100 mm and is tested for 600 strokes. The results of the test consist of measuring and recording the change in haze

Fig. 11—Taber Oscillating Sand Tester (courtesy of Taber Industries).

and light transmission of the test specimen. This tester is referenced in ASTM F735, Standard Test Method for Abrasion Resistance of Transparent Plastics and Coatings Using the Oscillating Sand Method.

COMPARISON OF ABRASION TESTERS

ASTM Subcommittee D-01.23 conducted a round robin to determine the comparative precision, sensitivity, and correlation of four wear abrasion testing procedures. The procedures were (a) air blast silicon carbide (ASTM D658—discontinued in 1996), (b) falling sand (ASTM D968), (c) falling silicon carbide (ASTM D968), and (d) Taber Abraser (ASTM D4060). The wear abrasion resistance of four coatings with significantly different apparent resistances to abrasion were tested with each device. The results obtained from these tests are recorded in ASTM Report RR D01-1037, which is available at ASTM Headquarters.

From the results, it was concluded that the air blast silicon carbide test and the cycles per mil Taber Abraser test had better sensitivity in differentiating coating abrasion resistances than the other test procedures. The falling sand test, air blast silicon carbide test, and Taber Abraser cycles per mil test ranked the coatings in the same order as the expected performance. The falling silicon carbide test reversed the ranking of two of the coatings. The precision exhibited by the four test procedures are as given in Table 1.

TABLE 1—Comparison of abrasion resistance test method precision

	Coefficients of Variation	
	Within Laboratory	Between Laboratories
Taber Abraser (ASTM D4060)	4 %	16 %
Air Blast Silicon Carbide (ASTM D658)	7 %	10 %
Falling Sand (ASTM D968)	9 %	35 %
Falling Silicon Carbide (ASTM D968)	11 %	45 %

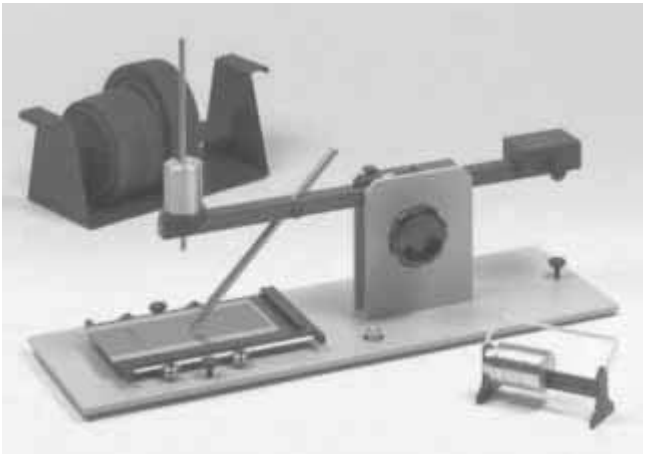

Fig. 12—Balanced Beam Tester (courtesy of Byk-Gardner).

TESTS FOR MAR ABRASION RESISTANCE

Balanced Beam Tester

A useful test for determination of mar resistance involves the use of a balanced beam scrape tester, seen in Fig. 12. ASTM D5178 was developed to determine the mar resistance on smooth, flat surfaces. Results are expressed in terms of force-to-mar films of organic coatings such as paint, varnish, and lacquer when applied to smooth, flat planar panel surfaces. This test is carried out by placing a coated test panel on a movable platform and a weight on the beam. The stylus is lowered gently onto the coated surface and then the platform is pushed against the stylus at a rate of 1/4 in. (6 mm) per second for a distance of at least 3 in. (75 mm). At the end of each stroke, the stylus is raised off the coated panel and the panel is moved slightly to the side to provide a new test surface. The coating is examined for marring. If none is visually observed in the initial scrape, successively greater weights are added to the beam until marring is apparent. If marring is produced in the initial scrape, testing is continued using successively lighter weights until the coating is not marred. The weight required to just produce visible marring is taken as the mar resistance value. Details about the balanced beam tester and its operation can also be found in ASTM D2197, Test Methods for Adhesion of Organic Coatings by Scrape Adhesion, ASTM D2248, Practice for Detergent Resistance of Organic Finishes.

Taber® Shear/Scratch Tester

The Taber Shear/Scratch Tester, seen in Fig. 13, is used to evaluate the scratch and mar resistance of organic coatings, slate, high pressure decorative laminates, and polymeric substrates. A specimen rotates at 0.5 or 5 rpm and the scratching/marring occurs as the specimen comes in contact with either the diamond or carbide tools. An adjustable load is applied to the scratch tool. Mar resistance is reported as the amount of weight required to just produce a barely visible scuffing or loss of gloss. This instrument is referenced in ASTM C217, Weather Resistance of Slate, EN 438-2 Decorative High Pressure Laminates—Resistance to Scratching, ISO 4586-2 High Pressure Decorative Laminates—Resistance to Scratching.

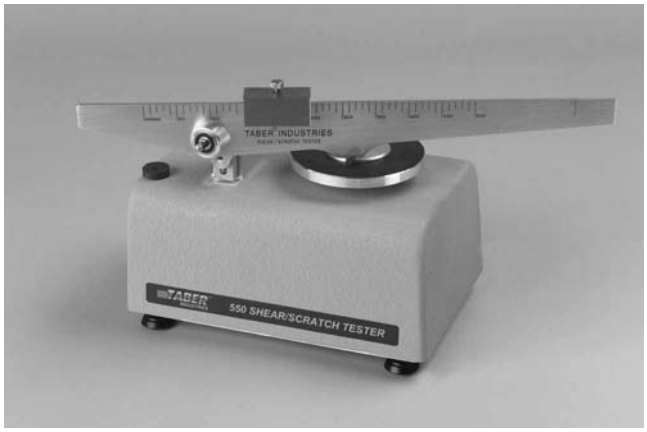

Fig. 13—Taber Shear/Scratch Tester (courtesy of Taber Industries).

Multi-Finger Scratch Tester (5-Finger Scratch Tester)

This testing device, made popular by the automotive industry, can be used for determining the scratch and mar resistance of molded-in-color automotive plastics by use of a linearly oriented, multi-fingered scratching device. Operation involves 1 or 7 mm, individually loaded, hemispherical tips scratching the surface at a constant speed of 100 mm per second. This testing device is seen in Fig. 14.

Coin Mar Test

This test consists of dragging the edge of a coin across the surface of a coated panel and visually determining the degree of marring produced. The procedure can be used as a "pass/fail" test or for comparing the mar resistance of coatings on a relative basis. Results will vary from laboratory to laboratory due to the particular coin used and the pressure used for contact.

Fingernail Test

In this test, the back of a fingernail is dragged across the surface of a coating and the degree of marring is visually observed. The procedure can be used as a "pass/fail" test or for comparing the mar resistance of coatings on a relative basis.

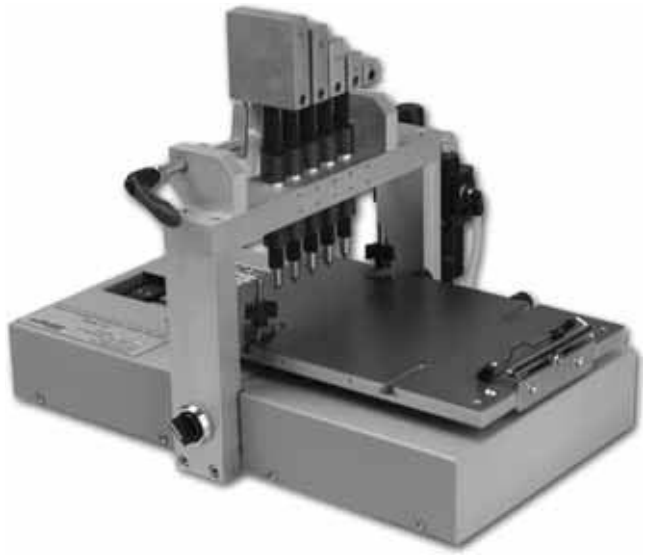

Fig. 14—Taber Multi-Finger Scratch Tester (courtesy of Taber Industries).

Paperclip Mar Test

This procedure is used to determine the ability of a surface to resist scuffing or marring. Scuffing is defined as permanent damage to the coating. An example of scuffing would be a break in the top-coat with visible flakes of coating caused by scraping by the paperclip. A paperclip remains in contact with the test specimen as the specimen is moved in four directions that are parallel to each of the edges of the specimen. The appearance is evaluated for evidence of scuffing or marring.

Nanoscratching

ASTM D7187 Standard Test Method for Measuring Mechanical Aspects of Scratch/Mar Behavior of Paint Coatings by Nanoscratching, covers the nanoscratch method for determining the resistance of paint coatings on smooth flat surfaces to scratch/mar. The loss of appearance is mainly due to surface damages created. This method uses a two step process to quantitatively and objectively measure scratch/mar behavior. Step one is to find the relationship between damage shape and size. Step two is to relate damage shape and size to visual loss of luster.

RAIN OR WATER EROSION

Rain erosion resistance of aircraft coatings has been studied in two types of testing machines [11]—whirling arm and jet. In the whirling arm tester, specimens having an airfoil contour are fastened to the leading edges of the two arms of a propeller-like blade that is rotated at angular velocities equivalent to flying speeds of up to 700 mph. Simultaneously drops of water fall on the whirling arms. Both the simulated air speed and the quantity of "rainfall" can be varied and closely controlled. In the jet-type tester, a high-pressure jet of water impinges on the specimen. A rotating slotted disk in the path of the water jet breaks the stream of water into individual drops to simulate rainfall.

In both of the above methods, having the water in the form of individual drops is a basic principle of the test. This is because the erosion that occurs on the leading edges of the airfoils on high-speed aircraft flying through rain is often the result of cavitation produced by the high-energy impacts of a multitude of individual droplets. At very high velocities, the water droplets, in effect, behave as tiny solid projectiles.

MISCELLANEOUS METHODS

PEI Abrasion Tester

Designed and developed by the Porcelain Enamel Institute to measure the abrasion resistance of porcelain enamels, this tester has also proven to be useful in determining the wet abrasion resistance of organic coatings. It is specified to be used in ASTM C448, Test Methods for Abrasion Resistance of Porcelain Enamels. The tester, which is pictured in Fig. 15, has a gyrating table with positions for nine specimens. Abrasive-retaining rings and lids are clamped over the specimen to form individual test chambers. Each chamber is charged with glass or stainless steel spheres, and a slurry of abrasive particles is added through a

Fig. 15—PEI abrasion tester. (courtesy of National Bureau of Standards).

filling aperture located in the lid. The table gyrates at 300 cycles per minute to cause abrasion of the specimens. The amount of abrasion is evaluated by measuring the loss of gloss or loss of weight in the specimens after a specified time period [12].

Sand on Wheel Tester

This test instrument is used for determining the resistance of metallic materials to abrasion by means of the dry sand/rubber wheel apparatus. The test specimen is pressed against a rotating rubber-rimmed wheel [13]. The test specimen is exposed to three-body scratch abrasion as abrasive grit is introduced between the specimen and rubber-rimmed wheel under a specified load. The intent of this method is to produce data that will reproducibly rank materials in their resistance to abrasion under specified conditions. Test results are reported as volume loss in cubic millimeters for the particular test procedure specified. Materials of higher abrasion resistance will have a lower volume loss. ASTM G65 Standard Test Method for Measuring Abrasion Using the Dry Sand/Rubber Wheel Apparatus.

END POINT MEASUREMENT

Any abrasion test is useless unless an accurate and repeatable endpoint can be reached. Without a precise end, the abrasion test results can be meaningless. The most common methods for determining endpoint are as follows; weight loss of the specimen after the abrasion test, visual loss by inspecting the specimen either with the naked eye or digitally. Those less common methods include gloss loss, haze loss, and change in coating thickness.

Calibration

An important aspect of today's quality systems is the traceability of testing instruments. Verification that the instruments, abradants, and scratch tools are within specification is the core to ensuring repeatable and reproducible test results. Precision testing instruments should be calibrated regularly to ensure accurate results.

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Dynamic Mechanical and Tensile Properties

Loren W. Hill[1]

DYNAMIC MECHANICAL AND TENSILE PROPERTIES are determined in all branches of materials science. There is a large body of published structure/property information that can be integrated with coatings research and development. By using structure/property information, coatings chemists can design and optimize chemical structures of the binder components of coatings. Purposeful and enlightened formulation with well-designed components makes it possible to obtain desirable coatings performance in many cases.

Determination of dynamic mechanical and tensile properties requires the use of free films. This requirement is a serious limitation because many, if not most, of the performance properties of coatings are influenced by coating-substrate interactions. Therefore, tests of coatings intact on their end-use substrates must be thoughtfully coupled with free film determinations. The practical utility of basic methods described in this section is greatly enhanced when results are interpreted in relation to results of adhesion, abrasion, hardness, flexibility, toughness, and internal stress tests as described elsewhere in the manual.

Dynamic mechanical analysis (DMA) and stress-strain analysis (SSA) of tensile properties are complementary methods in several ways. DMA involves very small strains, whereas SSA involves the maximum strain that the sample can withstand. Since the small strains used in DMA usually do not exceed the tensile strength or yield strength of the sample, the method is nondestructive. This feature facilitates property determination over a wide temperature range on a single sample, that is, DMA is often used as a temperature-scanning method. In contrast, SSA data are usually obtained at a single temperature, preferably on an instrument located in a controlled temperature and humidity room. Since the sample is broken in each test, it is very arduous to carry out SSA over a wide temperature range, and SSA is not amenable to temperature scanning.

DEFINITIONS

Tensile Versus Shear Tests

Two types of deformation of a block-shaped sample are depicted in Fig. 1. These deformations are used frequently in property determinations because they can be carried out reproducibly and treated by simple mathematics. In a tension test (Fig. 1 (A)), the sample is pulled apart with straight line application of force, called "uniaxial extension." In a shear test (Fig. 1 (B)), one face of the cube is held stationary and the sample is pushed sideways by application of force at the opposite face. Note that different symbols (ε epsilon or γ) are used for strain in these two tests. A single symbol is used for stress (σ sigma), but subscripts indicate the type of test. In Fig. 1, F is force and A, B, and C are initial sample dimensions. The product $A \times B$ is the initial cross-sectional area.

It is evident in Fig. 1 that strain is defined quite differently in tension and shear tests. In a tension test, strain is the fractional increase in sample length. In a shear test, strain is the distance moved by the movable face divided by sample thickness, i.e., the distance between the stationary and movable faces. In both tests, stress is force divided by cross-sectional area, and modulus is stress divided by strain. Since strain is unitless, stress and modulus have the same units (force/area). It is evident in Fig. 1 (A) that cross-sectional area will decrease as ΔC increases. If the initial cross-sectional area is used to calculate σ_t, the resulting E is called "engineering" modulus. If the change in cross-sectional area is incorporated in the calculation, the resulting E is called "true" modulus.

The relationship between tensile modulus and shear modulus is

$$E = 2(1 + \mu)\mathrm{G} \tag{1}$$

where μ is Poisson's ratio [1,2]. For materials that do not undergo change in volume with strain, $\mu = 0.5$, and Eq (1) becomes $E = 3G$. Experimentally, μ is very close to 0.5 for rubbery materials and slightly less than 0.5 for many thermoplastic polymers [1,2].

Definitions of Dynamic Properties

In dynamic testing, an oscillating strain is applied, and the resulting oscillating stress is measured, or conversely an oscillating stress is applied, and the resulting oscillating strain is measured. Definitions and mathematical treatments do not depend on which of these modes of operation is used. Definitions and symbols used here correspond to ASTM Standard D4092, Terminology Relating to Dynamic Mechanical Measurements in Plastics. Relationships between strain, stress, and time are sketched in Fig. 2 for tensile DMA with application of strain and measurement of stress. The maximum applied strain is ε_0. The maximum resulting stress is $\sigma_{t,0}$. Oscillation is depicted as a sine wave, but whether or not the driver of the instrument in use actually delivers a sine wave oscillation may depend on the particular instrument. The sample is held under sufficient tension so that it remains taut (not slack) even when the oscillating strain is at a minimum.

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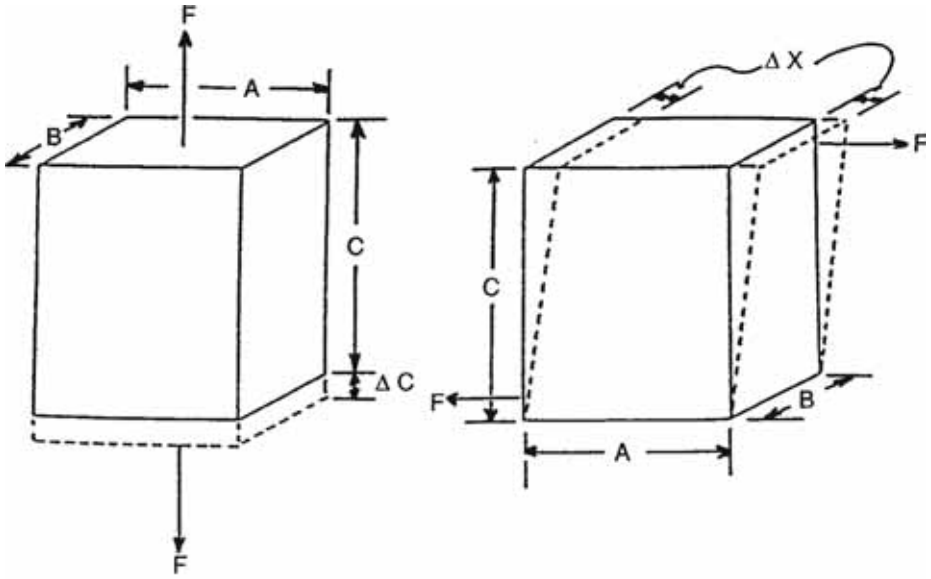

A. TENSILE

ϵ = Tensile Strain

σ_t = Tensile Stress

$$\epsilon = \frac{\Delta C}{C}$$

$$\sigma_t = \frac{F}{AxB}$$

E = Tensile Modulus

$$E = \frac{\sigma_t}{\epsilon}$$

B. SHEAR

γ = Shear Strain

σ_s = Shear Stress

$$\gamma = \frac{\Delta X}{C}$$

$$\sigma_s = \frac{F}{AxB}$$

G = Shear Modulus

$$G = \frac{\sigma_s}{\gamma}$$

Fig. 1—Deformations of test samples: A. tensile, B. shear. The two types of deformation have different definitions and different symbols for strain, stress, and modulus.

The sine waves for strain and stress have the same frequency, but for viscoelastic samples the waves are out of phase by an amount, δ, called the phase lag. Theoretically and experimentally, δ is zero for an ideal (Hookean) elastic solid. If an ideal (Newtonian) liquid could be tested in this way, δ would be 90°. For viscoelastic materials, δ lies between 0 and 90°, and the value of δ is a rather direct indication of viscoelastic character [1–4].

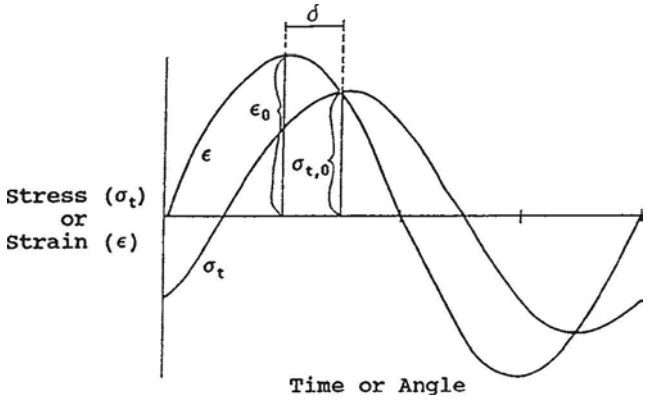

Fig. 2—Applied oscillating strain (ε) and resulting oscillating stress (σ_t) in a dynamic mechanical analysis experiment with tensile deformation. The phase lag (δ) and maximum values of strain (ε_0) and stress ($\sigma_{t,0}$) are indicated.

Definitions of dynamic properties depend on the concept of resolving the stress wave of Fig. 2 into two waves, one that is in phase with strain and one that is 90° out of phase with strain. The in-phase resolved plot represents elastic response, and the 90° out-of-phase resolved plot represents viscous response. In terms of modulus, the separated responses result in the following definitions

$$\text{Tensile Storage Modulus} = E' = \frac{\sigma_{t,0}\cos\delta}{\varepsilon_0} \quad (2)$$

$$\text{Tensile Loss Modulus} = E'' = \frac{\sigma_{t,0}\sin\delta}{\varepsilon_0} \quad (3)$$

$$\text{Loss Tangent} = \frac{E''}{E'}\tan\delta \quad (4)$$

The term "storage" is associated with the elastic part of the response E because mechanical energy input to elastic materials is "stored" in the sense of being completely recoverable. The term "loss" is associated with the viscous part of the response E'' because mechanical energy input to ideal liquids is totally lost through viscous heating. The ratio E''/E' is viscous response expressed relative to elastic response. This ratio reduces to sin δ/cos δ, which is tan δ. Thus, the name "loss tangent" is appropriate.

A check of limiting values of δ is consistent with assignment of elastic and viscous responses in Eqs (2) and (3). When $\delta = 0°$, cos $\delta = 1.0$ and sin $\delta = 0$. By Eq (3), E'' is zero and all of the response is elastic, i.e., E' from Eq (2). When $\delta = 90°$, cos $\delta = 0$ and sin $\delta = 1.0$. Now E' is zero by Eq (2) and all of the response is viscous, i.e., E'' from Eq (3).

DMA relationships in Eqs (2) and (3) relate directly to characterization of samples that are solid or semi-solid. Other objectives of DMA include following viscosity and elasticity changes as the cure of thermoset coatings takes place and determining the melt-flow properties of powder coatings before the onset of cross-linking. When viscous response is the main interest, DMA is often carried out in shear.

The treatment for shear DMA is identical, but with selection of appropriate shear symbols from Fig. 1, the definitions are:

$$\text{Shear Storage Modulus} = G' = \frac{\sigma_{s,0}\cos\delta}{\gamma_0} \tag{5}$$

$$\text{Shear Loss Modulus} = G'' = \frac{\sigma_{s,0}\sin\delta}{\gamma_0} \tag{6}$$

$$\text{Loss Tangent} = \frac{G''}{G'} = \tan\delta \tag{7}$$

Once the experimenters have values of $\sigma_{s,0}$, γ_0, and δ in hand, it is their choice whether to express results in terms of modulus values, Eqs (5) and (6), or in terms of "dynamic viscosity." For dynamic viscosity, the frequency of oscillation, ω in radians per second, is required, but this frequency is usually known. The frequency is required because viscosity is (shear stress)/(rate of shear strain). In a dynamic shear test, rate of shear strain is the product $\omega \times \gamma$. Definitions of dynamic viscosity are:

$$\text{Dynamic Loss Viscosity} = \eta' = \frac{G''}{\omega} = \frac{\alpha_{s,0}\sin\delta}{\omega\gamma_0} \tag{8}$$

$$\text{Dynamic Storage Viscosity} = \eta'' = \frac{G'}{\omega} = \frac{\sigma_{s,0}\cos\delta}{\omega\gamma_0} \tag{9}$$

$$\text{Loss Tangent} = \frac{\eta'}{\eta''} = \tan\delta \tag{10}$$

In the Newtonian liquid limit ($\delta = 90°$), η'' is zero by Eq (9), and all of the response is viscous, η' from Eq (8). Furthermore in this limit, G' is zero by either Eq (9) or Eq (5), and the viscous response could alternatively be expressed in terms of G'' from Eq (6). Thus, in dynamic shear tests, modulus and viscosity determinations are one and the same experiment. Usually experimenters will choose Eqs (5) and (6) when the sample has a lot of elastic character and only a little viscous character, whereas the logical choice for mainly viscous materials having only a little elastic character will be Eqs (8) and (9). In principle, it would be valid to express tensile DMA results in terms of dynamic viscosities as well. This is not done very often, probably because viscosity is strongly associated with shearing experiments, not with tensile experiments. The close association of viscosity with shear is the basis for omitting the word "shear" at the left in Eqs (8) and (9).

The relationships between modulus values defined in Fig. 1 and the dynamic modulus values are [1–4]:

$$E^2 = E^2 + E''^2 \tag{11}$$

$$G^2 = G'^2 + G''^2 \tag{12}$$

Use of complex numbers and quantities such as $i = \sqrt{-1}$ has been avoided here. If readers would like definitions of such quantities as the "complex tensile storage modulus," E^*, they should consult Refs. [1–4]. Complex notation may be convenient for mathematical derivations, but complex modulus values, with their imaginary parts, add little or nothing to the interpretation of structure/property relationships.

Definitions of Tensile Properties

The term "tensile properties" logically refers to all properties that can be determined in tests that involve tensile deformation as depicted in Fig. 1 (A). Common tests that involve tensile deformation include stress-strain tests, creep tests, and stress relaxation tests. Stress-strain tests are used much more frequently than the others. Therefore, the terms "tensile properties" and "stress-strain properties" are often used interchangeably. Creep and stress-relaxation tests are sometimes referred to as "transient tests" because responses, either elongation or stress, change with time and are determined as a function of time [5].

Terminology, definitions, and symbols for stress-strain tests have been taken from earlier editions of the *Paint Testing Manual*. Additional terminology was taken from ASTM standards for various polymeric materials:

D2370	Test Method for Tensile Properties of Organic Coatings
D638	Test Method for Tensile Properties of Plastics
D882	Test Method for Tensile Properties of Thin Plastic Sheeting
D412	Test Methods for Vulcanized Rubber and Thermoplastic Rubbers and Thermoplastic Elastomers—Tension
D883	Terminology Relating to Plastics

In a stress-strain test, the sample is elongated at constant rate. The force, also called "load," required to maintain constant rate of elongation is determined. Force is converted to tensile stress (σ_t) by division by the initial cross-sectional area ($A \times B$ in Fig. 1 (A)). Results are presented as a plot of stress (σ_t) on the vertical axis versus strain (either ε or $100 \times \varepsilon$ = % elongation) on the horizontal axis. A hypothetical example is shown in Fig. 3 [5,6]. The tensile modulus (E) is the slope of the initial, linear portion of the plot (see Fig. 3). If the initial part of the plot is not linear, several calculations for estimating E have been suggested in ASTM D638. Use of the slope for E amplifies the simple definition of tensile modulus given in Fig. 1 (A).

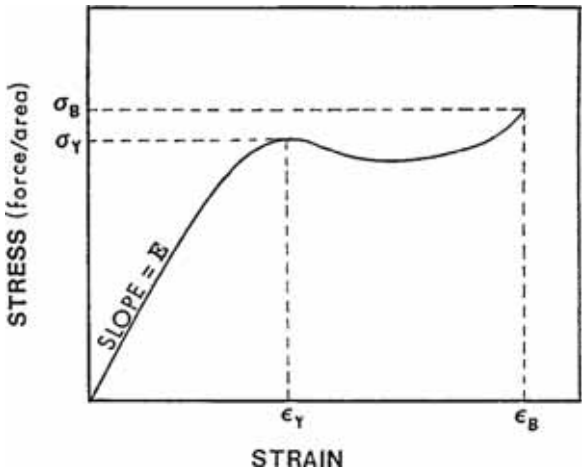

Fig. 3—A hypothetical stress-strain curve for a ductile film. Tensile properties are defined: tensile modulus (*E*), elongation at yield (ε_Y), elongation at break (ε_B), yield stress (σ_Y), and tensile strength (σ_B).

Other terms used for tensile modulus include "elastic modulus," "Young's modulus," and "stiffness."

The first point on the plot of Fig. 3 where the slope is zero is called the "yield point." Strain at the yield point is called "elongation at yield" (ε_Y). Stress at the yield point is called "yield strength" (σ_Y). Elongation is continued until the sample breaks. Strain at the break point is called "elongation at break" (ε_B). Stress at the break point is called "tensile strength" (σ_B) as shown in Fig. 3. However, in some cases (not shown) the stress is higher at the yield point than it is at the break point. In such cases, ASTM standards specify that the "tensile strength" be indicated as the higher value of stress and be designated as "tensile strength at yield." Practice is not uniform with regard to this latter "tensile strength" terminology.

Results of transient tests have not frequently been published for coatings. Such tests clarify viscoelastic character quite directly. Possibly unexpected field failures of coatings could be avoided in some cases if more attention were given to viscoelasticity. Only the most simple form of retardation and relaxation concepts are treated here.

In a tensile creep experiment, the sample is subjected to constant stress, σ_t, and elongation is determined as a function of time, $\varepsilon(t)$. Analysis of dependence of elongation on time yields "retardation time," τ. The simplest mechanical model that permits definition of τ is the Maxwell model as shown in Fig. 4. This model consists of a series connection of an ideal Hookean spring of modulus, E, and a dashpot that contains an ideal Newtonian liquid of viscosity, η. As indicated in Fig. 4, τ is the viscosity of the liquid in the dashpot divided by the modulus of the spring. τ has units of time. Results of the creep experiment for the Maxwell model can be expressed as

$$\varepsilon(t) = \varepsilon(0) + \frac{\varepsilon(0)}{\tau} t \tag{13}$$

When stress is first applied, the spring extends instantaneously by an amount $\varepsilon(0)$. Then retarded further elongation takes place due to flow in the dashpot. It is evident in Eq (13) that the retarded elongation is linear with time. The value of τ can be obtained from the product (reciprocal of the slope) × (intercept) [4,5].

In a tensile stress relaxation experiment, the sample is elongated instantaneously by an amount ε, and thereafter ε is held constant. Stress is determined as function of time, $\sigma(t)$. Analysis of the dependence of stress on time yields "relaxation time," τ. For the Maxwell model, τ values are the same whether from creep or relaxation. For real materials, experimentation is required to determine whether or not retardation and relaxation values are equal. Results of the stress relaxation experiment for the Maxwell model can be expressed as

$$\sigma(t) = \sigma(0) e^{-t/\tau} \tag{14}$$

When the instantaneous elongation is applied, the time zero response is entirely in the spring. Then the dashpot extends with time relieving stress on the spring. It is evident from Eq (14) that the value of τ can be obtained as the time at which stress has been reduced to $1/e$ (0.368) of its initial value. Alternatively, one can obtain the value of τ from the negative of the reciprocal of the slope of a plot of ln $\sigma(t)$ versus t [4,5].

To represent mechanical response of viscoelastic polymeric materials, it is usually necessary to use more elaborate mechanical models and to replace a single value of τ by "a spectrum of relaxation times" [1,2].

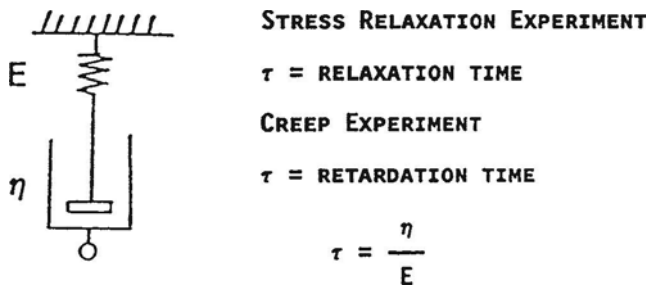

Fig. 4—A mechanical model consisting of a spring and a dashpot permits definition of relaxation time and retardation time.

PREPARATION OF FREE FILM SAMPLES

Methods for preparation and cure of adherent films are described elsewhere in the manual and in ASTM Standard Practice for Producing Films of Uniform Thickness of Paint, Varnish, and Related Products on Test Panels (D823). Since dynamic mechanical and tensile property determinations require free films, ASTM Practice for Preparation of Free Films of Organic Coatings (D4708), is also very useful. Details concerning thickness measurements, which are required for calculation of cross-sectional area, are given in ASTM Test Method for Measurement of Dry-Film Thickness of Organic Coatings Using Micrometers (D1005).

The most widely used method for free film preparation involves application on release substrates, i.e., low surface energy substrates. Four release substrates are described in ASTM D4708. Low surface energy results in poor adhesion so that the coating can be stripped from the release substrate after it is cured. Surface tension differences between the coating and release substrate must be carefully balanced. If the surface tension of the liquid coating is higher than the critical surface tension of the release substrate, the coating will crawl inward from the edges to

give nonuniform thickness. In extreme cases of crawling, the coating will break up into unconnected puddles. There are many types of release paper and many surface treating agents to convert glass or metal panels into low-energy surfaces. It is worthwhile to try several release surfaces to find the balance that will avoid crawling but will still permit separation. Tendency to crawl can be reduced by use of high-viscosity formulations. Viscosities for draw-down application (see ASTM D823) can be quite high compared to those required for spray application.

Thickness is an important consideration in preparation of samples for dynamic mechanical and tensile property tests. Usually tests are more reproducible if samples are thicker than normal coatings thicknesses. However, film formation seldom occurs in exactly the same way for thick films as for thin ones. Several reasons for dependence of cured film properties on thickness have been discussed [5]. In our laboratory, films of 1 mil (25 μm) and up have been analyzed routinely. It has not been possible to analyze or even handle very thin free films such as beverage can coatings, which are approximately 3 to 5 μm thick.

Coatings and thin plastic film samples are usually prepared as rectangular strips, whereas thicker materials are prepared as dogbone-shaped samples. The narrowing in the middle of the dogbone tends to control where failure occurs in tension tests, but for thin samples this narrowing causes the cross-sectional area to be too small for many load measuring cells. The dogbone shape also provides more area for clamping, which facilitates the balance between slip-free clamping and avoidance of rupture at the clamp.

There is extensive literature on the notch sensitivity of polymeric materials in stress-strain tests [7]. The challenge in preparation of high *Tg* coating samples is to avoid undesired notches, nicks, or cracks along the edges. Small edge cracks, which are very difficult to detect even with magnification, can cause premature failure in tension tests. Usually samples are die cut, and the sharpness and condition of cutting edges of the die affect uniformity of sample edges.

DMA

Instruments and Methods Used for DMA

Many DMA practices used for plastics have been applied to coatings as well. The broadest standard practice is:

ASTM D4065 Standard Practice for Plastics—

Dynamic Mechanical Properties: Determination and Report Procedures

Thirteen procedures for applying oscillating strain are diagrammed in D4065, and equations are given for calculating dynamic properties for each.

Other methods are specific to the type of oscillating deformation used:

Test Method for Plastics: DMA

D5023	Flexure—Three Point Bending
D5024	Compression
D5026	Tension (most common for coatings)
D5279	Torsion (sometimes called shear)
D5418	Flexure—Dual Cantilever Beam

One of the reasons for rapidly expanding use of DMA for coatings and other research is a rather long history of improvements in the quality of automation and computer-control of instruments. DMA instrumentation was undergoing rapid change and development in 1995 when the last edition of this manual was published. Eighteen DMA instruments were tabulated for coatings used prior to 1995. A great deal of consolidation has occurred in terms of instruments offered and instrument companies active in DMA. Table 1 lists the instruments used in eleven papers published from 2002 to 2006. A common feature of all these instruments is oscillatory deformation, an example of which is shown in Fig. 2. Variable features include: the type of deformation (tensile, shear, etc.), free versus forced oscillation, frequency scan versus temperature scan versus either, sensitivity for thin film analysis, capability of traversing the entire range of property behavior (glassy to transition to rubbery) during a single temperature scan, breadth and rate of temperature scan, breadth and rate of frequency scan or range and number of frequency settings, versatility of sample holding devices, ruggedness versus flimsiness, amount of attention required once a run has been started, accuracy and versatility of the associated software for control during the run and data treatment and plotting after the run. In several cases, newer models permit determination of properties at several frequencies during a single temperature scan.

TABLE 1—DMA instruments Cited, 2002–2006

Company	Model Number	Number of Citations	References
Rheometrics Scientific	DMTA—3	Four	[29–31,51]
Perkin Elmer	DMTA—7	Three	[35,54,55]
TA Instruments	2980	Two	[32,56]
Polymer Laboratories	PL & (England)	Two	[48,57]

The procedure for carrying out a DMA run on an automated instrument is rather simple, with details depending on the particular instrument. Usually the associated software includes a "run" program that prompts the operator to input sample data (e.g., thickness) and settings for the run such as initial and final temperatures, frequency of oscillation, heating rate, etc. After the input steps, there is usually a cooling period. The instrument takes over when the preset initial temperature is reached. Thereafter nothing is required of the operator until the run is finished. Usually initial and final temperatures are selected to span the glassy region, transition region, and rubbery plateau region. For direct tensile DMA, the run program usually contains a tensioning sub-routine, which provides constant static tension sufficient to avoid slack in the sample in the glassy region and then decreasing static tension as the sample softens in the transition region. Modification of the tensioning sub-routine is often necessary. If tension is too high, films break in the glassy region or are pulled apart in the transition region. If tension is too low, slack results or the oscillatory stress falls below measurable values. Skilled operators soon develop several modified run programs with different tensioning parameters that are suitable for samples of various properties and dimensions. Calibration of DMA instruments is described in E2254 Storage Modulus Calibration of DMA.

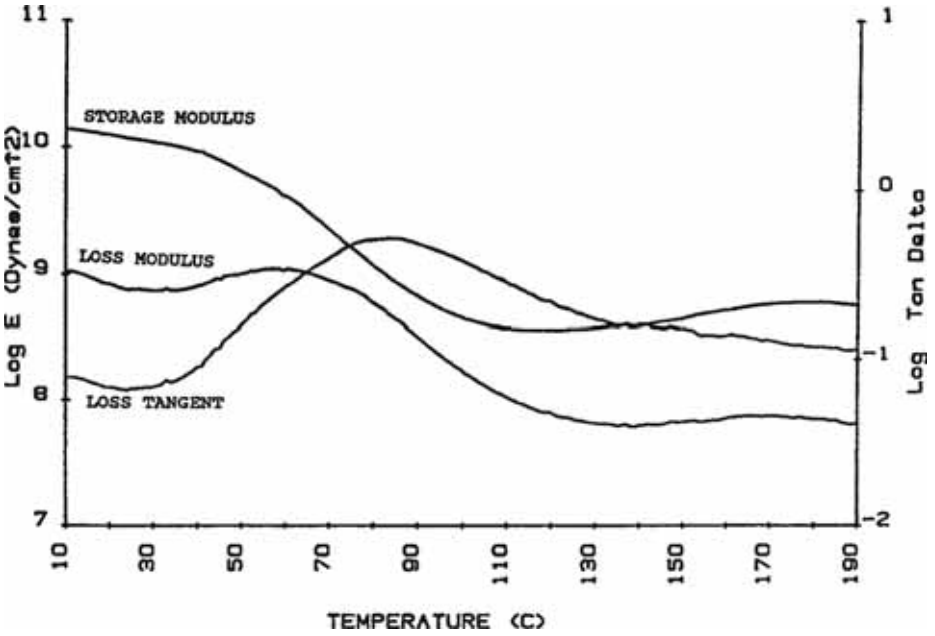

Fig. 5—DMA plots for a clearcoat prepared from an ACR and an etherified MF resin, ACR/MF 70/30. The film was cured before DMA for 30 min at 120°C with 0.5 % para-toluenesulfonic acid. DMA was carried out at 11 Hz. See Table 2 for dynamic properties.

Various support materials, such as glass braids and metal springs or shims, are used when the sample is a viscous liquid and the objective is to follow cure as the coating formulation is converted to a solid. Use of supports makes it difficult to obtain absolute values of E', but relative values are often sufficient for component optimization. The position of peaks in E'' or tan δ plots are usually not shifted when a support is used. When coating samples do not contain solvents, e.g., powder coatings and 100 % active coatings, parallel plate, and cone and plate geometries can be used.

In some cases, DMA is treated as an adjunct to thermomechanical analysis (TMA). The TMA probe is driven up and down in an oscillatory manner as temperature is scanned. General indications of liquid-like character during transitions can be obtained, but quantitative DMA data are not often obtainable in this manner.

Interpretation of DMA Plots

DMA plots are shown in Fig. 5 for a clear film prepared from an acrylic polyol (ACR) and an etherified melamine formaldehyde (MF) cross-linker. Plots are labeled according to Eqs (2)–(4). The storage modulus level at the left is typical of amorphous, unpigmented films in the glassy state. The 25°C data are of interest for comparison with modulus values obtained from the slope of stress-strain plots because SSA is usually carried out at 25°C. The value of E' (25°) from the computer printout corresponding to Fig. 5 is 1.38×10^{10} dynes/cm^2. The same value expressed in other units is 1.38×10^9 Pa or 2.00×10^5 psi (1 pascal = 1 newton/m^2 = 10 dynes/cm^2 = 1.45×10^{-4} pounds-force per square inch). The recommended SI unit is Pa. The value of E'' (25°) is 6.86×10^8 dynes/cm^2. Inserting E' and E'' (25°) values into Eq (11) and solving for tensile modulus, E, we obtain $E = 1.382 \times 10^{10}$. In this case $E = E'$ (25°) to a very close approximation, and the contribution of E'' (25°) to E is negligible. Hard, tough coatings often have tensile modulus values from SSA ranging from 1×10^{10} to 3×10^{10} dynes/cm^2 [5,7,8], in agreement with the DMA value. For a quantitative comparison of E from SSA and E from DMA via Eq (11), the strain rate from SSA would have to be matched with the oscillating frequency from DMA.

The viscous response is not always negligible relative to elastic response, of course. The E'' contribution is highest at the temperature of the maximum in tan δ, 79°C in Fig. 5. Note that E' (79°) is 1.04×10^9 dynes/cm^2, and E' (79°) is 5.15×10^8 dynes/cm^2. From Eq (11), $E = 1.16 \times 10^9$ dynes/cm^2, and E > E' (79°) for this case. If we actually carried out SSA at 79° and a strain rate corresponding to 11 Hz, we would expect to find $E = 1.16 \times 10^9$ dynes/cm^2. During the elongation in SSA, it would not be evident that a significant fraction of the resistance was viscous in nature. However, after the sample broke or was released from the grips, retraction would be delayed (not instantaneous) and part of the deformation would be permanent.

The middle portion of the plots in Fig. 5 represents the transition region where E' drops sharply and both E'' and tan δ go through a maximum. In coatings papers the glass transition temperature is usually taken as the temperature of the maximum in the tan δ plot, and the symbol used for this temperature is T_g. This definition will be used in this chapter. Different assignments and symbols of various transition temperatures are described in ASTM E1640 Standard Test Method for Assignment of the Glass Transition Temperature by Dynamic Mechanical Analysis:

Peak temperature of the loss modulus plot = T_1 (55°C in Fig. 5)

Peak temperature of the tan δ plot = T_t (79°C in Fig. 5)

Intercept of two E′ tangents= T_g (52°C in Fig. 5)

The two tangents in the last assignment are drawn (1) along the glassy portion and (2) through the inflection point in the transition region. The lower transition values

TABLE 2—Dynamic properties of acrylic/MF clearcoat

Frequency, Hz	T_g, °C	Tan δ, max	PW,[a] Δ,°C	E' (min), dynes/cm^2	Temperature of E' (min),°C
3.5	76	0.49	45	3.3×10^8	108
11.0	79	0.49	50	3.6×10^8	112
35.0	83	0.52	55	4.2×10^8	116
110.0	88	0.52	59	4.7×10^8	121

[a]PW is the peak width at half height.

agree more closely with that obtained from differential scanning calorimetry, but the highest value can be obtained with better reproducibility because the tan δ peak is prominent. Coatings often have several binder components, and many coatings are cross-linked. These structural features broaden the glass transition and favor use of the peak in tan δ for assigning T_g. Regardless of the data point selected to represent T_g, it is important to remember that T_g depends on rate of testing for viscoelastic materials.

The effects of changing rate of testing, i.e., frequency in DMA, are shown in Table 2. The 11 Hz data of Table 2 correspond to the run depicted in Fig. 5. A ten-fold increase in frequency results in a 7° to 9° increase in T_g with a slightly stronger dependence on frequency at the higher frequencies. Hartmann [9] noted that a 7°C T_g change per decade change in frequency is used as a "rule-of-thumb." Results of Table 2 are consistent with this generalization. The height of the tan δ peak is nearly independent of frequency, but the width increases with increasing frequency. Very similar dependence of height and width on frequency was observed for lightly cross-linked epoxy films [9]. Values of E' (min) increase slightly with increasing frequency (Table 2). The structural implications of E' (min) will be discussed in the next sub-section.

Height and width of tan δ peaks reflect structural homogeneity and cross-link density. Homogeneous, uncross-linked, noncrystalline polymeric materials of narrow molecular weight distribution usually have tan δ (max) values greater than one and sometimes greater than two. Such tan δ peaks are very narrow. A broader molecular weight distribution results in a wider peak and a lower value of tan δ (max). Introduction of cross-links invariably reduces tan δ (max) and usually increases peak width. For homogeneous cross-linked samples, peak width reflects the broadness of the distribution of lengths of chains between junction points in the network [2,3]. For sound and vibration damping, materials with both high and wide tan δ peaks would be desirable, but height and width cannot be adjusted independently [9]. High peaks tend to be narrow, and wide peaks tend to be low. These observations have resulted in speculation concerning a general comparability of peak areas of the glass transition. Eventually theoretical treatment of peak areas may prove to be useful for structure/property correlations.

Samples that undergo partial phase separation during molecular weight buildup and cross-linking often have very broad transitions [4,9,10]. Manson and Sperling [10] have described the use of interpenetrating polymer networks to limit and control the extent of phase separation. When T_g values of the separate domains are close to one another, a general broadening is observed. When T_g values of the separate domains are considerably different, tan δ plot shapes provide considerable structural information. Observation of two narrow peaks with low tan δ values between them indicates distinct phase separation with little mixing at domain boundaries. Observation to two broad and indistinct peaks with high tan δ values between them indicates diffuse domains with extended regions of varying composition at the boundaries [4,10]. Diffuse domains have also been created in multiblock uncross-linked polymers, and block design has resulted in controlled broadening of tan δ peaks [11].

The relationships between transition width and coating end-use performance have been presented for radiation-cured coatings [12], polyol/melamine thermoset coatings [13,14], gel coats [14], and can coatings [14]. Although the glass transition is emphasized in this section, many polymers are known to have multiple transitions. Low-temperature transitions are observed in DMA as tan δ or E'' peaks that are quite small compared to the glass transition peaks. As discussed in the section entitled "Relationship to Other Mechanical Properties," good impact resistance is often attributed to transitions that produce low-temperature loss peaks.

Interpretation of tan δ peak broadening in terms of structural nonuniformity requires considerable restraint because in some cases broadening is caused by physical or chemical changes that take place during the temperature scan. In some cases, DMA has its own uncertainty principle; the structural features that are under study are changing during the determination. Physical changes include loss of plasticizer or absorbed water and morphological changes such as partial crystallization. Chemical changes include additional cross-linking of thermoset coating during the scan and oxidative or thermal degradation. In general, if the temperature of processing the samples is well above the temperature of the tan δ peak under analysis, there is much less chance that properties are changing during the scan.

Determination of Cross-Link Density

For unpigmented, cross-linked coating films, the level of storage modulus, E', in the rubbery plateau region above T_g is an indication of cross-link density. A wide range of variation has been observed from approximately 4×10^7 dynes/cm^2 for lightly cross-linked films to approximately 2×10^9 dynes/cm^2 for every highly cross-linked films. Increases in E' values in the rubbery plateau have been attributed to increase in cross-link density for many types of studies: increasing cure temperature and cure time [13,16–18], increasing radiation dose in electron beam curing [15],

increasing the stoichiometric balance in epoxy films [2,19] and in polyol/melamine films [13,17,18], increasing the functionality of the cross-linker in radiation cure films [20] and in powder coating [21,22], and increasing the molecular weight of the main film former in acrylic clearcoats [23].

Quantitative aspects of the relationship between E' in the rubbery plateau and cross-link density have been clarified [18]. Cross-link density is defined as

$$\nu_e = \text{moles of elastically effective network chains per cubic centimeter of film} \quad (15)$$

Cross-link density can be calculated using Eq (16)

$$\nu_e = \frac{G'}{RT} = \frac{E'}{3RT} \quad (16)$$

where the storage modulus values, G' or E', are obtained in the rubber plateau, T is temperature in degrees K corresponding to the storage modulus value, and R is the gas constant (8.314×10^7 dynes/degrees K · mole in the cgs unit system). Inserting the 3.5 Hz data from Table 2 ($E' = 3.3 \times 10^8$ dynes/cm^2 and T = 108°C = 381°K) into Eq (16) gives $\nu_e = 3.47 \times 10^{-3}$ moles/cm^3. Since Eq (16) has no correction for frequency dependence of E', a more accurate value would be obtained if frequency were reduced until E' no longer depended on frequency. Extrapolation to zero frequency was used in cross-link density calculations for powder coatings [21]. For a polyurethane film of low T_g but relatively high cross-link density, E' plots were identical in the rubbery plateau at 11 and 110 Hz [18]; thus, no frequency extrapolation was necessary for the is case.

Equation (16) has been called "the ideal network law" with an analogy implied to the ideal gas law [18]. In an ideal network, all chains are elastically effective. Conversion in the network forming reaction is complete, and there are no small loops or dangling ends. For ideal networks formed by functional group reactions of terminally functional (telechelic) starting material, the value of ν_e can be calculated directly from Eq (15). The calculation requires only a balanced chemical equation and an experimental determination of cured film density. For example, consider a tetrafunctional coreactant B_4 (M_n = 3000) cured by a trifunctional cross-linker A_3 (M_n = 300) $4A_3 + 3B_4 \rightarrow$ Ideal Network (density = 1.10 g/cm^3).

The mass of the network formed by this reactions is 10,200 g ($3 \times 3000 + 4 \times 300$), and the volume is 10,2001/.10 = 9273 cm^3. This volume of cured film contains 24 mol of chain ends ($4 \times 3 + 3 \times 4$) coming into junction points in the network. By definition, a chain has two ends; therefore, there are 12 mol of elastically effective chains in 9273 cm^3 of ideal network film. From Eq (15), $\nu_e = 12/9273 = 1.29 \times 10^{-3}$ mol/cm^3.

Equation (17), attributed to Scanlon [18,24], formalizes this type of calculation

$$\nu_e = \frac{3}{2}C_3 + \frac{4}{2}C_4 + \frac{5}{2}C_5 + \ldots = \frac{1}{2}\sum_{f=3}^{\infty} fC_f \quad (17)$$

where C_f is the concentration of *"f"* functional reactant expressed in unusual units, i.e., moles of reactant per cubic centimeter of *final film*. Difunctional reactants contribute to volume but do not increase the number of moles of chains. Therefore, there is no C_2 term in Eq (17).

Ideal network calculations have been carried out for several types of coating such as polyester polyol/melamine films [17], epoxy/diamine films [19], and powder coating films [21,22]. The ν_e values calculated from reactant structures agree remarkably well with experimental ν_e values from Eq (16).

Although ν_e is useful for network characterization, most coating chemists can more easily visualize a network based on the value of M_c

$$M_c = \text{weight of sample in grams that contains one mole of elastically effective chains} \quad (18)$$

If chain lengths in the network vary, one can place a bar over M_c and refer to this quantity as "number average molecular weight of effective network chains." Based on Eqs (15) and (18), the relationship between ν_c and M_c is

$$M_c = \frac{\rho}{\nu_e} \quad (19)$$

where ρ is film density in g/cm^3. For the $4A_3 + 3B_4$ example, M_c =1.10/1.29 $\times 10^{-3}$ = 853 g/mol. For the film of Table 2, the experimental density is 1.12 g/cm^3, and M_c is $1.12/3.47 \times 10^{-3}$ = 323 g/mol. Or course, a high value of M_c corresponds to a loose network and a low value to a tight network.

Equation (16) can be considered empirical or the result of kinetic theory of rubber elasticity [20,24–28]. The theory was developed for networks that have very long chains between junction points. For long chains, conformations can be treated by statistical-mechanics concepts. The chains in networks of greatest interest for coatings are much too short for such treatments. For long chains between junction points, results of the theory are of ten expressed as [20]

$$\nu_e = \nu_c + \nu_p = \frac{G}{gRT} \quad (20)$$

where ν_e is sum of a chemical contribution, is ν_p. The physical contribution is attributed to chain entanglements [28] or physical constraints [25–27]. The factor, g, is related to junction point displacement under stress and is reported to depend on functionality [20,25]. If the reader chooses to use rubber elasticity theory, Eq (16) is obtained from Eq (20) with g = 1.0, $G = G'$, and $\nu_p = 0$ (relative to ν_c). It has been shown that Eq (16) can be derived rather directly for networks made up of short chains such that chain entanglements are minimal [18].

For many years DMA has been used to determine the extent of cure of thermoset coatings. Cross-link density (Eq (16)) and glass transition temperature (from the maximum in the plot of tan δ versus temperature) are used as measures of extent of cure. Recent examples include:

Acrylates cross-linked by hydroxyl alkyl amides [29] (2006)
Catiionic UV curable coatings [30] (2004)
UV cured acrylate/hyperbranched polyester coatings [31] (2003)
Urethane/acrylic hybrid coatings [32] (2005)
Alternative UV cure methods for automotive clearcoats [33] (2004)
High performance all-acrylic coatings [34] (2003)

Pigmented or nanoparticle-reinforced coatings, of course, do not have a direct relationship between E' (min)

and cross-link density. Finely divided particles, as well as cross-links, cause an increase in E' (min). Rodriguez et al. [35] have reported on the effects of varying Pigment Volume Concentration (PVC) on dynamic mechanical properties of epoxy coatings. Soucek and Ni [36] have reported the effect on dynamic properties of varying the content of oligosiloxane ceramer in a polyurethane coating for aircraft.

RELATIONSHIP TO OTHER MECHANICAL PROPERTIES

Knowledge of dynamic properties is useful for optimizing the chemical structure of coating components. When the binder is a copolymer, monomer ratios can be altered to control thermosets, increasing the functionality of the cross-linker is expected to cause an increase in cross-link density. DMA is a very direct method for determining whether purposeful structural changes have actually had the desired effects.

In addition to general structure/property use of DMA, progress is being made in establishing relationships between dynamic properties and the results of paint test methods for hardness, flexibility, impact resistance, and solvent resistance. DMA has some inherent limitations in the establishment of these property/property relationships. The oscillatory deformation, e.g., ε_0 in Fig. 2, is very small. If the paint performance property depends critically on large deformations, a property/property correlation should not be expected. Results of paint performance tests usually depend to some extent on interactions between coating and substrate. When dependence on coating-substrate interactions is dominant, a free film method such as DMA should not be expected to correlate with results of paint tests.

DMA has helped elucidate the causes of reversals in rank orders of hardness among films when different tests are used [5,37]. As described elsewhere in the manual, hardness is determined by penetration, pendulum, and scratch test methods. The most important property for influencing hardness is T_g. However, even for a series of films that have the same T_g, considerable differences are sometimes observed in hardness test results. We have observed that penetration hardness depends more directly on the E' (25°) value than on T_g. Films of the same T_g can have quite different values of E' (25°). Pendulum hardness depends more directly on E'' values than on E' values. This result is expected because damping of the swings of a pendulum depends on conversion of mechanical energy into heat through viscous effects in the coating. As noted earlier, E'' is a measure of viscous response. Films that have nearly the same E' (25°) values and the same penetration hardness can have quite different E'' (25°) values and quite different values of pendulum hardness. The back and forth rolling motion of a Sward Rocker is also damped by viscous effects, and therefore depends strongly on E'' values. In this case, there is also a contribution from sliding friction. Usually pendulum hardness is determined at a single temperature, but Sato [37] describes studies of damping time as a function of temperature. Plots of the reciprocal of damping time versus temperature have exactly the same shape as the tan δ plot for the same films. Both glassy and rubbery materials have low tan δ values as shown in Fig. 5. If a pendulum hardness test is carried out at room temperature on a material that is in its rubbery region at room temperature, a careless interpretation of results is likely to conclude that rubber is very hard. This example illustrates that DMA can be used to understand the results of paint tests more fully.

Among the many scratch tests that have been devised, the most widely used is pencil hardness. Although pencil hardness results are quite reproducible when carried out by one skilled in the art, these results sometimes do not correlate with either penetration or pendulum hardness results. Furthermore, there is no known dynamic property that correlates well with pencil hardness. The plowing action in pencil hardness failures involve large localized deformations. A relation to stress-strain analysis, which also involves large deformation, is more likely.

Flexibility of coatings is often measured by mandrel bend tests and falling weight impact test (see a previous chapter in this book). In thermoplastic polymer studies, good flexibility and impact resistance are often associated with low temperature peaks in E'' and tan δ plots [38]. Rubber-toughened epoxy coatings clearly show the low temperature peak attributable to the rubber phase [39]. Polyester/melamine films have much better mandrel bend performance than do acrylic/melamine films of similar T_g and cross-link density. DMA scans beginning at –100°C show a weak tan δ peak at –70°C for the PE/MF films, but no such peak is observed for the ACR/MF films [18]. In some cases [12,13], extreme broadening of the peak in the E'' plot has been associated with improvements in flexibility of coatings.

Pigments often increase the toughness of coatings without broadening the transition or introducing low-temperature loss peaks [15]. The main effect of increasing pigment volume content (PVC = 0 to 55 %) on DMA plots is to increase E' values moderately in the glassy region and strongly in the rubbery plateau [15]. Values of T_g often increase by about 5 to 10°C at PVC = 0.4 relative to the corresponding clear coatings [15].

Solvent resistance as measured in methyl ethyl ketone (MEK) double rub tests is related to E' values in the rubbery plateau, i.e., to cross-link density [5,13]. MEK resistance also depends on the solubility parameter of the coating. Although the double rub test is widely used to determine the degree of cure of thermoset coatings, the only ASTM method adopted relates to zinc-rich primers (D4752). Relationships between the number of double rubs and E'(min) values are quite reproducible within a coating type but not from type to type. For example, with acrylic clearcoats, 200 double rubs are obtained when E'(min) = 2×10^8 dynes/cm^2 [13]. Films of this type having 50 to 100 double rubs typically have E' (min) values in the range of 5×10^7 to 1×10^8 dynes/cm^2. In contrast, polyester polyol powder coatings, cured with several types of cross-linkers, yielded 200+ double rubs despite having E' (min) values as low as 5×10^7 dynes/cm^2 [22]. The lack of generality in the relationship of MEK resistance to E' (min) for various coatings types is believed to result in part from differences in solvent-polymer interactions. There may also be a weak dependence of MEK resistance on T_g as well as a strong dependence on E' (min).

DETERMINATION OF TENSILE PROPERTIES

Description of SSA

Instrumentation for SSA is described in detail in the ASTM test methods listed in the section of this chapter entitled

"Definitions of Tensile Properties." In most cases, specific instruments are not identified, apparently to avoid commercial implications, but it is generally known than Instron® instruments (Instron Engineering Corp.) are widely used. For organic coatings, the most suitable test method is usually ASTM D2370. However, other tension test methods contain additional useful information. ASTM D638 is useful for selection of metric units and units consistent with SI recommendations. ASTM D882 has rather extensive data on statistical treatments for plastic sheeting, but the statistical methods could be beneficially applied to coatings films. For certain types of coatings, such as flexible primers or coatings for plastic substrates, rubbery behavior is expected, and ASTM D412 provides useful information such as data treatment when a crack moves slowly across the sample as opposed to the more usual instantaneous failure mode. Often stress-strain curves do not start out with constant slope as shown in Fig. 3, but instead have an initial curvature caused by takeup of slack. The initial curved portion is called a "toe," and toe compensation is described in ASTM D638 and in ASTM D882. Some stress-strain curves have no linear (i.e., no Hookean) region from which to calculate the slope for modulus values. In such instances, the "toe corrected" origin and another point on the curve are joined by a straight line. The slope of the line is reported as the "secant modulus." The elongation percentage at the second point selected is always reported along with the value of secant modulus. Graphical illustrations of secant modulus determinations are given in ASTM D638 and in ASTM D882. Among the various test methods, D638 contains the most complete list of definitions and symbols.

Determination of "tensile energy to break" is described in ASTM D882. The area under the stress-strain curve, e.g., see Fig. 3, is divided by sample volume to obtain this quantity, which has also been called "work-to-break" or "toughness" [5]. Recommended units are megajoules per cubic meter. ASTM D882 describes how an integrated chart paper area (distance^2) can be converted to energy/volume by using the ordinate setting (force/distance of chart paper), the abscissa setting (distance of elongation/distance of chart paper), and the sample dimensions. Now that computers are used to control operation and to treat data for SSA [40], numerical integration is nearly instantaneous, and tensile energy to break is likely to be reported more often. This SSA property may prove to be useful for correlations with paint test results.

Interpretation of Stress-Strain Curves

Schematic stress-strain curves for various types of polymeric materials are shown in Fig. 6 [2]. This extremely wide range of property variation is represented in coatings of various types. Scales on the graphs give an order-of-magnitude indication of property values. Brittle materials (6*A*) have high modulus values (initial slope), tensile strengths up to about 8000 psi (5.5×10^7 Pa = 5.5×10^8 dynes/cm^2), and elongations below 10 %. Ductile materials (6*B*) usually have lower initial slopes, tensile strengths in the 4000 to 6000 psi range, and elongations of about 100 %. The upper plot in 6*B* corresponds to yielding with uniform sample deformation between the grips. The lower plot in 6*B* corresponds to a ductile sample that necks down at the yield point, and further elongation (~40 % to 110 % in Fig. 6) occurs with increase in length of the necked part of the sample. Elastomeric (rubbery) samples (6*C*) have much lower initial slopes than brittle materials, tensile strengths of about 2000 psi, and elongations of the order of 400 % to 500 %. The upward curvature near the end of the lower plot in Part C is attributed to strain-induced crystallization [2].

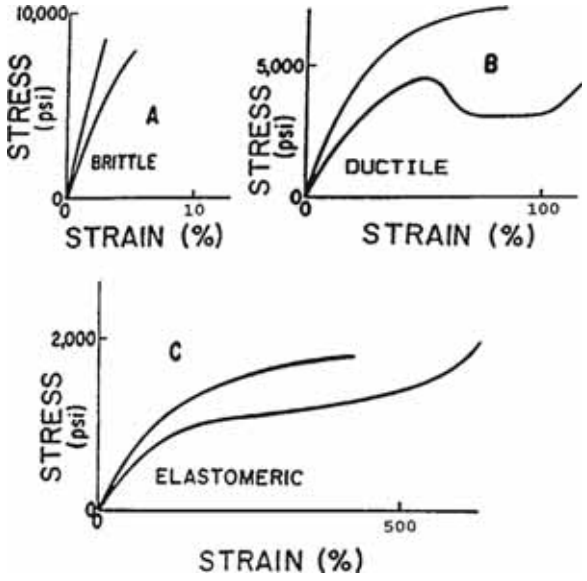

Fig. 6—General kinds of stress-strain curves for various types of coatings. Scales indicate order-of-magnitude values.

Materials represented in 6A and 6B of Fig. 6 have T_g values above the test temperature. Therefore, modulus values depend on secondary interactions of polymer chain segments and partial crystallinity, if any exists. The elastomeric material (6*C*) has T_g well below the test temperature. Therefore, modulus values depend in part on cross-link density, chain entanglements, or both.

Stress-strain curves are carried out at a constant rate of strain and results depend on strain rate selected. In general, a higher rate results in higher modulus. The two curves in 6*A* could represent the same material strained at different rates. In fact a large increase in strain rate could cause the plots of 6*B* to be converted to the plots of 6*A*. Dependence on strain rate is evidence of viscoelasticity. Strain rate dependence in SSA, therefore, has the same origin as dependence on oscillatory frequency in DMA (see Table 2).

A recent study of silicone-epoxy resins cross-linked with amines of various functionality [40] illustrates the extreme range of stress-strain properties exhibited by coating films. Tensile strength ranged from 31 to 4418 psi. Percent elongation ranged from 7 % to 177 %. Unfortunately, neither modulus values nor tensile energy to break were reported. Property variations were attributed to differences in degree of entanglement and to partial phase separation. In a network-forming thermoset system, it would be impossible to get a tensile strength as low as 31 psi unless incompatibility had prevented occurrence of the network-forming reaction.

Examples of all types of behavior shown in Fig. 6 are represented in a single figure for coatings used on naval aircraft [41] (see Fig. 4, Ref. [41]). One plot shows results for a polysulfide sealant that has a tensile strength of about 250 psi and an elongation >130 %. Results for a flexible polyurethane primer are a tensile strength of 3500 psi, a

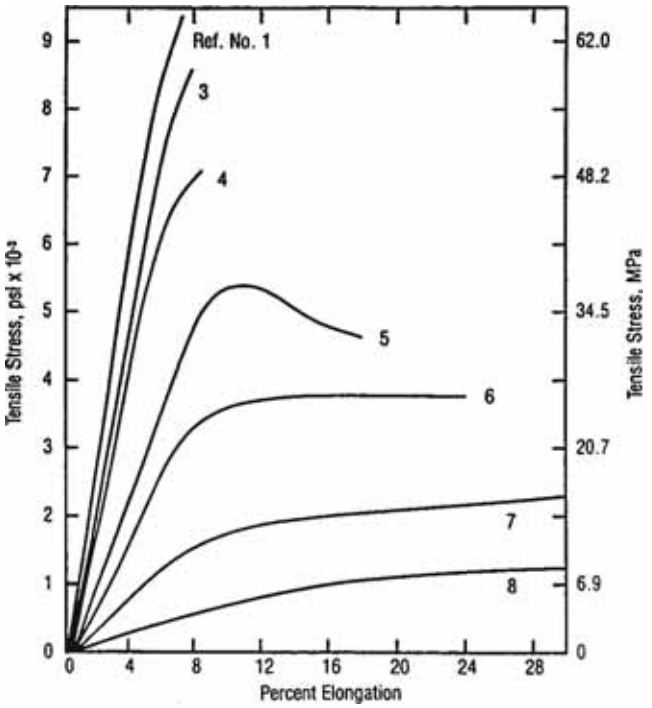

Fig. 7—Stress-strain curves for UV-cured cycloaliphatic epoxide films flexibilized with oligomeric propylene oxide triol. Strain rate is 40 % per minute. See Table 3 for tensile properties.

yield strength of 3200 psi, an elongation at break of 90 %, and an elongation at yield of 40 %. The plot shows that a polyurethane topcoat yields and breaks at about the same point: 4000 psi and 22 % elongation. The plot for an epoxy primer shows brittle behavior (no yield point), a tensile strength of 2300 psi, and an elongation at break of 7 %. The authors [41] report that replacing the epoxy primer by the flexible polyurethane primer eliminated the need for the sealant coat.

SSA has been used extensively to characterize cationic UV-cured cycloaliphatic epoxy/polyol coatings [42–44]. The mechanism of introduction of polyol is a chain transfer step [34], which permits use of a wide range of epoxy:polyol ratio without need for stoichiometric balance. Selection of flexible polyols with this wide formulating latitude permits preparation of cross-linked films with an extremely wide range of mechanical properties. Numerous stress-strain curves have been presented for this type of system with oligomeric propylene oxide polyols [43] and with oligomeric caprolactone polyols [44]. Examples of stress-strain curves for a cycloaliphatic diepoxide (CYRACURE® UVR-6110, Union Carbide) and a propylene oxide triol (*MW* = 702) are shown in Fig. 7 [43]. The corresponding tensile properties are given in Table 3. Films from Compositions 1 through 4 all give brittle failure (compare Fig. 6(A)) and only moderate changes in tensile properties (Table 3) despite a large change in composition. At Composition 5 (70/30 epoxy:polyol, see Table 3) a yield point is first noted, and thereafter very large property changes occur despite relatively small changes in composition. Compositions in the 4 to 6 range (see Table 3) are reported to give excellent post formability, as required for coatings on beverage can ends, while maintaining adequate hardness and solvent resistance [42–44].

Relationship to Other Mechanical Properties

SSA is used in a general way to assess suitability of a binder for various coating end uses. Most coating chemists associate modulus with coating hardness and percentage elongation at break with coating flexibility. Quantitative correlations of these properties are not published very often, however. The lack of published correlations may result from the fact, noted above, that paint tests of adherent coatings depend on coating-substrate interactions, whereas SSA is carried out on free films. ASTM Test Method for Elongation of Attached Organic Coatings with Conical Mandrel Apparatus (D522) describes how to calculate percent elongation from the crack length in a conical mandrel bend test. Comparison of elongation of adherent coatings by the conical mandrel method and elongation of the same coating as a free film from SSA would certainly be of interest, but such comparisons were not found in the literature.

TABLE 3—Tensile properties (strain rate, 40 %/min) of UV-cured cycloaliphatic epoxide films flexibilized with oligomeric propylene oxide triol

Film Number[a]	Composition[b]		Tensile Modulus,[c] psi	Tensile Strength, psi	Elongation, %
	Epoxide, wt %	Triol, wt %			
1	90.0	10.0	3.88×10^5	9.5×10^3	6.6
2	85.0	15.0	3.72×10^5	8.9×10^3	6.6
3	80.0	20.0	3.33×10^5	8.4×10^3	7.4
4	75.0	25.0	2.95×10^5	7.0×10^3	8.1
5	70.0	30.0	2.05×10^5	4.3×10^3	16.2
6	66.7	33.3	1.48×10^5	3.7×10^3	24.3
7	63.4	36.6	0.70×10^5	2.5×10^3	54.0
8	60.0	40.0	0.26×10^5	2.0×10^3	88.4

[a]Keyed to the plots in Fig. 7.
[b]Weight % of polymeric binder. (Films also contain 2.9 wt % photoinitiator and 0.5 wt % flow agent.)
[c]1% secant modulus. (The modulus range expressed in pascals is 2.68×10^9, No. 1, to 1.79×10^8, No. 8.)

The logic of associating yield behavior in SSA with post formability of coil coated metal was noted in 1977 [45].In 1987, Koleske [43,44] confirmed that compositions that exhibited a yield point performed well in the demanding post-forming operations carried out on beverage can ends.

Evans and Fogel [46] provided convincing evidence that gloss retention during abrasion of floor coatings is related to the area under stress-strain curves. This area, divided by sample volume, is called "work-to-break" or "toughness" as noted previously. The authors provide a clear example of the need to match strain rates when attempting to correlate SSA results with paint test results.

The field of Fracture Mechanics was well established for analysis of cracking of plastics by the 1980s, but coatings publications using Fracture Mechanics concepts began in the 1990s. In 1992 Gregorovich and McGonigal [47] reported that "the essential work to break," obtained from SSA plots with notched samples, correlated with resistance to car wash marring of automotive topcoats. In 2005, Sadati et al. [48] analyzed scratch resistance of clear coats based on fracture energy. In 1998 Nichols et al. [49] analyzed the fracture energy of automotive clearcoats using Fracture Mechanics, and in 2002 Nichols [50] used Fracture Mechanics concepts for anticipating paint cracking during weathering. In 2006 Skaja et al. [51] combined DMA and SSA data in analysis of mechanical property changes during accelerated weathering of polyester-urethane coatings. In 2001 Soucek et al. [52] analyzed fracture toughness of inorganic-organic hybrids, and in 2002 Soucek and Ni [36] used SSA and Fracture Mechanics to determine mechanical properties of nanostructured polyurethane ceramer coatings for aircraft.

Failure of attempts to correlate pencil hardness with penetration hardness, e.g., Tukon Hardness, probably result because the former has a strong requirement for toughness, whereas the latter is more dependent on the modulus value at room temperature.

DMA is much more generally applicable to determination of cross-link density (see the chapter subsection entitled "Determination of Cross-Link Density") than is SSA. If the *Tg* of a coating binder is well below the temperature at which SSA is carried out, then the modulus from the initial slope of the stress-strain curve is a rubbery plateau modulus and Eq (16) is valid at least in principle. In practice, curvature in stress-strain curves and permanent deformation usually result in inappropriate modulus values. An innovative approach to avoiding the permanent deformation problem consists of reversing the extension mode of SSA so that a retraction plot is also obtained. Hergenrother [53] has applied this tensile retraction method for determination of cross-link density of elastomeric polyurethanes.

CONCLUSIONS

A wide range of automated and computer-controlled instruments is available for determination of dynamic mechanical and tensile properties. Careful review of variable features is necessary to insure suitability for property determinations on coating samples of normal thickness. Determination of basic physical properties makes it possible to integrate structure/property knowledge from many polymer fields with coatings research and development. Free film coating data are much more useful when thoughtfully interpreted in relation to results from tests carried out with films intact on their end-use substrates. This review includes many examples that illustrate the benefits of combining DMA or SSA data with results from well controlled and documented tests as provided by the ASTM. The goal of much of the discussion provided here is better understanding of hardness, flexibility, post-formability, solvent resistance, and abrasion resistance.

DMA and SSA are often complementary because strains imposed on test samples are very different. SSA provides information on yield behavior and failure at high strains. DMA provides low strain properties and reveals the viscoelastic nature of coatings very directly and quantitatively.

For unpigmented thermoset coatings, values of storage modulus, E', in the rubbery plateau can be used to calculate cross-link density. Determination of cross-link density usually makes it possible to confirm or deny that purposeful reformulation or changes in resin structure have had the desired effects.

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Flexibility and Toughness

John Fletcher[1] and Joseph Walker[2]

PREFACE

IN PREPARATION OF THIS CHAPTER, THE CON-tents of the fourteenth edition were extensively drawn upon. The authors acknowledge the author of the fourteenth edition, Mark P. Morse. The current edition will review and update the topics as addressed by the previous author, introduce new technology that has been developed, and include up-to-date references. This chapter is an abridged and modified version of the chapter entitled "Flexibility," written by Garmond G. Schurr, found in earlier editions of this manual.

DEFINITIONS

For a coating to meet its service requirements it must exhibit appropriate properties of flexibility and toughness to withstand cracking when it is subjected to stresses produced by shrinking or swelling, forming, mechanical abuse, and weathering. Flexibility is the ability of a material to be bent or flexed without cracking or undergoing other failure. Toughness is the strength and resilience of a material; it is the material's ability to withstand great strain imposed in a short time period, such as an impact, without tearing, breaking, or rupture.

INTERPRETATION

The flexibility of a coating applied to a substrate depends not only on its ability to expand by pressure from within the film, distensibility, but also on the coating thickness and on the adhesion between coating and substrate. Good adhesion tends to give better apparent flexibility than does poor adhesion. The toughness of a coating is dependent on its hardness, stiffness, resiliency, distensibility, and the existence of an energy dissipation mechanism that operates at temperatures far below room temperature and is discernable by dynamic mechanical measurements made over a broad temperature or frequency range.

Generally, the bend and impact tests used to evaluate flexibility and toughness are much more severe than actual service conditions. This is because the tests are usually performed on relatively fresh, un-aged coating films. Since coating films tend to lose flexibility during use due to the loss through volatilization of free plasticizing components and chemical changes such as degradation, cross-linking, and the like, these severe tests that exceed normal operational expectations are useful in predicting long-term serviceability [1].

BASIC PROPERTIES AFFECTING COATING PERFORMANCE

Both flexibility and toughness depend on very basic properties: the viscoelastic behavior of the coating and its physical transitions and relaxations. The following is a discussion of these properties taken from a paper by Skrovanek and Schoff [2].

Coatings, as the polymers from which they are prepared, are viscoelastic in nature, that is, they behave both as viscous liquids and as elastic solids. The coatings have elastic recovery and yet will flow with time when placed under a stress. In general, viscoelastic behavior and mechanical properties are markedly affected when a coating enters the glass transition, softening point, or other relaxation. To be certain that the properties of a coating will fulfill the needs of its intended use, the viscoelastic behavior of the coating should be measured, controlled, and designed to meet the particular end use.

The softening point of a coating can be used as an index of flexibility. The softening point is between the temperature where the coating changes from being hard and glassy and the temperature where it is leathery or rubbery. For example, if a coating has a softening temperature region near the temperature of the forming operation, the coating is less susceptible to failure by cracking or a similar mechanism than if the softening region is above the forming temperature. Measurement of energy storage (related to elasticity) and energy loss (related to viscous losses) as a function of temperature is a means of predicting impact resistance.

Impact resistance of a paint film can be considered as energy dissipation by vibration or rotation of various molecular segments so that at no time will sufficient energy be focused to cause fracture. Since the impact tests performed on paint films often produce deformations beyond the elastic limit of the films, flow within the films must take place or fracture will occur [3].

To obtain good impact resistance, the paint film must consist of a polymer that has a sufficiently high molecular weight to have strong intermolecular entanglement (and therefore, high tensile strength), but sufficiently low viscosity (by choice of proper molecular constituents and limiting molecular weight) that flow and accompanying energy dissipation will take place.

Polymer viscosity increases as molecular weight increases so that polymers with very high molecular weights will have greater flexibility than those polymers

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with intermediate or low molecular weights. At the same time, molecular weights below the critical molecular weight for entanglement lead to very low tensile strengths and the mechanical behavior observed is brittleness. It has been found that modulus is the dominant factor in the relationship between the tensile properties of a coating and its impact resistance [4].

In addition to dynamic mechanical behavior, the relaxation behavior as measured by dissipation or damping of coatings has been determined by application of dynamic electrical tests [5]. In a dielectric relaxation test, a periodic electrical potential is applied to the sample coating situated between a pair of electrodes. The dielectric constant and dissipation factor are measured as a function of frequency and temperature.

TECHNIQUES FOR MEASURING BASIC VISCOELASTIC PROPERTIES

Thermal Mechanical Analyzer (TMA)

This instrument employs transducers to sense the position of a vertical rod that rests on the surface of a coating sample. The instrument is usually equipped with a furnace and program planner so that heating, cooling, and isothermal temperature operations can be employed.

With its use, softening points and glass transitions can be determined from plots of coating indentation as a function of temperature. Also, changes in stresses within a coating at a constant temperature (creep) can be determined from plots of indentation versus time [2].

Dynamic Mechanical Thermal Analyzer (DMTA)

This instrument produces vibrations in a coating film over a wide frequency range and/or temperature range. It can scan a wide range of sample temperatures at different rates. The resulting deformations from the sinusoidal applied stresses are analyzed to compute values related to energy storage and energy loss [2].

Tensile Testing

Tensile testing of organic films can measure tensile strength, modulus and elongation of the coating materials. The area under the stress-strain curve can be used as a measure of the toughness of the coating.

EXTERNAL FACTORS AFFECTING FLEXIBILITY AND TOUGHNESS

Flexibility and toughness are not constant characteristics of a specific coating. A number of external factors affect these properties.

Humidity

Water is a good plasticizer for almost all paint films in that it preserves the flexibility and adhesive power of the film. A change in relative humidity of as little as 2 % can be detected in flexibility measurements. Some paint films, such as those based on latexes, imbibe moisture very rapidly, whereas others reach equilibrium with the atmosphere very slowly. It is imperative that tests for flexibility and toughness are conducted in an atmosphere of controlled relative humidity and that the specimens are conditioned in that atmosphere for a day or more before the tests are performed. Generally, flexibility and toughness tests are carried out at a relative humidity of 50 ± 5 %. The 10 % tolerance is needed because of the difficulty in more accurately controlling relative humidity in most laboratories. If the environment cannot be controlled at this recommended level, then the relative humidity should be measured and reported along with the mechanical properties.

Temperature

The flexibility and toughness of coatings are dependent on temperature. This is particularly true of thermoplastic coatings, but it also is a factor for thermoset coatings. These coatings have a definite second order transition temperature known as the glass transition temperature, T_g. Coatings at a temperature below T_g are hard and brittle with poor flexibility and impact resistance unless there is an auxiliary loss mechanism below T_g or below the temperature at which the coating is used, as exists in polycarbonates that have a high T_g of about 160°C (at 1 Hz) and yet have excellent impact resistance because of a relaxation that occurs at about –90°C (at 1 Hz). If coatings do not have this type loss mechanism, at temperatures just above T_g they are flexible, and at temperatures substantially above T_g they tend to develop viscous rather than elastic properties. There is a tendency for all thermoplastic coatings to have identical flexibility properties if these properties are measured at the same temperature relative to T_g, for example, at 10°C above T_g [1,6].

Flexibility and toughness measurements are usually made at a temperature of 25 ± 1°C after the coatings are conditioned at that temperature. However, there are many instances when test are performed at lower temperatures as might be encountered in cold climates.

Strain Rate

Strain rate is the rate at which a coating specimen is elongated and is usually expressed in percent per minute, in./in./ min or cm/cm/min. This is the rate of extension relative to specimen size. That is, if a specimen 10 cm long is elongated at a rate of 1 cm/min, it is the same as a specimen 1 cm long being elongated at a rate of 0.1 cm/min (1 mm/min). In both cases, the strain rate is 10 % per min.

Strain rate has a great influence on the flexibility and toughness of a coating. In general, the effect of increasing the strain rate is similar to decreasing the coating temperature, that is, as the strain rate is increased, flexibility and toughness decrease.

There can be critical strain rates where flexibility has sharp changes, which are very similar to the effects produced at the glass transition temperature [7]. This means that the strain rate used in a test must be closely controlled. In some tests, such as a bend test, this is difficult to do. This also means that tests performed at a low strain rate (cupping test) are likely to produce different flexibility ratings than those produced by a high strain rate (conical mandrel test) [1,7].

It should also be noted that the temperature and humidity of the test are significant in the results that are obtained and should be noted as part of the test result.

FLEXIBILITY AND TOUGHNESS MEASUREMENTS

Mandrel Bend Tests

Both conical and cylindrical mandrels are used for evaluating the flexibility of coatings. Even though it is difficult to control the strain rate in these manually operated tests,

Fig. 1—A conical mandrel bend tester (Reprinted by permission of Elcometer Inc.).

they can provide very useful flexibility ratings and are often used to evaluate coatings applied to metal test panels.

Conical Mandrel Tests

A conical mandrel test consists of manually bending a coated metal panel over a cone. As described in ASTM D522, Standard Test Methods for Mandrel Bend Test of Attached Organic Coatings, Test Method A, a conical mandrel tester consists of a metal cone, a rotating panel bending arm, and panel clamps. These items are all mounted on a metal base as illustrated in Fig. 1. The cone is smooth steel 8 in. (203 mm) in length with a diameter of $\frac{1}{8}$-in (3.2 mm) at one end and a diameter of 1.5 in. (38 mm) at the other end.

When a coating is applied on a $\frac{1}{32}$-in (0.8 mm)-thickcold-rolled steel panel, as specified in ASTM D522, a bend over the mandrel produces an elongation of 3 % at the large end of the cone and of 30 % at the small end of the cone. The coated panel is bent 135° around the cone in approximately 1 s to obtain a crack resistance rating under simulated abuse conditions. In some instances, longer bend times have been found to be useful. For example, if the percent elongation of the coating at the point of cracking is to be determined, the method specifies a bend time of 15 s. ASTM D6905, Standard Test Method for Impact Flexibility of Organic Coatings, describes a procedure for determining the ability of a coating and its substrate to resist shattering, cracking, or chipping when the film and the substrate are distended beyond their original form by impact. This test method references D522 but states that D6905 is perhaps a better way to apply the test using a rapid application of the force. Since the impact is almost instantaneous the problems associated with time variables in the mandrel tests are eliminated.

Since variations in temperature and humidity can affect mandrel bend tests, it is imperative that the coated panels be conditioned at a standard temperature and relative humidity before performing the test, which is conducted under the same conditions.

Film thickness will also influence the results of the test and therefore the thickness of the film should be reported along with the temperature and humidity conditions.

The crack resistance value of a coating is obtained by measuring the distance from the furthest end of the crack to the small end of the mandrel. This distance is converted to cone diameter by means of a plot given in ASTM D522. The mandrel diameter at which cracking occurs is taken as the crack resistance value.

If the elongation of the coating at the onset of cracking is to be reported, a bend time of 15 s is used and the diameter at which the onset of cracking occurred is converted to percent elongation from a plot given in ASTM D522 Test Methods for Mandrel Bend Test of Attached Organic Coatings.

Cylindrical Mandrel Bend Tests

When executing cylindrical mandrel flexibility tests, a coated panel is bent manually over one or more cylindrical rods or surfaces of different diameters. ASTM D522 Method B states that the testing device should include mandrels with 1-in. (25 mm), $\frac{3}{4}$-in. (19 mm), $\frac{1}{2}$-in. (12.7 mm), $\frac{3}{8}$-in. (9.5 mm), $\frac{1}{4}$-in. (6.4 mm), and $\frac{1}{8}$-in (3.2 mm) diameters. Examples of cylindrical mandrel testers are given in Figs 2 and 3.

The panel should be bent over a mandrel with the uncoated side of the panel in contact with the mandrel surface. The panel should be bent approximately 180° around the mandrel at a uniform velocity in a time of 1 s. If cracking has not occurred, the procedure is repeated using successively smaller and smaller diameter mandrels until cracking is apparent. The cracking-resistance value of a coated panel is the minimum diameter at which cracking does not appear.

Fig. 2—A cylindrical mandrel bend tester (Reprinted by permission of Elcometer Inc.).

Fig. 3—Simple cylindrical mandrels test apparatus. (Reprinted by permission of Elcometer Inc.)

This testing procedure can be applied as a "pass/fail" test by determining whether cracking is produced by bending over a specified mandrel diameter.

A table for converting mandrel diameter to percent elongation is given in ASTM D522. Schuh and Theuerer [8] derived the relationship between the diameter of a mandrel and the elongation of a coating to be as follows:

$$\text{Persent Elongation} = 100(t/(2r + r)) \quad (1)$$

where t is the thickness of the coated panel and r is the radius of the mandrel.

Observed elongations are greater than values calculated from the above expression and vary with different types of metal substrates.

Crack resistance of a coating is dependent on its thickness. That is, the thicker the film, the lower the crack resistance. Values of crack resistance obtained by the mandrel bend tests should be corrected for film thickness when comparisons are made between different coatings. ASTM D522 contains corrections to be added to elongation values obtained with coatings having a thickness greater than 1 mil (0.03 mm) when applied to 1/8-in (0.8-mm)-thick steel panels.

Conical mandrel bend test procedures, similar to those given in ASTM D522, are found in ISO 6860 and BS 3900 E11. Cylindrical mandrel bend test procedures, similar to those given in ASTM D522, are found in ISO 1519, DIN 35 152, and BS 3900 E1.

T-Bend Tests

T-bend tests are a means of evaluating the flexibility of coated strip metal that is to be formed during a fabrication process (Fig. 4). Multiple 180° bends of the coated metal are made, and the amount of cracking produced at each bend is visually determined. Ratings are classified as 0T, 1T, 2T, 3T, and so on. The 0T (pronounced zero T) bend consists of making a 180° bend with the paint on the outside of the bend and pressing the bend flat so there is no space between the metal surfaces. This operation is

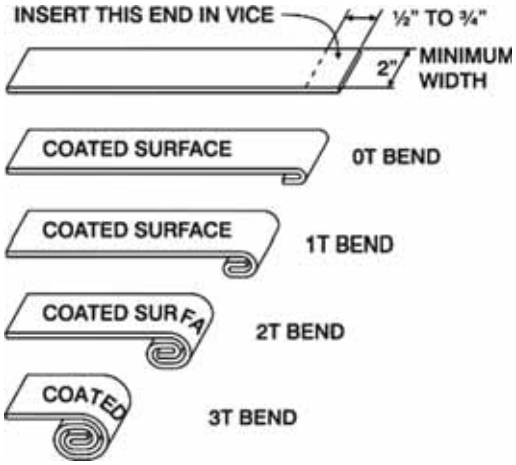

Fig. 4—T-Bend test bending the coated sheet on itself (ASTM D4145: Standard Test Method for Coating Flexibility of Prepainted Sheet).

repeated successively to produce a 1T (pronounced one T), 2T, 3T, etc. bends. These successive bends result in two, three, etc. thickness of the metal around the first bend. It should be apparent that the greater the number of thicknesses around which the coated metal is bent, the less severe the test.

Test results are reported as passing the smallest T-bend on which cracks are observed. In some cases, cracking must be detected by removal of the coating using a pressure-sensitive tape placed on the bend edges and observing the degree of removed coating particles. ASTM D4145, Test Method for Coating Flexibility of Prepainted Sheet, describes this test procedure.

A triangular-shaped specimen has been found to be convenient for making T-bend tests as this shape leaves a portion of each bend exposed for later examination and for permanent record.

Alternatively the T-bend test described in D4145 can be carried out using a die around which the deformation is

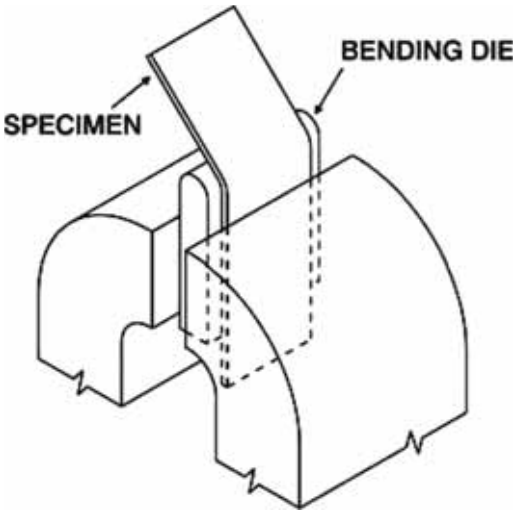

Fig. 5—T-Bend test using a die around which the specimen is bent (ASTM D4145: Standard Test Method for Coating Flexibility of Prepainted Sheet).

Fig. 6—Motorized Cupping Tester fitted with a web-cam to record the onset of cracking in the coating. (Reprinted by permission of Elcometer Inc.)

made (Fig. 5). Progressively larger dies are used to progress the test to the point where no damage to the coating results from the bending.

Cupping Tests

A test using a relatively slow rate of forming can be conducted with a Cupping Tester (Fig. 6) that pushes a punch into the unpainted side of a coated panel until the increasing deformation produces cracks in the coating. Test procedures are given in ISO TC 35, BS 3900 E4, NFT 30–019, SIS 18 41 77, DIN 50 101, and DIN 50 102. Cupping testers can be used to simulate different forming operations. The motorized Cupping Tester uses a spherical punch and a range of cupping speeds can be achieved. The maximum cupping depth is approximately 18 mm (0.7 in.). The cupping action is stopped when cracking in the coating is detected visually. The depth of cupping at that point is indicated on a dial gage and is considered to be the flexibility rating. The cupping tester can be equipped with a magnifier, a stereomicroscope, or a web-cam for observing the onset of cracking.

Forming Tests

In many industrial operations, metal is coated flat and then formed into various shapes by drawing the coated metal. This can be simulated directly or by elongating a coated metal sheet. Any tension-testing instrument capable of rapidly elongating a metal strip can be used for determining the ability of a coating to be drawn (drawability). A coated metal strip is elongated at a high rate of strain until cracking occurs. The elongation can be measured with an extensiometer [1]. Drawability would be reported as the percent elongation obtained just before cracking is observed. Since elongation is rate dependent, the rate of elongation used in the test should be reported.

ASTM D4146 Test Method for Formability of Zinc-Rich Primer/Chromate Complex Coatings on Steel provides a procedure for determining the formability of coated strip metal. An outline of a testing machine that can produce a sufficiently high pressure for pressing a 1 5/8-in (41-mm)-diameter indenter ball into the coated metal is provided. The rate of forming can be adjusted over a range of 0.2 to 1.0 in./min (4.8 to 25 mm/min). A dial gage monitors the movement of the indenting ball. Adhesive tape is applied over the dome formed in the metal, and the tape is rapidly removed. The amount of coating removed is given a rating by comparing it with a set of photographic standards.

Impact Resistance Tests

The most commonly used impact testers drop a weight onto an indenter resting on the surface of a coated panel that is resting on a platform (Fig. 7). A die in an opening in the platform allows the panel to be pushed down by the indenter to form a dimple in the panel. The weight is dropped through a guiding tube whose height is marked in increments.

There are a number of possible combinations of weights, indenter sizes, die sizes, and weight heights that can be used in performing impact tests. The tests can be performed by impacting either the coating directly (coating facing upward) or indirectly (coating facing downward).

Cracking observed on or around the impact-produced dimple is considered failure, and the force to produce the cracking is given in inch-pounds (kilograms-meters), that is, weight times height. The test can be performed either to determine the inch-pounds required to produce cracking or to determine whether a coating passes or fails at a specified inch-pound value. ASTM D2794, Standard Test Method for Resistance of Organic Coatings to the Effects of Rapid Deformation (Impact), describes such a test procedure and offers three procedures for determining the degree of cracking produced in an impact deformation: (a) visual inspection with a magnifier, (b) visual inspection after application of an acidified copper sulfate solution, and (c) use of a pin-hole detector.

The General Electric Impact Flexibility Tool is used for simultaneously making several indentations of different sizes. From these indentations, conclusions can be made regarding crack resistance and the amount of draw that a coating applied to sheet metal can tolerate. This tester consists of a steel cylinder that has knobs (segments of spheres) of different radii machined on each end. The cylinder is dropped onto a coated panel that is supported coating side down by a rubber pad. The height of drop is adjusted so that the boundary of the cylinder is just discernible. This procedure assures that each knob is used to its limit. Eight knobs cover a range of 0.5 to 60 % elongation. See Federal Test Method Standard 141C, Method 6226.

ASTM G14, Standard Test Method for Impact Resistance of Pipeline Coatings (Falling Weight Test), describes a test procedure for determining the impact resistance of pipe coatings. A fixed weight of 3.0 lb (1.36 kg) and having a 5/8-in. nose diameter is dropped through a guide tube onto a coated pipe specimen. The height of the weight is adjusted until the minimum height at which cracking appears is attained. A wet-sponge pinhole detector is used to determine the presence of cracks in the coating on the impacted pipe. An equation is given for calculating the impact resistance from the weight and its height of drop required to just produce cracking.

Fig. 7—Falling weight impact tester. (Reprinted by permission of Elcometer Inc.)

A different type of impact tester was developed and is being used at the Bell Laboratories of AT&T. A coated panel is subjected to repeat glancing blows by a case-hardened steel ball at the end of a short arm that is pivoted to another arm connected to a rotating shaft. During the test, the coated panel is mounted on a platform that moves so that successive blows do not strike the same spot. The energy level of the blows may be held constant, as in a "pass/fail" test, or it can be adjusted by changing the speed of the rotating shaft to determine the onset of cracking. If the hammer energy level required to destroy the coating is desired, a transparent, calibrated scale of shaft speed in revolutions is superimposed over the impact pattern. This tester is not commercially available.

There are a number of other impact testers that have been developed over the years and used to some extent. These include the Parlin-duPont Tester, Camp Impact Test, Hart Impact Tester, Ball Punch, General Electric Ball Drop, and Navy Falling Ball test. None of these testers are commercially available now.

The ISO 6272 standard, Rapid-deformation (impact resistance) tests is made up of two parts, part 1, Falling-weight test, large-area indenter and part 2 Falling-weight test, small-area indenter. Part 1 uses a 1 kg weight with the 20 mm diameter spherical indenter attached, whereas part 2 is based on ASTM D2794-93 (2010) and uses either a 12.7 mm or 15.9 mm indenter.

Testing of Free Films

ASTM D2370, the Standard Test Method for Tensile Properties of Organic Coatings, covers the elongation, tensile strength and stiffness (modulus of elasticity) of organic coatings when tested as free films. The method for preparing the uniform free films of organic coatings is given in ASTM D4708, Standard Practice for Preparation of Uniform Free Films of Organic Coatings using substrates that can be peeled from the cured film. Procedures are given for preparing free films on three alternative substrates. These substrates are treated FEP (fluorinated ethylene-propylene) sheet, silicone coated paper, and halo-silane coated glass plates. (Note: The dental foil that used to be included as one of the substrate has been removed from this practice because it contains mercury and is therefore hazardous.)

Cold Crack Resistance Tests

Tests in which coatings on substrates are cycled through elevated temperature, low temperature, and room temperature environments are called cold crack tests. They have been used in the coatings industry for many years as an indication of the ability of a coating to resist cracking in service and therefore are considered to be tests of coating flexibility.

ASTM D1211 Standard Test Method for Temperature-Change Resistance of Clear Nitrocellulose Lacquer Films Applied to Wood is an example of such a cold crack test, however this Standard Test Method was withdrawn without a replacement in 2006. It described a procedure for testing lacquer coatings applied on wood. The testing cycles consist of 1 h at 120°F (49°C), 1 h at –5°F (–21°C), and ½ h at room temperature. The results were reported as the number of cycles required to produce visible cracking in the coating.

Automotive coatings are subjected to cold crack cycle tests. A typical test for exterior coatings on metal panels consists of (1) equilibration at room temperature, (2) exposure in a humidity cabinet at 100°F (38°C) and 100 % relative humidity for 20 h, and (3) exposure in a freezer at –22°F (–30°C) for 4 h. After removal from the freezer, the coated panels are allowed to stand at room temperature for 2 h. Then the coatings are visually rated for cracking. In some cases, an exposure of 2 h in an oven at 150°F (65°C) is introduced into the above cycle conditions.

A rapid cold crack test that has been developed is based on the use of cooled air entering a transparent, insulated box. Cold air that has been cooled at a rapid controlled rate is introduced into the box, and the coatings are observed for cracking. The coatings are then rated by determining the temperature decrease from room temperature that is required to produce visual cracks in the coatings [4].

Effects of Aging and Weathering

The ultimate measure of satisfactory flexibility and toughness of a coating applied to a substrate is performance under service conditions. Most flexibility and toughness tests are performed on relatively fresh-coated panels, that is, tests are usually performed after the panels have been conditioned in a specified atmosphere for a specified period between 24 h and 7 days. The results obtained are applicable to service conditions if these are concerned with post forming or service indoors without a degrading atmosphere, since most coatings do not change appreciably in their physical service properties under such conditions. However, if the service conditions include exposure to weathering, this factor can cause appreciable changes to occur in the coatings properties.

The effects of moisture, temperature changes, and exposure to sunlight (ultraviolet wave lengths) encountered in outdoor exposure generally reduce the flexibility and toughness of organic coatings. Therefore, it often is desirable to conduct tests for flexibility and toughness after periods of weathering to determine how a coating will perform under actual weather conditions [1].

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Understanding Osmotic Activity in Paint Films and Determining Cause by Systematic Analysis of Blister Fluids and Blistered Coatings

George Mills[1]

INTRODUCTION

A PROBLEM OFTEN OBSERVED WITH PAINT FILMS is the development of domed blisters. Usually these "bubbles" in the paint film are the result of osmotic activity. Understanding the osmotic process will be very helpful in the investigation of the cause(s) or driving force with this mode of paint failure. Osmotic blisters may develop between the primer paint and base substrate, between coats of applied paints, or within the matrix of a single layer of the composite (single or multi-coat) paint film. Although in most cases the blisters are easily seen, it is possible to experience osmotic activity under paint films when a domed blister is not elevated enough to be visible. When this occurs on a steel substrate, typically, corrosion will develop under the film. The osmotic process may be represented by the following graphic. It is most important to appreciate that potential solvent molecules will migrate through the paint film "one molecule at a time." One will remember that a collection of single, individual molecules is defined as a gas. For this reason, osmosis follows, and is controlled by, the general gas laws.

A common "definition" of osmotic activity in paint films describes the migration of solvent molecules through the film and dissolving one or more solutes forming the blister fluid solution. This process then continues in an effort to dilute the blister fluid solution to the point that it has the same concentration (actually, same vapor pressure) as the outer contact solvent liquid. It is this differential in vapor pressures that drive the osmotic activity.

Osmosis involves a semi-permeable membrane (as with a paint film), a solvent, and one or more solutes. To understand the potential interventions and investigation of the driving forces, knowledge of the basics of osmosis are extremely useful. Within this chapter we will review the chemistry and physics controlling the osmotic phenomena and present the analytical techniques that will allow one to determine the source, or driving force, of the osmotic activity. After determining the driving force one then has the ability to modify the paint formulation, application procedures, surface preparation, or service restrictions if any of these are shown to be the cause (source). If a coating failure has occurred one may determine where the liabilities lie as well as the extent of remediation that will be required to allow a true long-term fix of the problem. Problems associated with faulty application such as improper surface preparation are frequently claimed as the culprit. But, the inclusion of a water soluble thinner or chemical reaction under, or within, the coating matrix that produce water soluble materials are possible. Examples of some of these will be discussed later. Other potential sources of osmotic problems include deficiencies in the paint specification and unanticipated service conditions. Paint formulations that include pigments, resins, or additives that are soluble, or convert to a form that is soluble in service, can cause osmotic problems. On rare occasions manufacturing anomalies may lead to osmotic activity.

The investigation of osmotic activity in paint films should involve the systematic collection of samples from the site along with attentive observation of the blister location, size, and shape. If within a tank, note if blister predominance is in the liquid or vapor phase of the tank (or at the vapor/liquid interface). Are there temperature differentials that would cause condensation? Data relating to cargo history may be needed in tank lining failures to recognize and explain unusual solutes found in the blister fluid and/or coating dome analysis. The collected samples should include blister fluid withdrawn from blisters, recovered paint chip film blister domes, paint film samples collected away from blistered areas, and, for internal tank lining failures within non-aqueous tank lining failures, a sample of the material within the tank leading to the osmotic problem.

Sometimes, solutes found in the blister fluid are the result of chemical reaction products. These reaction products may be generated in the blister fluid over time or generated within the coating matrix itself producing a solute *in situ*. Examples of these include the highly alkaline fluid on an underground pipeline or ship's ballast tank caused by the reduction of oxygen in systems under cathodic protection (CP). This high *pH* fluid may hydrolyze bound chlorine from an epoxy resin or bromide from the blue-green pigment in the fusion bonded epoxy (FBE). Tank linings exposed to chlorinated solvents will experience generation of hydrochloric acid (HCl) from hydrolysis of the material within the coating film. Hydrolysis of acetate solvents

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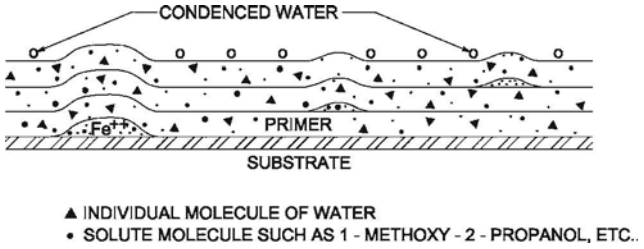

Fig. 1—Osmotic blisters can form at various interfaces. This includes under the initial primer coat at the substrate or between intermediate coats. Individual molecules of the solvent migrate through the polymer forming the paint film. Some of these molecules of solvent coalesces to a liquid forming the blister and disolves one or more solutes. The difference in vapor pressures between the fluid in the blister and the migrating solvent controls the direction of solvent flow. (Graphics done by George Mills, Jr.; Building Design Solutions, LLC.)

generates acetic acid. When blister fluids are low *p*H, often there will be an iron corrosion product as a solute as well. These will be discussed later (Fig. 1).

Chemical analysis of the blister fluid along with thermal out-gassing of the blister dome film, usually, will define the cause of the osmotic activity. When "strange" or unexpected solutes are seen, the investigator may be required to review some of the chemical reactions that could produce these solutes in the blister fluid. While the solvent is often water, tank linings and internal pipe coatings in non-aqueous service may experience osmotic activity wherein the solvent of the osmotic blister is the product of the contact service media. The solutes may be occluded previous cargo materials or lower molecular weight polymer fractions generated by the cargo material. These will be discussed in detail later.

Most domed paint blisters will be present with the liquid that caused the blister, although some blister domes may be found after the liquid has escaped from the coating. The disruption in the paint film often leads to severe corrosion of the substrate as seen in Fig. 2 within a ballast tank of a large ocean going tanker.

As discussed previously the cause (driving force) of osmotic blister formation may originate as a result of numerous sources. While the applicator often is accused of improper surface preparation, the service conditions encountered and the paint's formulation may be responsible. The real driving force, and hopefully a correction in the future, may be determined by systematically analyzing the blister fluids and understanding some of the complex chemistry that may be operative.

The physical development of osmotic blisters in a paint film requires that a solvent be available having marginal transmission within the paint film. This solvent will dissolve one or more solutes under the film at the substrate, between applied coats, or within the matrix of a single layer of the paint film. Usually the source of the solvent is not a mystery. Typically, it is water from condensation or immersion when water contact is possible. For tanks in non-aqueous service, the linings may experience osmotic blister formation wherein the materials in the tank constitute the solvent. For these situations, the contact solvent will be known or discovered upon chemical analysis. The identification of the solutes, and the source of these solutes, may present the investigator with a challenge. While in some cases, salts over-coated during application have been cited as the driving force, the real picture, usually is considerably more complicated. The solutes may involve the generation of ions, with time, under the film. A good example is the osmotic blisters often discovered in the lining of potable water tanks at the "one year" guarantee inspection after use of hypochlorite as the purification agent. Through multiple chemical steps, hydrochloric acid is generated at the steel interface leading to iron chloride salts under the blisters. Fig. 3 depicts the blisters formed in such a way within the potable water tank onboard a very large passenger cruise ship.

The blister fluid may have become strongly acid or strongly alkaline by generating an acid or alkali under the film after gas phase transmission of the acid or alkaline precursors. Acids and alkalis are both strong ionic solutes and may drive osmotic blister enlargement once initiated. Water soluble solvents included in the paint formulation by the manufacturer, or added at application, are another source of solutes in which there is no additional ionic activity.

Fig. 2—Osmotic blisters in the ballast tank of a large marine tanker. Note that many blisters have broken open and corrosion of the substrate is substantial. Some of these may be driven by cathodic protection anodes installed in the tanks that are operative only when the tank is with ballast water.

Fig. 3—Osmotic blisters in a potable water tank within a large cruise ship. Notice rust staining coming from broken blisters. Often these initiate from water soluble solvents formulated into the epoxy or added during application. Analysis of the blister fluid will indicate the source of the osmotic blister formation.

OSMOSIS IN PAINT FILMS

When a practitioner is asked to define an "Osmotic paint failure," the typical response is "… the passage of water through a semi-permeable membrane to dissolve salts under the paint thereby forming blisters under the film." While this might describe a portion of such failures, the picture is much broader than this description might imply. The term "semi-permeable" is in common usage although, often, there is little, or no, thought as to the considerable significance of the numerical value of the "semi-" in this common definition. This is true as it relates to the material acting as the solvent as well as the materials acting as the solutes driving the osmotic activity. It is important to appreciate that this variability in migration rate/ability through the paint film applies to both the solvent and (the often neglected) solute(s), when these solutes are water-soluble solvents included in the paint formulation, added during application, or generated in service.

In this chapter on methods of determining the source of osmotic activity in paint films, the terms "blister fluid" and "blister solution" represent the mixture of the solvent and one or more solutes found in the blister. By convention, the material present in this solution in the largest amount is considered to be the solvent. Generally speaking, the value of the vapor pressure of the solvent in the blister fluid solution as compared to the vapor pressure of the solvent outside the blistered film dictates the direction of the solvent flow. One must remember that a solvent's vapor pressure will always be depressed when the solvent has any solutes added. In the production of pickles, the cucumber is soaked in a strong salt brine solution wherein the water of the brine has a lower vapor pressure than the water inside the cucumber. In this case, the water flows out of the cucumber causing it to shrivel to a much smaller size.

Within the blister fluid, all of the dissolved materials are considered as the solutes and will act to depress the solvent's vapor pressure. Many only think of salts, over-coated at the time of application or included in the formulation, as potential solutes and water from either surface condensation or immersion service as the solvent. While water soluble salts are a common and strong osmotic driving force, water soluble solvents, such as oxygenated alcohols, have been shown to present a serious osmotic driving force. Oxygenated alcohols are alcohols (already containing at least one oxygen atom) that contain additional oxygen in the form of ethers or ketones. These materials are excellent solvents for the epoxy coatings as they cure and may be employed in the paint formulation, but they are typically not very volatile and remain within the coating matrix for long periods of time. Their added oxygen in the molecule as ether linkages (–COC–) usually render them water soluble. Their water solubility also aides in displacing moisture at the interface during application over damp surfaces. Unfortunately, since most are totally water soluble, they can become the osmotic driving force when liquid water condenses on, or comes into contact with the coating, especially when insufficient time is available to allow escape during the drying stage [1].

Water soluble reaction products such as acetic acid remaining after hydrolysis of acetate solvents or microbial digestion of sugars have also been seen as solutes. Acid solutes usually cause additional corrosion of steel substrates under coatings with the initially formed iron salts becoming solutes in the osmotic process. The ferrous (Fe^{+2}) corrosion product soon converts to an insoluble ferric (Fe^{+3}) corrosion product after reaction with oxygen in the air. If the adhesion is good and the blister dome breaks from internal pressure, osmosis cannot continue at that blister location since osmosis requires movement of one molecule at a time.

There are a number of factors that dictate the degree and speed of damage to a coating system that is experiencing osmotic activity. This communication is intended to present some important aspects useful in understanding the process of osmosis, its damaging effects upon paint films, and a methodology that has proven useful in the systematic elucidation of the source of the osmotic driving force. Osmotic activity in paint films is a very common failure mode. This chapter is intended to assist the coatings formulator, the application contractor, the failure analysis practitioner, and the end user in understanding the operative driving forces and demonstrate methodology useful in determining the source of the osmotic activity after coating failure.

Osmotic activity in paint films will be addressed in the following steps: (1) discuss the chemistry/energetics of the osmotic process and other chemical processes that may accompany and exacerbate this coating failure mode; (2) discuss some of those factors causing, or accelerating, osmotic activity in paint films; (3) discuss a proven methodology employed in the systematic chemical analysis of the osmotic blister fluids to identify the source of the activity and the significance of the analytical data as it relates to potential problems with the paint formulation, the specific application, and/or the service leading to the paint failure; and (4) present some case history examples to demonstrate the data developed in identifying the source of the osmotic activity.

Water is the most common solvent encountered in paint film osmotic activity. For this reason, water systems, primarily, will be discussed in this communication. It is important to appreciate that other solvent/solute systems may be encountered and are just as damaging. A common example exists with marine epoxy tank linings containing benzyl alcohol or nonyl-phenols and cargo materials having marginal transmission coefficients such as the fuel additive methyl-t-butyl ether (MTBE) and some lower molecular weight alcohols sequenced with the presence of water.

THE CHEMISTRY OF THE OSMOTIC PROCESS

In simpler terms, osmosis is the natural process of *individual* solvent molecules migrating through the film, condensing, and dissolving some solute to form a solution. For osmosis to be possible, molecules of solvent MUST travel through the paint film ONE MOLECULE AT A TIME. By definition, this makes the process a "Gas Phase Transition" since a "gas" is a collection of individual molecules. For this reason osmotic activity follows the general gas laws of chemistry.

It is more understandable to say that the vapor pressure of the pure solvent (outside the coating film) is greater than the vapor pressure of the diluted solvent in the blister fluid solution. This difference in vapor pressure thereby forces the solvent towards the osmotic solution. This is due to the depression in vapor pressure of the blister fluid caused by

the solutes present as opposed to the pure solvent. Just as dissolved solutes will depress the freezing point, or elevate the boiling point of a solvent (by depressing its vapor pressure), the energy required to perform the chemical work, or, simply, the osmotic driving force, has its origins in the similar basic laws of chemistry [2].

This then leads one to the more common "definition" of osmotic activity. The solvent molecules migrate through the film and dissolve into the blister fluid solution in an effort to dilute that solution to the point that it is the same concentration (same vapor pressure) as the outer contact liquid. More precisely, the process continues until the vapor pressure of the blister fluid solution equals the partial vapor pressure of the solvent outside the blister. (The physical chemistry purist will speak of equating the chemical potential of the two.)

Because osmotic activity is a "colligative property" of the solution, the driving force is based on the number of individual species dissolved in the solution rather than the individual solute's molecular weight, size, or chemical structure. In general, this means that the effect of one mole (90 g) of 2-butoxy ethanol/liter has the same damaging effect as a half "mole" (about 29 g) of sodium chloride/liter since the sodium and the chloride ions are each separated in the osmotic solution and the total sum of the number of individual species dissolved (ions) are equal to the number of the 2-butoxy ethanol molecules in solution.

Individual movement of molecules of the solvent through the paint film is an important concept to appreciate. By definition, this is a gas phase transition since a gas, also, exists as individual molecules. For osmotic blisters to form in the first place there must be sufficiently compromised adhesion for a condensed (liquid) phase to exist, even if over an extremely minuscule area. Once a liquid solution is present, at an interface (base substrate, inter-coat interface, particle inclusion, etc.), the volume and, usually, the pressure of the condensing fluid will continue to increase until two conditions exist collectively.

In osmotic activity, the first condition is that the concentration of the solute within the blister fluid decreases as the volume of pure solvent passing through the film increases. When this concentration of driving solute in the blister fluid equals that in the external contact fluid, the process will stop. More precisely stated, the osmotic driving force diminishes as the partial pressure (chemical potential) of the solution in the blister and the partial pressure of the liquid outside the film approach the same value.

The second condition occurs when the actual pressure that is gradually created in the osmotic blister reaches the value that will force the pure solvent (or solutes) back through the film. This is the process of reverse osmosis used to purify water in certain desalination systems.

When the adhesion of the paint film is good and the film cannot be peeled easily from the substrate by the internal osmotic pressure generated, the pressure may become sufficient to rupture the blister. When this occurs, if the crack remains open and liquid solvent can pass, osmotic activity is no longer possible. This is because liquid phase movements (as opposed to gas phase) are now operative since there is no semi-permeable membrane. Osmosis requires that individual molecules (i.e., separated from each other) move through the semi-permeable membrane (paint film) thus acting as a vapor phase transmission.

FACTORS CAUSING VARIATION IN OSMOTIC ACTIVITY IN PAINT FILMS

While most osmotic activity in paint films is clearly visible, osmotic activity can, and does, occur without the appearance of visible domed blisters. The development of osmotic blisters at the coating/substrate interface, whether visible or not, depends on a large number of factors. A few of these include: (1) the value of the paint's adhesion force at that location; (2) the degree of the depression of the glass transition temperature, T_g, and/or plasticity of the paint film caused by the water (or other solvent) and any migrating solutes; (3) the concentration, and location, of available solutes; (4) the transmission coefficients of the solvent, and solutes, within the paint film at that location and under the local ambient cure conditions.

For coatings like epoxies, the actual variation in transmission rates are possible within a single formulation and depend on numerous application variables. Solvent and molecular solute transmission coefficients within a paint film will depend on variations in the degree of mixing prior to application, closeness to true mixed chemical stoichiometry of the base and converter resins, temperature of the substrate (and, therefore, the reacting paint mixture) during curing, ultimate cross-link density of the formulation, amount of carbon dioxide (CO_2) stripped from the air by the amino functional converter during mixing and application, and a myriad of other variables.

Although rare, osmotic activity can occur within the matrix of the paint film as opposed to an interface. When this happens, bubbles of liquid will form within the coating matrix, usually from condensation of water (or the solvent) on the surface of some occluded particle. This requires the osmotic pressure to develop to a value greater than the tensile strength of the paint matrix at the location of the formed bubble. Osmotic activity in this form is typically present as very small bubbles within the paint film. The bubbles are not spherical in nature, and they are best viewed under a microscope. It is important to emphasize that osmotically driven bubbles have nothing to do with any air or gas bubbles or voids that may have been trapped during application and are present in the applied film [3]. Osmotically generated voids or bubbles within the coating matrix will show, microscopically, a fractured edge as opposed to a smooth surface for air trapped bubbles. The size of the bubbles formed from osmotic activity that occur within the coating matrix depends largely on the tensile strength of the coating matrix at the inclusion and the distribution of water soluble inclusions, either salts, pigments, or converter fractions. Water soluble low molecular weight amine converters have been seen in blister fluid when application occurred at cold temperatures. Typically, these are usually at an interface as opposed to within the film matrix and occur as a result of reaction of the alkaline amine functional cross-linker and the acid gas carbon dioxide.

From the above discussion, it is evident that for osmotic activity to occur at an interface where adequate solute is available, the value (strength) of adhesion is the major factor that will dictate the size of the blisters formed. When blisters form, areas having very good adhesion will yield small blisters. Areas having compromised or lower values of adhesion will yield larger blisters. Very large blisters (16 in. diameter and greater) have been observed when CP produced alkali salts *in situ* under FBE pipe coatings.

Fig. 4—Blisters as large as 20 in. have been seen on cathodically protected pipelines. The fluid from the blister on the FBE coated pipe above was highly alkaline from the reduced oxygen production of hydroxide.

These coatings were applied over salt contaminated areas of a pipe and developed within a few years time. This very common example typically is the result of applied cathodic protection and the production of hydroxide ion (salts) from reduction of oxygen gas passing through the coating and dissolving into the blister fluid. See Fig. 4.

All amorphous (i.e., non-crystalline) organic coatings and plastics will allow small molecules to migrate within, or diffuse through, the plastic matrix. This is the same mechanism that allows a freshly applied coating, after gelling, to lose most of its included solvents as it cures and dries. The rate, or speed, of passage of these individual molecules through a coating film is called its transmission coefficient for that material and depends on numerous factors. These include the solute size and molecular weight. Ficks Law dictates that the diffusion rate through a polymer matrix is inversely proportional to the square root of the molecular weight of the migrating molecule. Diffusion rate is also impacted by the cross-link density of the film. The transmission coefficient of migrating molecules is often related to the glass transition temperature, T_g. Migration rates are also impacted by the chemical and structural nature of the matrix as well as the migrating specie's polarity, polarizability, and chemical stability. This migration within a coating matrix is normal and to be expected, although sometimes it is undesirable. When sufficient volumes are lost after reaching the gelled state in its curing process, cracking of the coating from shrinkage stress development may occur. No coating stresses can develop from volume loss before the gel point is reached since liquid mechanics are operative within the freshly applied paint. The inclusion of these migrating species within a coating matrix causes a decrease in the cured film's glass transition temperature, T_g. This dynamic, constant movement within the coating film is the same as experienced with migrating plasticizers, chemically blocked cross-link accelerators/enhancers, molecular catalysts, as well as binder extenders such as benzyl alcohol, nonyl-phenols, etc.

The past experience of the author has shown that the water-soluble solutes causing osmotic blisters can come from a number of sources. Some typical sources include the following:

1. Water-soluble solvents purposefully formulated into the paint by the manufacturer. The most common are oxygenated alcohols such as 1-methoxy-2-propanol and 2-butoxy ethanol. Some are listed in the product's material safety data sheets (MSDS) while some paint manufacturers are reluctant to identify their presence.
2. Water-soluble solvents added at application (thinners). While the paint or the manufacturer's recommended thinners may not contain the oxygenated alcohols, the manufacturer's recommended wash thinners may contain these solvents. These have been detected in applied paint films in past blister fluid analyses, apparently from inadvertent inclusion by the applicator when the wash thinner was used to thin the paint at application.
3. Salts remaining on the substrate at the time of application. All water-soluble salts, whether sodium chloride, sodium/potassium/lithium hydroxide, or whatever the ionizable water-soluble salts may be, these can become solutes in the osmotic blister fluid. Most water based zinc silicate formulations use a binder that originates as a water glass. This is a silicate dissolved by alkali hydroxide. Shop primers often are not formulated above the critical pigment volume concentration (CPVC) and allow the hydroxide salts to become trapped within the matrix of the shop-primer coating. These are slowly released when used in immersion or damp, water-condensing service. Usually, efforts are made to water rinse any soluble salts from the primers prior to over-coating but with systems formulated below the CPVC, this cannot be done effectively. Even with systems formulated above the CPVC, extended curing times are always required to minimize the availability of the soluble alkali hydroxides. Rinsing should continue until the dampened surface has a *p*H equal to the rinse water. The lack of porosity makes this task difficult (or impossible). In these cases, the blister fluid will be of a high *p*H, high conductivity, and the ion analysis will indicate the presence of the alkali metal (Na, K, or Li) from the water based zinc silicate primer. Ethyl silicate based zinc primers are not as prone to the blistering in this way, although the mineral acids used to stabilize the silicate binder in the storage container may present a problem if not rinsed away prior to over-coating and immersion.
4. Hydroxide salts generated in the blister fluid. The continuous generation of hydroxide ion in blister fluid will occur when two conditions are met: (a) a liquid water filled area exists at the steel or zinc primer interface irrespective of how small (as opposed to intercoat delaminated areas) allowing oxygen to migrate in; (b) a cathodic potential exists of sufficient voltage to reduce any oxygen that migrates into the blister fluid. The oxygen is converted to hydroxide as it migrates into the blister fluid.

$$2H_2O + O_2 \rightarrow 4OH–$$

This represents the in situ production of a salt that will drive osmotic blister activity. The blister fluid will present with high conductivity and a high *p*H but may also contain dissolved organic and inorganic moieties from the paint. Benzyl alcohol is more soluble in alkaline blister fluid than in neutral *p*H water and has been seen in high *p*H blister fluid.
5. Hydrolysis of formulated, or cargo absorbed, materials such as ester solvents or chlorinated solvents. Esters are the reaction product of an acid and an alcohol.

Hence, butyl acetate is the reaction product of butanol and acetic acid. When this has been a cargo in a lined tank, after washing with water we have seen hydrolysis within the coating matrix. The butyl alcohol and acetic acid are regenerated by soponification reaction with a water molecule. Acetic acid that migrates to the steel interface may produce a corrosion product with iron that is itself somewhat soluble and becomes one of the osmotic driving solutes. Chlorinated solvents hydrolyze to HCl. The rate of hydrolysis is a function of the specie undergoing hydrolysis and the alkaline strength of the nucleophilic centers (nucleophilicity) within the coating matrix that catalyze the hydrolysis. The blister fluid will be of a low *p*H (less than 7 depending on acid content). Fermentation of sugars, as in molasses cargoes aboard ships, also produces acetic acid. Acetic acid will migrate through the coating and initiate corrosion at the steel interface. Analyses of the solid iron corrosion product recovered from under ruptured blisters will give a strong indication of acetic acid when utilizing the pyrolysis function of the gas chromatograph mass spectrometer (GC/MS) if this has occurred.

6. Production of sulfuric acid (H_2SO_4) within the slime layer of an internal lined sewer pipe caused by the bio-oxidation of hydrogen sulfide (H_2S). This leads to low *p*H blister fluids, and often perforation of the pipe.
7. Low molecular weight amine functional curatives that have been blocked from the epoxy reaction by carbon dioxide (CO_2) or other blocking agents. For CO_2 blocked converters, this is typically the result of cold temperature application wherein the epoxy-amine reaction slows or stops and the acid gas CO_2-amine reaction continues reasonably fast. During mixing of the amino side of the epoxy coating or the "A" + "B" mix, if a vortex is drawn on the mixing paint and air is mixed into the paint, most of the CO_2 in the air will be stripped and the resulting blocked curative will not be available for reaction with the epoxy. This is one of the sources of variability in the ultimate T_g of the cured coating. Inclusion of ketones in the amino side of an epoxy curatives is another potential source of failures. This happens when the amino functionality is blocked by the formation of ketimines in the can during storage. In this case, the length of time since curative manufacturer and the past thermal history will influence the amount of ketimine that has developed in the can. Ketimines require moisture from the atmosphere to cure and are the curatives used in "moisture cured" epoxy systems.

The data developed by the blister fluid analysis, on occasion, will indicate additional tests useful in confirming the source of the water soluble solutes found. This is true when their presence cannot be explained by the MSDS of one of the paint products involved. The MSDS for the coating material does not always include non-hazardous water-soluble solvents. Evidence developed from work by this laboratory on ship-bottom paints has shown that solvents from any coat of applied paint will migrate throughout all prior applied old layers allowing blisters to form at the steel interface. This was demonstrated after the fresh application of a topcoat containing an oxygenated alcohol was applied to a ship's hull over three layers of five year old, pre-existing paint that never blistered. The analysis of the blister fluid collected from below the original paint system indicated the water-soluble alcohol that was present in the new paint application. On occasion, chemical reactions in or about the osmotic blister area will be producing the solutes. For this reason, to establish liability, the investigator must be prepared to accept the data from the blister fluid analysis and seek the true chemical pathways to these solutes, even if he must revisit his chemistry textbooks.

THE SYSTEMATIC CHEMICAL ANALYSIS OF OSMOTIC BLISTER FLUIDS AND BLISTERED COATINGS

A systematic analysis of the fluids removed from osmotic blisters will provide the answers as to what drives the osmotic activity and therefore assist in establishing liability. In addition, the analysis often will indicate ancillary chemistries occurring within the blister fluid itself and/or within the coating matrix forming the blister dome. The following analytical methodologies have been found to provide sufficient data to identify the material(s) initiating the activity and any additional driving forces that might be developed after blister formation.

The collection of blister fluids is best done using a hypodermic syringe after first producing a small hole through which the needle may be placed as seen in Fig. 5. Usually, the coatings are too hard and brittle to force the needle through the coating film itself. For this reason, to minimize the chance of destroying, bending, or plugging the needle, drilling or puncturing with a sharp nail at the edge of the blister may be best. The solution should be collected and stored in glass vials since many of the solvents will migrate through plastic containers if the chemical analysis is not done timely.

Ideally, many answers are provided by using a GC/MS having the ability, first, to out-gas and identify the lower molecular weight volatiles followed by a separate, second, analysis of the fragments after pyrolysis at elevated temperature of the residues. The pyrolysis, then, is done without opening the thermal extraction (TE)/pyrolysis (Pyro) oven. This is useful in solving some of the mysteries when the solutes are organic in nature. Higher molecular weight water soluble materials may be identified that are not seen on direct injection. When this type of equipment is not available, gas chromatograph/mass spectrometers utilizing

Fig. 5—Blister fluid is being removed under water using a small hypodermic syringe. This is in the coating within a large concrete pool at a state aquarium. Note sharp wood chisel used to first produce a very small hole in the coating at the edge of the blister.

direct injection of the blister fluid is an alternative that will provide good definitive data for some of the cases, but the solvent portion is always much greater than the molecular solutes. The ionic solutes will not volatilize and cannot be seen by the GC. These are identified by ion chromatography or by scanning electron microscope (SEM) with energy dispersive x-ray (EDX) after drying the blister fluid residues (Fig. 6).

Knowing potential sources of osmotic activity allows narrowing the search. The sequence of procedures followed in the blister fluid analysis yielding the most data will include the following steps.

1. GC/MS analysis by low temperature TE/desorption (water soluble solvents).
2. GC/MS analysis by pyrolysis analysis of non-volatiles remaining after TE (higher molecular weight, water soluble reaction products); Done without opening TE/ Pyro oven.
3. Determination of electrical conductivity and *p*H
4. Ion chromatography to identify the specific ions other than OH^- and H^+ ions seen in the *p*H determination. When not available, SEM/EDX analysis of the dried blister fluid residue will reveal the inorganics present.

While the mass spec detector suffers in its being more difficult to perform finite concentration determinations, its ability to provide the identity of unknown water soluble organic solutes from their specific mass fragment fingerprint is excellent. Although it may be useful in some cases, the absolute concentration of the specific solutes in the blister fluid is not required to determine the source of the osmotic activity.

After analysis of the blister fluid, additional analyses of related coating materials will allow determining the source of the water soluble solvents. These analytical techniques include thermal extraction and pyrolysis analysis of the coating materials forming the dome of the blister, as well as coating material in the near vicinity of the blister. Testing wet, un-applied, un-mixed coating materials from the can will pinpoint specific problems if these are from the paint formulation. If a water soluble solvent is found to be the osmotic driving force, the comparison of the analyses of the applied coating and the unapplied coating material will indicate whether this bad solvent was added during application or was included by the manufacturer in the paint formulation. Occasionally a review of the MSDS for the coating product will indicate the water-soluble solvent, though from experience we have seen that the paint manufacturer often does not identify these solvents (Fig. 7).

GC/MS Analysis by Low Temperature Thermal Extraction/Desorption (TE/GC/MS)

Often, the amount of available blister solution is small. Because of the large amount of data provided by the GC/MS thermal desorption and pyrolysis techniques, these analyses should be performed first if only one drop of blister fluid solution is available. When salts are the primary osmotic driving force, usually there will be ample blister fluid sample available (Fig. 8).

The ideal GC/MS analytical instrument used for the thermal extraction and pyrolysis analysis is a combination of four instruments linked together. It has been described in detail previously [4,5]. Briefly, it is a late-model GC with a mass spectrometer used as the detector. Integrally attached to the GC inlet is a heated transfer line of deactivated fused silica maintained at about 325°C (620°F) connecting the computer controlled TE/ Pyro oven. The very small TE/ Pyro oven has a stream of Helium sweeping any volatilized materials into the cryogenic trap in the GC. The separation

Fig. 6—The ideal analytical instrument configuration for identifying the source of osmotic activity in paint films is a gas chromatograph having a mass spectrometer as a detector, a thermal out-gassing/pyrolysis attachment, and a liquid nitrogen trapping section at the head of the GC column. To the right is the pyrolysis and thermal out-gassing attachment. The liquid nitrogen cryogenic focusing on capillary column is within the GC oven as seen in Fig. 6. The components of the analytical system are as follows: 1. Gas chromatograph; 2. Mass spectrometer; 3. Pyrolysis-outgassing controller for solid samples; 4. Liquid nitrogen cryogenic controller; 5. Heated crossover line from pyrolysis oven to cryogenic trap in the GC oven; 6. Liquid nitrogen supply line from outside LN2 storage.

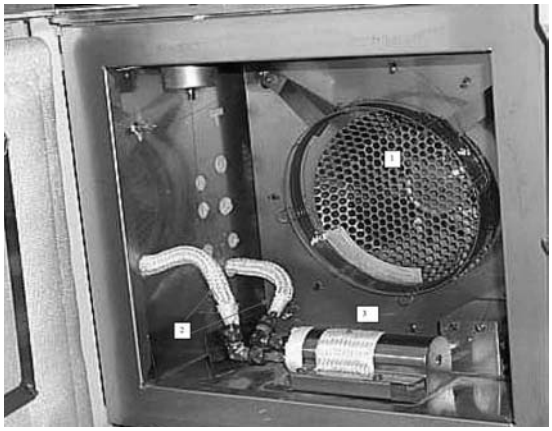

Fig. 7—Oven of gas chromatograph housing quartz capillary column (30 m) and quartz cryogenic focusing chamber. The components are: 1. 30 m capillary column passing through liquid nitrogen (LN2) cryogenic trap; 2. LN2 inlet and outlet fed by thermostat control of LN2 valve; 3. Quartz LN2 cryogenic chamber with electrical resistance heater to flush trapped components onto the column at the start of the GC analysis. Capillary column passes through the LN2 cooled cryogenic trap. An alternative "home-made" cryogenic trap is a simple styrofoam cup containing liquid nitrogen. This is placed in the GC oven allowing a short section of the capillary column to be manually submerged during sample out-gassing. The LN2 is removed at the start of the GC analysis.

Fig. 8—A conductivity meter requiring only one drop of blister fluid is used to determine electrical conductivity. Conductivity of the blister fluid solution is a measure of the total number of ions or salts present. Specific identification of the ions is provided by SEM/EDX or ion chromatography. (Photo provided by HORIBA Instruments, Inc., www.horiba.com)

Fig. 9—A *p*H indicating a paper strip is used to determine the *p*H of the blister solution. The fluid from the conductivity meter is adequate for this determination. If there is minimal blister fluid available, a very small spot from the hypodermic syringe will suffice.

column used is a 30 m DB-5 capillary column. About 4 in. of the front end of the column passes through a quartz chamber plumbed to receive liquid nitrogen. This chamber also contains a wire resistance heater capable of heating the frozen column to 275°C (527°F) very quickly. A separate computer controller is programmed to maintain –125°C (–193°F), initially to cryogenically trap the volatilized components or thermally degraded fragments from the heated polymer. The thermal desorption/pyrolysis oven operates for about 6.5 min, going from ambient to 125°C (257°F) for TE or ambient to 500°C (932°F) for pyrolysis. This drives off any materials volatile at these conditions. The cryogenic trap maintains its cold –125°C (–193°F) temperature for 10 min. At the end of the 10 min. collection period, the controller shuts off the LN2, the resistance heater quickly takes the cryogenically cooled trapped section of the column to 275°C (527°F), the GC is automatically switched on, and the mass spectrometer starts to collect data. An alternative cryogenic trap that works very well is a simple styrofoam cup placed in the GC containing liquid nitrogen. A loop of the GC column is then submerged under the LN2. To start the analysis the cup of LN2 is removed and the GC started after the out-gassing/ pyrolysis. This provides –190°C (–310°F) cryogenic trapping. At this temperature, all products of interest will be stopped, including carbon dioxide and acetone.

Frequently, solutes identified by the low temperature TE analysis include the oxygenated alcohols (2-butoxy ethanol, 1-methoxy-2-propanol, etc.), the butanols, benzyl alcohol, the xylenes, ketones, acids (both organic and mineral), and any solutes volatilized at the 125°C (257°F) TE condition. If the blister is being driven by hydroxyl ion being leached from the substrate (as with some water based zinc silicates) or generated from CP impressed currents, the *p*H will be high. For high *p*H blister fluids, the solubility of any benzyl alcohol binder extender and other alcohols become much greater. These may then be seen. Typically, their concentrations will not be sufficiently great to continue the development of the blisters in neutral (water) blister fluid. Tank linings used in organic solvent service can generate blisters from the alcohol extenders depending on the coating and service (Fig. 9).

GC/MS High Temperature Pyrolysis (PYRO/GC/MS)

To identify the higher molecular weight solutes, without opening the TE/Pyro oven system after the TE run, the TE/Pyro oven controller is set for the pyrolysis programmed conditions. The cryogenic trap is brought back down to –125°C (–193°F) or the cup of LN2 is re-inserted. When the cryogenic section of the separation column reaches the low trapping temperature, the pyrolysis oven containing the dried blister fluid sample is heated to 500°C (932°F). Any organic materials that were dissolved in the blister fluid but did not volatilize during the warming thermal extraction procedure are now subjected to the potential thermal degradation temperature of 500°C (932°F). Any heavy organic solutes will degrade to volatile components. The identification of these components allows one to visualize their precursors.

Determination of Electrical Conductivity and pH

If there is sufficient blister fluid, one drop is used to determine the electrical conductivity and *p*H. When the conductivity is high, there is ionic activity. If the *p*H is alkaline, the ionic source could be from applied CP, or a source of stray current potential sufficient to reduce molecular oxygen to the hydroxide. The coating may have been applied over a water based zinc shop primer wherein all of the sodium or potassium hydroxide could not be rinsed away. There is a very low probability that some of the amine curative may have been solubilized.

If the conductivity is high and the *p*H is neutral, as may be the case between coating layers, the salts may be organic acid or carbonated amine curatives. An exception is in areas where wind blown salts are available, as on offshore facilities and in marine applications.

If the conductivity is high and the *p*H is low, there is some source of acid causing the *p*H depression. Unlike the clean, non-corroded metal seen under high *p*H blister

fluids, typically, the low *p*H fluids cause the steel to corrode. The source of acid must be determined from past history or pyrolysis of the iron corrosion product. For cargo tank linings, this is a common problem and may be deduced from cargo histories that are available. Acetic acid is especially problematic. Cargoes of molasses and natural sugar products often contain acetic acid that is the result of bio-degradation. The transmission coefficients for acetic acid through most tank linings are such that it often becomes the primary solute in the osmotic activity. After desolution of iron, additional soluble iron (II) complexes add to the solute mix dissolved in the blister fluid. As oxygen transports across the paint film to the blister fluid, the soluble iron (II) complex is converted to iron (III) and precipitates out of solution. Analysis of the rusty iron scrapings from under the blister area by pyrolysis GC/MS will often reveal which acid has been operative, even if it is hydrochloric acid. Hydrochloric acid results from the hydrolysis of chlorinated solvents. There are many different chlorinated organic solvents stored in coated tanks as well as transported in coated marine tankers. All will hydrolyze to some degree to produce the HCl. The most problematic chlorinated solvent seen by this laboratory is the cargo material allyl chloride, $CH_2{=}CH_2CH_2Cl$. This material absorbs into the tank lining and within hours after water washing, liberates HCl.

Hydrogen sulfide, H_2S, may be generated within sewer systems that are not properly treated to control the condition. Since this is an anaerobic action (occurs in the absence of oxygen), to stop this H_2S formation, sewer operators will sometimes attempt to maintain a sufficient amount of dissolved oxygen (DO) in the effluent to disallow attack of the sulfates. Another practice is the addition of nitrates into the effluent, since the bacteria prefer nitrates to sulfates as their hydrogen acceptor in the energetics of their life cycle. If the sewer system has not been properly controlled for the production of hydrogen sulfide, sulfuric acid will be produced from any H_2S after reaching aerobic conditions. This occurs readily in the crown of partially filled pipes where air is available above the wastewater. The resulting corrosion is called "Crown Corrosion" for this reason [6]. This can destroy both steel and concrete pipe systems after loss of coating by osmotic blister formation.

Ion Chromatography

The use of ion chromatography usually will identify the specific ions causing the high conductivity in blister fluids. Past experience of this laboratory has shown that the presence of hydroxyl ions from a CP induced high *p*H blister fluid often will cause an increase in additional ionic species in the blister fluid. Under blue or green coatings, bromine may be hydrolyzed from the phthalo blues and greens pigments. Chlorides may be hydrolyzed from epoxy resins in high *p*H blister fluids. For this reason, the presence of the chloride or bromide ion in the blister fluid is NOT, conclusively, indicative of salts over-coated during application although these may have contributed to the diminished adhesion exacerbating the osmotic activity. Sulfates will be seen in oxidation of the H_2S in sewer pipes. Sea water evaporation and blown sea salts will contain chlorides, bicarbonates or carbonates (depending on *p*H), sulfates, and all other ions typically seen in seawater.

CASE HISTORIES OF OSMOTIC ACTIVITY PAINT FAILURES

Case Number 1: A series of barges employed in fresh water river trade developed blisters after being in service a number of months. The time to discovery was about a year. The paint system included the use of a water based potassium silicate zinc shop primer applied to the steel plate upon arrival at the fabrication facility. After application of the shop primer, the steel was fabricated into barges within about a month. After fabrication of the barge, and just a few days before launch, the finished barge was high-pressure fresh water rinsed, allowed to dry, and over-coated with an epoxy coating. Blisters were discovered during dry-docking about a year later. There were no cathodic protection anodes used. The declaration was made that there had been no cathodic protection potentials applied to the vessel during its moorings. Grounding a vessel to the CP system of a dock is a practice that often occurs with vessels that trade in flammable cargo. These barges traded in dry cargo.

Fluid was collected from a number of the blisters on the bottom of a barge. The blister fluid was clear, the *p*H of the fluid was about 13, the conductivity was measured at 19 200 μS (microsemins). Chemical analyses of the fluid by GC/MS TE followed by PYRO indicated that a small amount of organic solubles was present in the fluid. These were all alcohols that had migrated from the epoxy paint topcoat. There were no heavier molecular weight materials seen during the pyrolysis analysis.

The analyses indicated that the water based zinc silicate still contained sufficient water-soluble potassium hydroxide to become the solute in the osmotic blisters. It is extremely difficult to extract all alkali from these types of silicate films in one short rinsing. Additionally, the curing of the silicate film may require months to fully bind the potassium and allow loss of the excess alkali to become minimally soluble-salt free. (It cannot become salt-free.) The driving force to produce blisters is just as strong for the salt potassium hydroxide as it is for the salt sodium chloride. One would never consider over-coating high concentrations of sodium chloride salt. Because zinc metal is amphoteric (i.e., can be dissolved by either acid or base) the tetrahydroxy zinc (II) ion is just another solute driving the osmotic activity. The organic solutes seen in the GC/MS analysis are, in part, because of their increased solubility as the pH of the blister fluid increases. The butanol and benzyl alcohol have limited solubility in neutral water. The 1-methoxy-2-propanol is 100 % water-soluble and can be a problem in certain scenarios. This water soluble solvent is sensitive to length of drying time and ventilation. The transmission coefficient for this oxygenated alcohol is greater than the 2-butoxy ethanol and often will not be sufficient to generate visible osmotic blisters. The exception is in well cross-linked epoxy systems where its mobility is more restricted. This is an example of the importance of the numerical values of the "semi" in the "semi-permeable membrane" part of a typical definition of "osmosis." In this case, although the concentrations were relatively small for all alcohols, the 1-methoxy-2-propanol exacerbated the blister formation and the hydroxide ion provided the driving force for the continued osmotic activity (see Fig. 10 and Fig. 11).

Case Number 2: Blisters developed within the coating system of a large floating offshore drilling platform. The

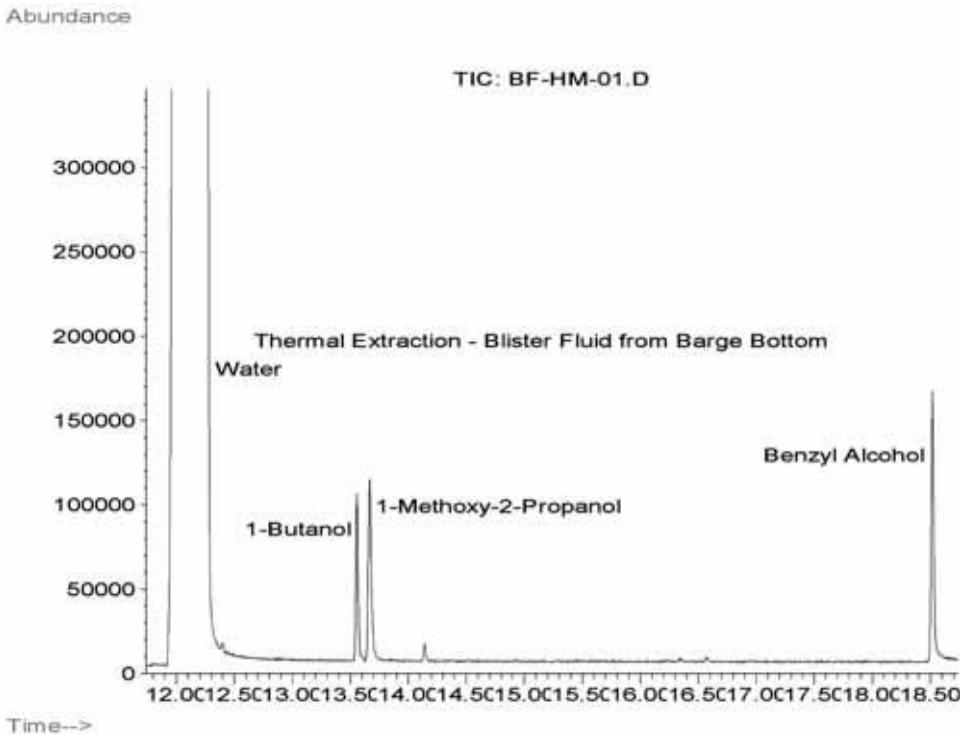

Fig. 10—GC/MS response from the thermal extraction of blister fluid collected from the bottom of a barge. Alcohols that normally are not appreciably soluble in water are more soluble in alkaline blister fluid. The scan is magnified to reveal the small amounts of organic solutes.

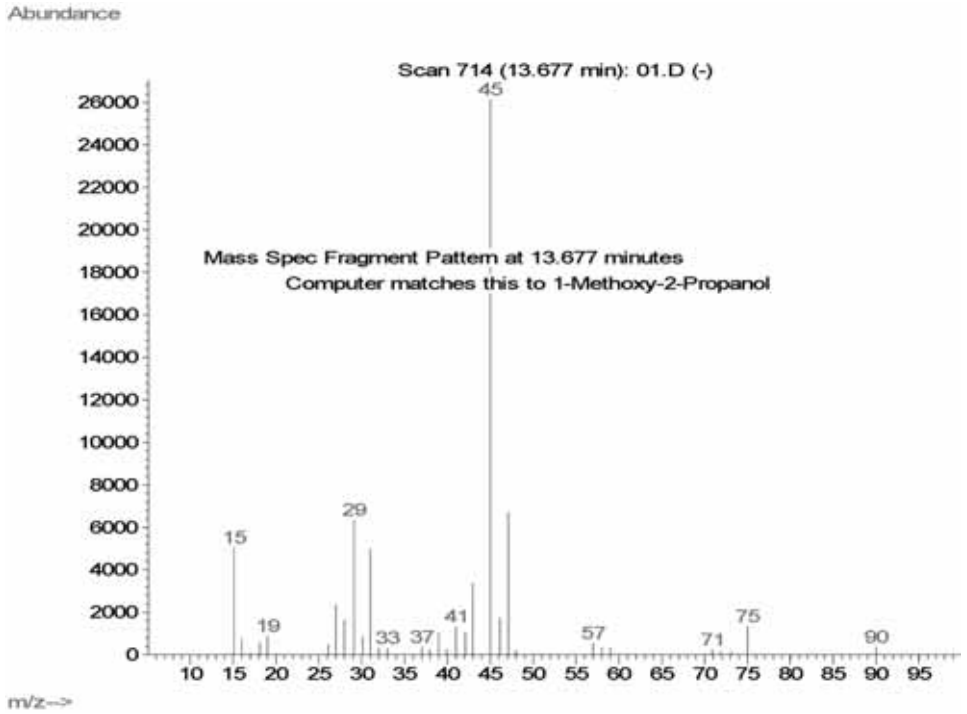

Fig. 11—Fragment pattern collected by the mass spectrometer at 13.677 min. The computer matched this pattern to 1-Methoxy-2-Propanol, a water soluble epoxy thinner. This "oxygenated" alcohol can cause osmotic blisters when condensed water is possible.

paint system was similar to Case Number 1 with the exception that the zinc silicate was applied as a holding primer after construction. It was a solvent based, ethyl silicate zinc coating. The two-coat epoxy topcoat was applied during colder months in Europe. Severe blistering occurred after flooding the tanks for testing. The drilling platform was delivered to the US for completion and an investigation of the cause of the osmotic activity was done [7].

Blister fluids were collected from two types of blisters based on their development location. Type one were blisters that originated at the metal interface and were under the full thickness of epoxy paint. Type two blisters were between the layers of the epoxy coating. Both blister fluids were clear as they were removed using hypodermic syringes. These fluids were analyzed separately. The blister fluid removed from the metal interface had a relatively high *p*H of greater than 12. The *p*H of the fluid extracted from blisters between layers of epoxy was neutral, *p*H of 7.

The GC/MS chemical analysis of the two blister fluids was very similar even though there was a large difference in their *p*H. There was a very large peak of 2-butoxy ethanol in each. It was very evident that the driving force for the blister formation was the oxygenated alcohol, 2-butoxy ethanol. A review of the MSDS for the reported coating material did not indicate the presence of this alcohol in the coating formulation. For this reason, it was first suspected that the applicator might have used this water-soluble solvent during application. This was shown to not be the case when retained samples of the actual coating materials used became available for GC/MS analysis. These were tested and found to contain the 2-butoxy ethanol as part of the paint formulation. The coating manufacturer was able to determine that there was a difference in the solvent system of the European produced material as opposed to that manufactured in the US. The high *p*H of the blister fluid removed from contact with the metal substrate was the result of sacrificial anodes installed during the construction of the platform. Oxygen that migrates into the blister fluid at the metal interface experienced sufficient electrical potential to cause the oxygen to be converted to hydroxide ion producing the high *p*H. For blisters formed between paint layers, there could be no electrical potential felt between layers, although there was compromised adhesion that allowed the delamination between coats of epoxy at the blister site [8].

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Stress Phenomena in Organic Coatings

Dan Y. Perera[1]

PREFACE

THIS CHAPTER REVIEWS AND UPDATES THE TOPICS addressed by the previous authors, including up-to-date references and expanded to include stress in multi-layer systems and stress in physical aging.

Interest in the stress phenomena in organic coatings is relatively new. The importance of understanding and measuring this stress became evident as facts accumulated about its role in coating degradation [1–10]. This is also supported by the fact that many coatings used today (e.g., thermosets) are more susceptible to developing high stresses than traditional ones (e.g., alkyd paints). It is now quite clear that stress can affect coating adhesion and/or cohesion and provoke delamination and/or cracking.

Since the development of stress is involved in practically all stages of coating life (film formation, exposure to various climatic conditions), its measurement is essential for a better understanding of coating behavior.

In addition, the measurement of stress can be used to evaluate other important characteristics of a coating, such as the glass transition temperature (T_g) and the critical pigment volume concentration (CPVC).

ORIGINS OF STRESS IN ORGANIC COATINGS

Stresses originate in organic coatings as a result of their adhesion to the substrate. Good adhesion is, on the one hand, indispensable for adequate substrate protection, but on the other hand prevents the normal movement of a coating.

The three main causes which provoke stress in an organic coating are [11]:

1. Film formation.
2. Variation in temperature.
3. Variation in relative humidity (RH).

The stresses induced by film formation, variation in temperature, and variation in RH are known, respectively, as internal, thermal, and hygroscopic. The latter two stresses are also referred to as hygrothermal (S^{HT})

It is important to realize that, due to the coating adhesion to its substrate, stress exerts its action mainly in a plane parallel to the substrate [6,12,13]. Therefore, one can write

$$S = \frac{E\varepsilon}{1-\nu} \tag{1}$$

where

S = stress,
E = elastic modulus,
ε = strain,
ν = Poisson's ratio.

This relationship represents the stress equation for an uni-axial deformation adapted for a bi-axial deformation by dividing it with $1 - \nu$. It is therefore considered that the coating can contract or expand only through its thickness. In practice this might not always be so, i.e., in addition to tangential stresses, the coating can also be subjected to normal stresses.

Stresses are especially damaging at edges [14] where they cannot cancel each other or in the middle of the plate if defects or heterogeneities are present.

Film Formation

During film formation and regardless of the mechanism involved (evaporation of solvent, coalescence, chemical reaction, or their combination), in almost all cases the coating tends to contract. If this contraction is prevented by coating adhesion to its substrate and/or the mobility of macromolecular segments is hindered, a tensile stress will develop in the coating.

In the literature certain confusion reigns about the denomination of the stress arising during film formation. For example, for solvent-based coatings an author may use these terms: cure stresses, solvent removal stresses, residual stresses, shrinkage stresses, internal stresses. For simplification, I suggest referring to the stress arising during film formation as internal stress (S^F).

If a liquid paint is applied on a substrate [8] and the development of stress is measured as a function of time, a number of stages can be observed (Fig. 1).

In Stage 0, the coating is still liquid and is mobile enough to permit volume contraction, and consequently no stress develops.

In Stage 1, the film starts to form, the volume contraction is restricted, and stress develops.

In Stage 2, a number of processes can occur. Depending on the coating composition, the evolution of stress can include various combinations of increasing, decreasing, and stationary stress levels. If no damage occurs to the film (cracks, microfissures, loss of adhesion), a decrease in stress results from relaxation processes which occur from the moment the stress develops but only become evident at this stage. It also follows that the measured stress values are a result of two opposite processes, one tending to develop stresses in the coating (in this case due to the volume shrinkage) and the other tending to decrease them (due to stress relaxation).

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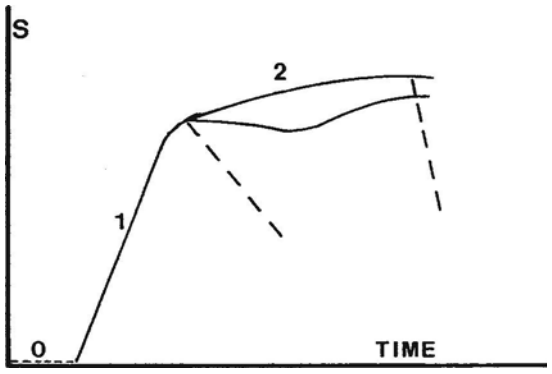

Fig. 1—Schematic description of stress (*S*) dependence on time.

Examples of stress development as a function of time for latex coatings [15] above and below the CPVC are shown in Fig. 2.

It is important to add that stress starts to develop in a coating when its T_g is at least equal to the experimental temperature [6]. For solvent-based coatings (Fig. 3), this is also confirmed by the fact that stress appears when Phase 2 of the evaporation kinetics (the diffusion process) starts [16]. At this point in the evaporation, referred to as solidification, the solvent volume fractions are equal to the solvent concentration necessary to bring the T_g of the coating to a temperature equal or higher than the experimental one [6,17].

The stresses arising in the different stages of the film formation of the polymer lattices are also discussed in Ref. [18]. The paper provides evidences of lateral dilatation stress occurring during the initial stage that is attributed to the capillary pressure.

If Eq (1) is extended to accommodate the specific effect of internal strain, ε^F [6], then

$$\varepsilon^F \approx \frac{V_s - V_t}{3V_s} = \frac{\Delta V}{3V_s} \tag{2}$$

where

V_s = volume of coating at solidification, and
V_t = volume of coating at time t after solidification.

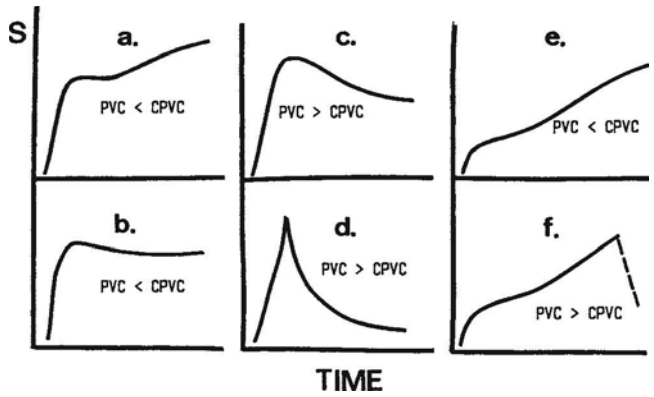

Fig. 2—Schematic description of stress (*S*) dependence on time for latex coatings: (a) and (b) PVC < CPVC; (c) and (d) PVC > CPVC; (e) PVC < CPVC in the presence of a poor coalescent; (f) PVC > CPVC in the presence of a poor coalescent.

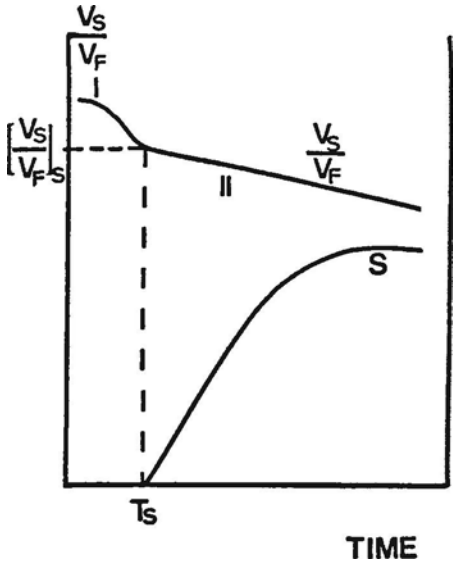

Fig. 3—Schematic representation of the dependence of V_S/V_F and stress (*S*) on time, V_S = volume of solvent present in the film; V_F = volume of the dry film.

One can write [19] that

$$S^F = \int_{V_t}^{V_S} \frac{E}{1-\nu}\frac{1}{3V_s}dV \tag{3}$$

Despite the limitations of Eq (2), which assumes that the strain is isotropic and linear, Eqs (2) and (3) enable one not only to better understand the factors affecting the S^F but eventually to calculate it approximately.

Variation of Temperature

When coated substrates are exposed to variations in temperature, dimensional changes are induced. If the thermal expansion coefficients of the coating $\left(\alpha_F^T\right)$ and the substrates $\left(\alpha_S^T\right)$ are different, which is usually the case, a thermal stress (S^T) will develop in the coating [2,7,11,20,21].

Since the thermal strain, ε^T is given by

$$\varepsilon^T \approx \left(\alpha_F^T - \alpha_S^T\right)\Delta T \tag{4}$$

the combination of Eqs (1) and (4) gives

$$S^T = \int_{T_2}^{T_1} \frac{E}{1-\nu}\left(\alpha_F^T - \alpha_S^T\right)\, dT \tag{5}$$

Determination of T_g

A schematic description of the stress dependence on temperature [19] is represented in Fig. 4.

Such dependence indicates the possibility of determining the T_g of a coating from the stress measurement. This is due to the fact that E, α_F^T, and ν (see Eqs (1) and (5)) also show a profound change at T_g.

Below temperature ***a*** the coating is in the glassy region, and above temperature ***b*** the coating is in the rubbery region.

The linear dependence of S on temperature in the glassy region greatly facilitates the measurement of T_g. This linearity is due to the fact that in this region E, α_F^T, and ν are practically independent of temperature.

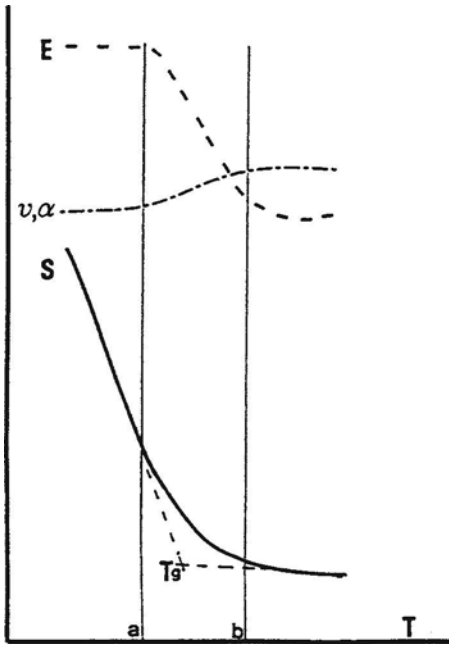

Fig. 4—Schematic representation of dependence of S, *E*, α, and *v* on temperature (*T*).

Three examples of the stress dependence on temperature and T_g determination by thermal stress measurements [19] are shown in Fig. 5.

When the stress magnitude in the rubbery region is small (e.g., elastomers, coatings with a low degree of cross-linking), the T_g can be determined with fair accuracy just by carrying out a few measurements in the glassy region and then extrapolating the straight line to $S^T = 0$.

For coatings subjected to a significant stress in the rubbery region (e.g., highly cross-linked thermosets), the measurement of stress in this region might provide a way to approximately determine the cross-link density, v_e [22].

Since in accordance with the molecular theory of rubber elasticity in its simplified form [23,24]

$$E_r = 3v_e RT_r \tag{6}$$

and

$$S_r = 2E_r\varepsilon_r \tag{7}$$

giving

$$v_e = \frac{E_r}{3RT_r} = \frac{S_r}{6RT_r\varepsilon_r} \tag{8}$$

where R, S_r, E_r, and T_r are, respectively, the gas constant, the stress, the elastic modulus, and the temperature at the beginning of the rubbery region. If S_r is measured and ε_r is known or determined from separate measurements (e.g., by thermomechanical analysis), v_e can be calculated.

Others have used the evaluation of T_g by stress measurements to investigate the effect of a pretreatment on certain pigments [25], the state of cure of baking enamels [22], and the modification of epoxy coatings [20,26].

Variation of Relative Humidity

Dimensional changes induced by absorption and desorption of water as a result of variation in RH is another cause of stress development in a coating [11,27,28]. As in the case of temperature, if a mismatch between the expansion coefficients of the coating and the substrate exists, a hygroscopic stress (S^H) will arise in the coating.

Since the hygroscopic strain ε^H is given by

$$\varepsilon^H \approx \left(\alpha_F^H - \alpha_S^H\right)\Delta H \tag{9}$$

one can write that

$$S^H = \int_{RH_1}^{RH_2} \frac{E}{1-\nu}\left(\alpha_F^H - \alpha_S^H\right) dRH \tag{10}$$

where α_F^H and α_S^H are, respectively, the hygroscopic expansion coefficients of the coating and the substrate.

Some examples of the S^H dependence on RH are given in Fig. 6.

INTERDEPENDENCE OF STRESSES

While in previous sections the various stresses (S^F, S^T, S^H) were discussed separately, in practice they can act together in such a way that the total stress (S_{tot}) is small or, as in many cases, very important [11]

$$S_{tot} = S^F \pm S^T \pm S^H \tag{11}$$

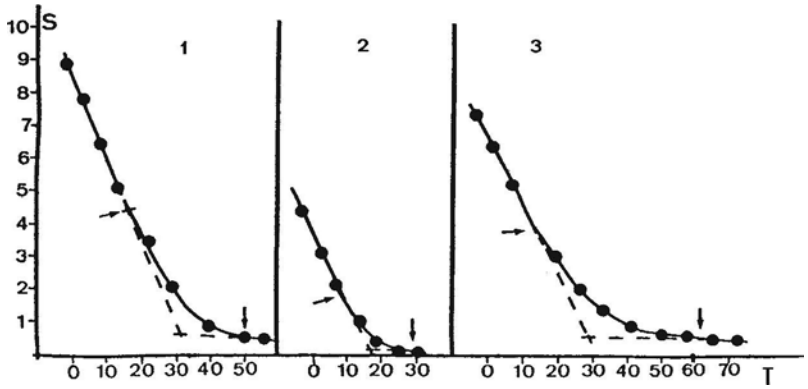

Fig. 5—Stress (*S*, MPa) dependence on temperature (*T*, °C) for three coatings at RH ≅ 0 % [an epoxy (1), a polyurethane (2), and an epoxy/melamine system (3)].

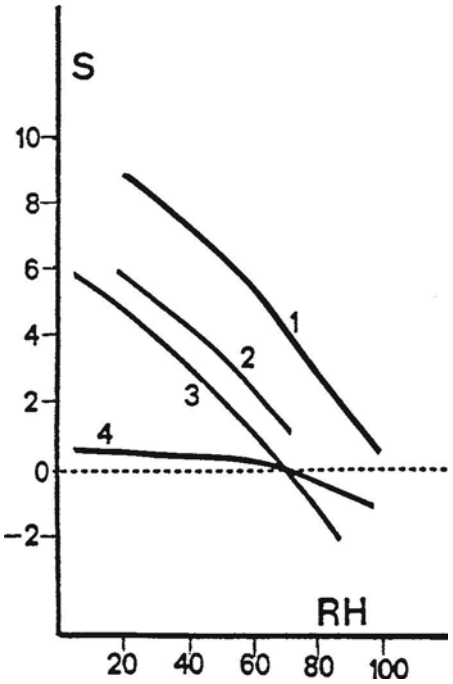

Fig. 6—Stress (*S*, MPa) dependence on relative humidity (RH, %) for a polyester powder coating (1); an epoxy (2); a polyurethane (3); and a latex coating (4).

The positive and negative signs are arbitrarily chosen. The positive sign denotes a coating tendency to contract (tensile stress) and the negative sign a coating tendency to expand (compressive stress). S^F is practically always positive.

Equation (11) indicates the existence of two climatic conditions which might provoke a high stress in a coating:

1. Low temperatures and RH's induce high tensile stresses (e.g., a dry, cold winter).
2. High temperatures and RH's induce high compressive stresses (e.g., a humid, warm summer).

According to Eq (11) and depending on the type of coating and the way it was cured, a number of situations can arise. For example, for a thermosetting coating cured at a high temperature (i.e., at $T > T_g$, RH = 0 %) and then exposed to different RH's, since $S^F \approx 0$ (except for highly cross-linked coatings), the S_{tot} is given by

$$S_{tot} \approx S^T - S^H \tag{12}$$

In Fig. 6, for one coating, the stress is positive regardless of RH, meaning that S^T is always higher than S^H; but cases where negative stress values are obtained are not rare.

It could be demonstrated [11] that the same coating conditioned in an identical environment but with different previous histories can develop different values of stress. Thus, a coating cured under isothermal and constant RH conditions (e.g., 21°C and 50 %) will develop a total stress given by

$$S_{tot} \approx S^F - S^H \tag{13}$$

Now, if the coated substrate is first heated at $T > T_g$ for sufficient time to enable a maximum stress relaxation and then brought back to the initial conditions (i.e., 21°C and 50 % RH)

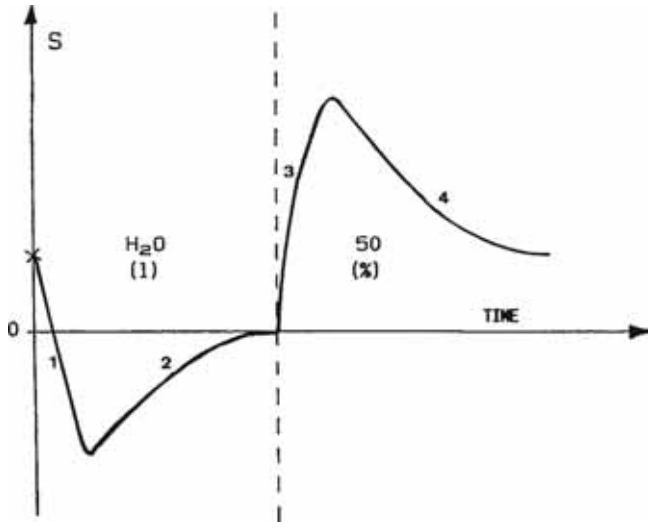

Fig. 7—Schematic description of the stress (*S*) dependence on time at two experimental conditions (water and 50 % RH). *X* = the initial stress.

$$S_{tot} = S^T - S^H \tag{14}$$

The results obtained [11] show that in certain cases (e.g., for an epoxy coating), the S_{tot} can be very different [S_{tot} (Eq (13)) = 5 MPa; S_{tot} (Eq (14)) = 0.4 MPa].

Interesting cases are those where the T_g of a coating is close to or below the experimental temperature once they are immersed in water or exposed to a high RH [29]. Under such conditions S^F or S^T can relax and therefore $S_{tot} \approx S^H$.

Such a situation is illustrated schematically in Fig. 7 and for a particular epoxy coating in Fig. 8.

Once a coated substrate is immersed in water one can observe first the development of a hygroscopic compressive stress followed by its decrease. The time necessary to reach zero stress is mainly dependent on the type of coating. The withdrawal of the coated substrate from water provokes first the development of a relatively high tensile hygroscopic stress followed by its decrease. The decrease in stress (Curves 2 and 4 in Fig. 7) is due to relaxation processes facilitated by the low T_g of the coating. The much higher stress values attained after the immediate withdrawal of the

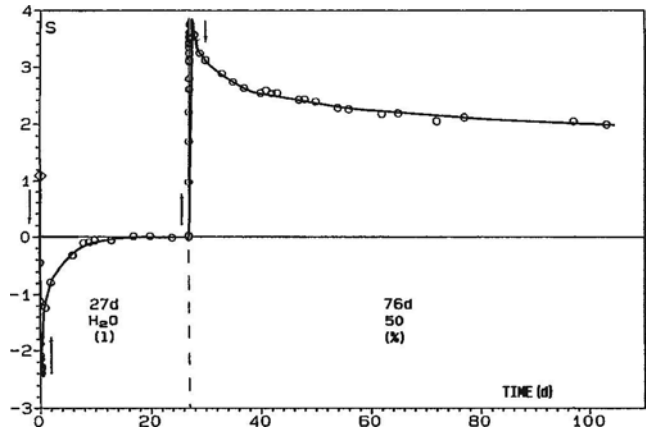

Fig. 8—Epoxy coating. Stress (*S*) dependence on time (*t*) at two experimental conditions (water and 50 % RH).

coated substrate from water (Curve 3 in Fig. 7), in comparison with the initial stress ($S_{tot} \approx S^F - S^H$ or $S_{tot} \approx S^T - S^H$) are due to the high hygroscopic tensile stress $\left(S_{tot} \approx S^H\right)$.

The above findings are important not only for understanding the mechanism of the stress development in organic coatings but also for practical reasons such as choosing the experimental conditions of natural or accelerated weathering tests, i.e., the magnitude of stress developed in a coating might depend as much on natural climatic conditions as on the type and order of cycle selected in the laboratory.

STRESS MEASUREMENT

Equations (1), (3), (5), and (10) show that, if one knows the values of E, ε, and v of a coating, then in principle the various stresses can be calculated. However, except for relatively simple cases, this is difficult because the above coating characteristics can be time, temperature, and relative humidity dependent.

Therefore, efforts were made to directly determine the stress arising in a coating. Among the methods one can find in the literature are: optical [30–33], strain gages [20,34,35], brittle lacquer materials [36], x-ray diffraction [37], and cantilever (beam) [2,4,8,11,27,38–45].

The cantilever (beam) method appears to be the most widely used and is suitable for determining the stress in an organic coating. This method makes use of the fact that for a coating under stress, applied on a substrate, the coated substrate will deflect in the direction which relieves the stress. Since the deflection can be measured and the elastic properties of the substrate are known from separate determinations, the stress can be calculated.

Two variations of the cantilever (beam) method are described in the literature: a one-sided coated substrate either (1) fixed vertically at one end [4,8,27,38] (Fig. 9) or (2) freely supported on two knife edges [2,11,43,45] (Fig. 10).

The stress analysis of (1) is more complicated and shows that to eliminate the effect of clamping on the coated substrate deflection, its measurement should be made at a distance higher than 80 mm from the clamping point [8]. Variation (2) is much simpler to analyze and can be designed to eliminate the effect of weight loss on the coated substrate deflection by choosing the right distance between the two knife edges [45].

Each variation has its advantages, but if correctly used they should give identical results. For example (1) is more suited to evaluate stress in water [29] and (2) to determine the effect of temperature [2,11].

Among the techniques used to measure the deflection of coated substrates, one can mention: capacitive transducers [44,45], laser [46], traveling microscope [4,8,27], automatic micrometer [11]. A variety of flexible substrates can be used, such as cold laminated steel, stainless steel, aluminum, copper, and silicon wafers.

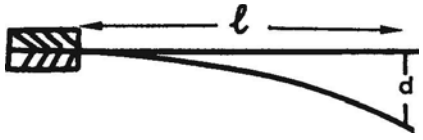

Fig. 9—Schematic description of the vertically fixed at one end cantilever (beam) method.

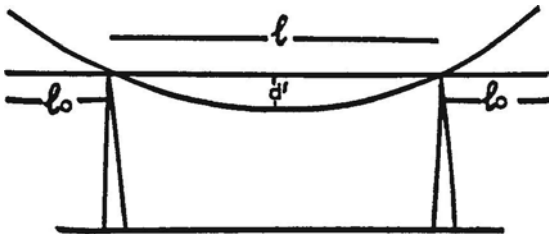

Fig. 10—Schematic description of the freely supported beam method.

A commercial apparatus, the CoRI Stressmeter (Fig. 11), is based on variation (2) and the mathematical analysis described in Ref. [45]. This apparatus is almost completely automatic and enables one to measure the stress from about –5 to 110°C under a variety of RH's. This instrument requires the use of substrates that are electrically conductive, e.g., cold laminated steel, stainless steel, aluminum, and copper.

In certain cases, such as for investigating the stress arising in ultraviolet cured coatings, the stress measurement might necessitate an elaborate set-up. In this case the set-up might include, among others, a UV lamp, a controlled flow gas and temperature device, an application chamber and a video camera monitoring the deflection of the coated substrate [47].

Mono-Layer Systems

A number of mathematical equations are proposed in the literature to calculate the stress in a mono-layer system [41,42], but in the author's opinion those proposed by Corcoran [41] are the closest to the real situation (e.g., considers the fact that stress develops in two directions)

$$S = \frac{dE_S t^3}{3l^2 c(t+c)(1-v_S)} + \frac{dE(t+c)}{l^2(1-v_S)} \tag{15}$$

$$S = \frac{4d'E_S t^3}{3l^2 c(t+c)(1-v_S)} + \frac{4d'E(t+c)}{l^2(1-v_S)} \tag{16}$$

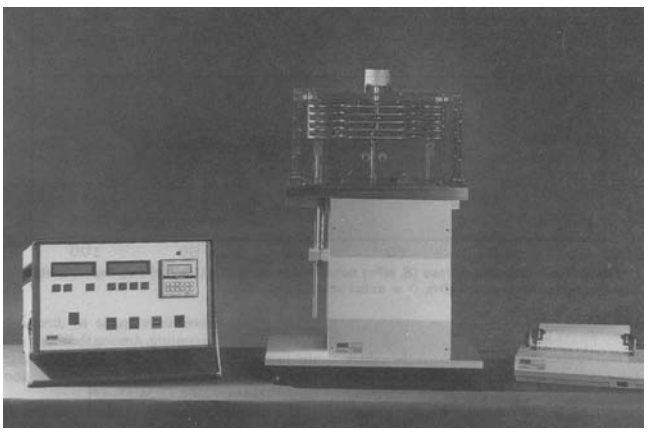

Fig. 11—CoRI Stressmeter apparatus (Courtesy of Elcometer, Liège, Belgium).

where

d = deflection of the substrate (Fig. 9),
d' = deflection in the middle of the substrate (Fig. 10),
E_s = elastic modulus of the substrate,
E = elastic modulus of the coating,
ν_s = Poisson's ratio of the substrate,
t = thickness of the substrate,
c = thickness of the coating,
l(Eq 15) = length of the coated substrate between the point at which it is clamped and the point at which the deflection is measured (Fig. 9), and
l(Eq 16) = distance between the two knife edges (Fig. 10).

Equations (15) and (16) assume, among other things, good adhesion between the coating and the substrate, isotropic elastic properties of the coating and the substrate, the elastic limit of the substrate is not exceeded, and the stress is constant throughout the coating thickness. If the last condition is not fulfilled it means that the coating is heterogeneous through the film thickness. Therefore, the measurement of stress as a function of film thickness might enable one to determine, depending of the film composition, the distribution of the solvent, cross-link density, pigmentation, etc., through the film thickness [8,15,16,68,76(a),76(b),77,79–81].

The second term in Eqs (15) and (16), which contains a number of coating properties difficult to determine, can be neglected if $E_S \gg E$ and $t \gg c$.

Since the substrate is flexible and deflects during a stress measurement, in principle, part of the stress relaxes. This relaxation is however negligible with respect to the stresses arising in the coating. An approximate calculation, by considering even a high elastic modulus ($E \approx 2$ MPa) and strain ($\approx 6\times10^{-6}$) values, induces a negligible stress relaxation (0.01 MPa $\ll$) with respect to stresses usually arising in the coating.

Most commonly, stainless steel or cold laminated steel [4,8,11,27,44,45] shims are used. Other substrates such as aluminum and copper can also be used.

The elastic modulus, E_s, of each shim can be determined prior to use with the CoRI Stressmeter by applying Eq (17)

$$E_S = \frac{Pl^3}{4d't^3b} \tag{17}$$

where

P = weight placed in the middle of the substrate,
b = width of the substrate, and
d', l, t = as in Eq (16).

It is important to add that, although it is not difficult to make the measurements, nevertheless great care is necessary. One should always use the correct substrate thickness, adequately condition it, and precisely calibrate the apparatus.

Multi-Layer Systems

In many cases multi-layer systems are applied on substrates to protect them against a variety of aggressive factors. Since the mechanical characteristics of each layer are usually different, one can expect that the stresses arising in each layer be also different. Furthermore, a monolayer system might become a multi-layer one if part of it acquires mechanical characteristics different from that of the bulk. This is typical of coatings subjected to chemical changes when submitted to natural or accelerated weathering.

To the author's knowledge, all the relationships for calculating the stress in multi-layer systems found in the literature [48–52] necessitate the determination of elastic properties of each layer, coating characteristics not always easily measurable.

To enable the determination of stress in each layer of multi-layer systems mathematical equations that do not necessitate the knowledge the elastic characteristics of each layer were derived [53]:

$$S_2 = \frac{4E_S t^3}{3l^2c_2\left(t+2c_1+c_2\right)\left(1-\nu_S\right)}\left(d_2-d_1\right) \tag{18}$$

$$S_3 = \frac{4E_S t^3}{3l^2c_3\left(t+2c_1+2c_2\right)\left(1-\nu_S\right)}\left(d_3-d_2\right) \tag{19}$$

where

c_1, c_2, c_3 = thickness of individual layers,
d_1, d_2, d_3 = deflection of the coated substrates (d′ in Fig. 10) with one, two, and three layers,
S_2 (Eq (18)) and
S_3 (Eq (19)) = stress in a top coat of two- and three-layer systems, respectively.

For a three-layer coating system whose composition is unaffected by multiple applications and curing, the determination of stress in each layer is as follows:

—application of the first layer and its curing,
—measurement of the deflection d_1 and of the thickness c_1,
—calculation of stress S_1 from Eq (16),
—application of the second layer and its curing,
—measurement of the deflection d_2 and of the thickness c_2,
—calculation of stress S_2 from Eq (18),
—application of the third layer and its curing,
—measurement of the deflection d_3 and of the thickness c_3,
—calculation of the stress S_3 from Eq (19).

Procedures for coatings affected by successive applications and curing are described in Ref. [53].

Two examples by applying Eqs (18) and (19) are presented in Figs. 12 and 13, respectively. Fig. 12 shows that for a three-layer system the highest thermal stresses are arising in the primer. Fig. 13 illustrates the case when a single layer system of 77 μm becomes a multi-layer one, due to its exposure in an accelerated weathering device. After seven days of weathering the thermal and hygroscopic stresses arising in the first 27 μm are much higher than in the bulk.

STRESS AND PHYSICAL AGING

We are associating the stress development with physical aging because both phenomena are mainly occurring in the glassy region, and they are therefore unseparated.

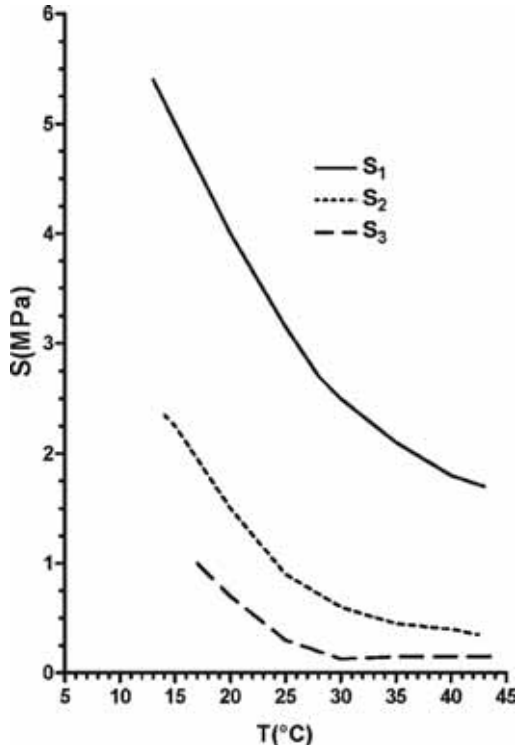

Fig. 12—Stress (*S*) dependence on temperature (*T*) for a three layer acrylic/melamine system. S_1, S_2 and S_3 indicate the stresses arising in the primer, middle, and top layers, respectively [53]. (With kind permission of Springer Science + Business Media.)

Physical aging is a general term that includes relaxation processes of a material in the glassy state, caused by its non-equilibrium state [54]. This process is easily explained by considering the dependence of volume (*V*), enthalpy (*H*), and entropy (*S′*) on temperature (*T*) above and below T_g (Fig. 14) [54–58]. During cooling at $T > T_g$, due to the great mobility of polymer chain segments, *V*, *H*, and *S′* can follow the decrease in temperature. Below T_g the

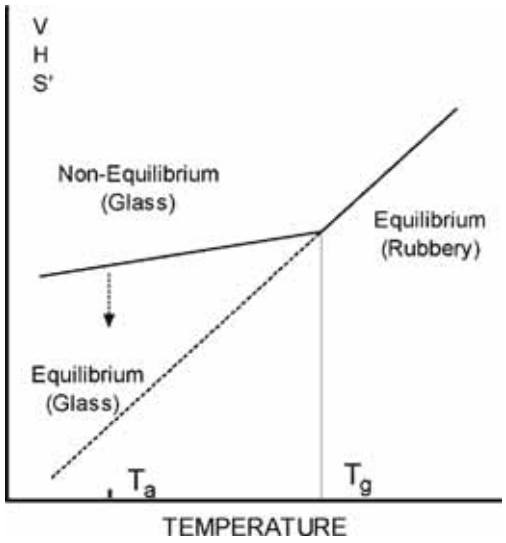

Fig. 14—Schematic description of the dependence of volume (V), enthalpy (H), and entropy (S′) on temperature. T_a = physically aging temperature.

mobility of polymer chain segments is reduced, and *V*, *H*, and *S′* cannot follow any more the decrease in temperature, meaning that the material departs from its equilibrium state. The values of these thermodynamic quantities being higher than in equilibrium state they will continuously decrease until the equilibrium state is reached. The closer the aging temperature to T_g the higher the aging rate and the smaller the change in property. Since the studies made by Struik [54], this relaxation toward equilibrium is known as physical aging.

In contrast with chemical aging that induces irreversible changes, physical aging is a reversible process. It can be eliminated by heating the samples to $T > T_g$ for sufficient time. More than 800 studies have been dedicated to various aspects of physical aging. While certain phenomenological models (e.g., Kohlrausch—Williams—Watts) describe

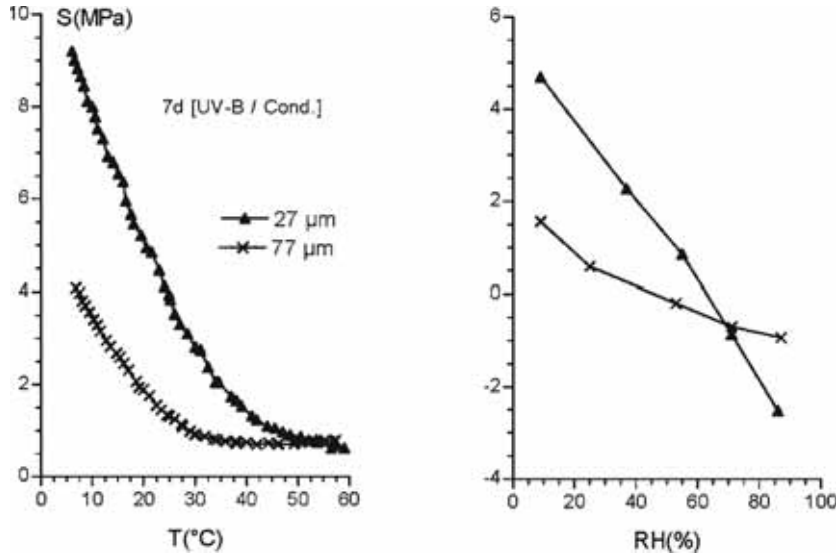

Fig. 13—Stress (*S*) dependence on temperature (*T*) (left) and on relative humidity (RH) (right) for an acrylic/melamine system after an exposure of 7 days in a Q-Lab Corporation (QUV) device.

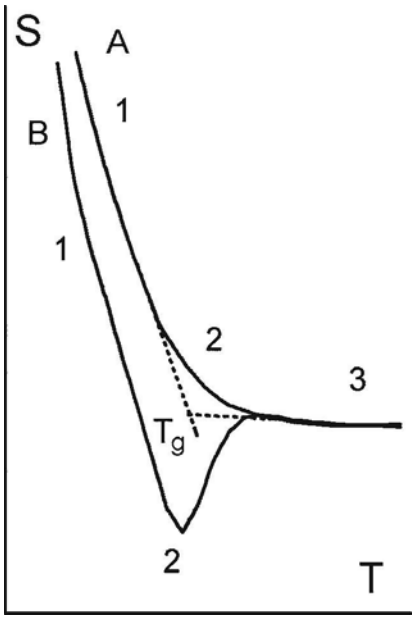

Fig. 15—Schematic description of the stress (*S*) dependence on temperature (*T*), for physically unaged (A) and aged (B) organic coatings. Segments 1 and 3 represent the glassy and the rubbery regions, respectively. Segment 2 represents the glass transition region [59].

well its kinetics, this process is not very well understood on a molecular scale. Nevertheless, it is associated with increased molecular packing and densification, processes that can greatly affect important coating properties like mechanical, thermal, and electric. Concerning mechanical properties, which directly affect coating integrity, densification causes the coating to become harder and more fragile.

To describe the interdependence between stress and physical aging the thermal stress will be considered. This interdependence was discussed in detail in Refs. [59,60] and is schematically described in Fig. 15. Curves A and B are typical of physically non-aged and physically aged coatings obtained during their heating. The U-shape curve is mainly due to the increase of E with physical aging which in turn induces higher compressive thermal stresses (see Eq (5)). The right side of the trough represents the decrease of this stress with temperature due to the stress relaxation in the rubbery region.

Studies made with thermoplastic (e.g., latex paints) and thermosetting (e.g., waterborne, powder coatings) systems show that the coating composition (type of binder, presence of coalescents, degree of film cross-link density, presence of pigments) affects the physical aging process [61,62]. Physical aging also influences the coating durability by increasing the stress magnitude and by decreasing the stress relaxation rate. There are indications that physical aging affects the late stages of coalescent process.

EFFECT OF COATING COMPONENTS

Since E, ε, and ν (Eqs (1), (3), (5), and (10)) are known to be affected by the coating components, one should expect the same to hold for stress development. This section will briefly review the influence of pigmentation, solvents, and binder.

Pigmentation

It has been shown that pigmentation, both the pigment volume concentration (PVC) and the type of filler (i.e., pigments and extenders), affects the development of internal stress [7,43,63–68]. To illustrate this, examples are presented in Figs. 16–21.

Figs. 16 and 17 show, respectively, the stress dependence on time for a thermoplastic binder in solution and a latex, filled with a titanium dioxide (TiO_2). Some PVCs are above the CPVC, and some are below the CPVC.

The different stages occurring during the film formation, discussed previously, can be recognized. In Stage 1 stress increases relatively rapidly. For latex coatings, this stage corresponds to the transition phase of the evaporation kinetics when the greatest part of the coalescence occurs.

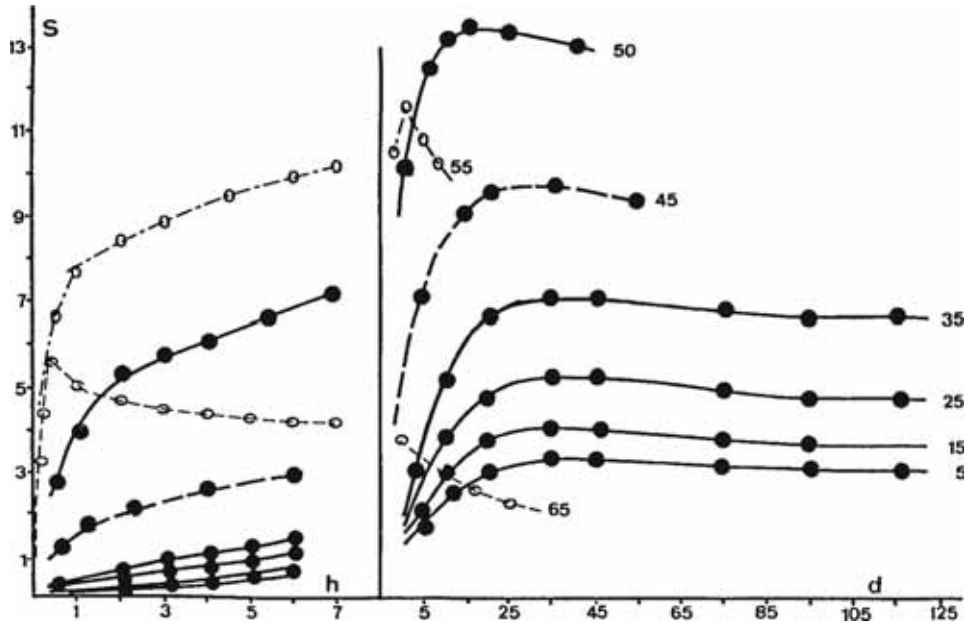

Fig. 16—Stress (*S*, MPa) as a function of time [hour (h) and day (d)] for a polyisobutyl methacrylate filled with TiO_2. The numbers in the figure indicate the different PVCs (%) investigated. CPVC = 51 %.

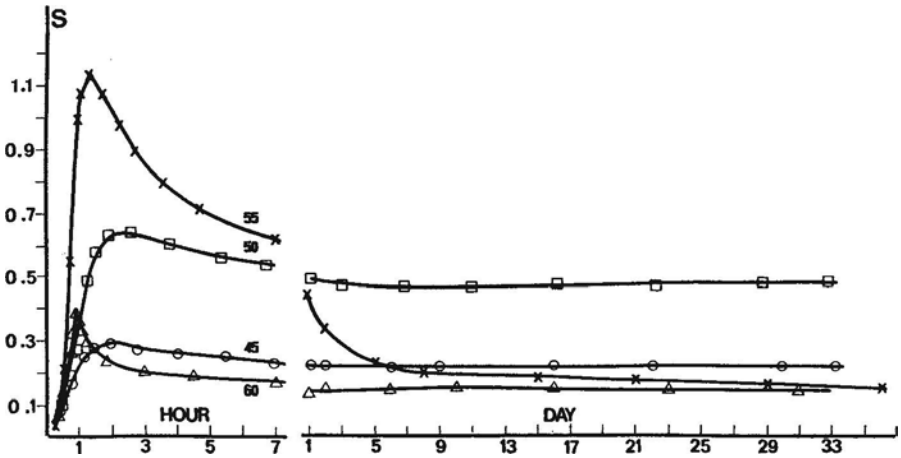

Fig. 17—Stress (*S*, MPa) as a function of time for a latex (vinyl acetate/vinyl versatate copolymer filled with TiO_2):45 % (○); 50 % (□); 55 % (X); 60 % (Δ). CPVC = 52 %.

In Stage 2 (which corresponds to Phase 2 of evaporation kinetics), depending on the PVC and the type of filler, the stress can decrease or first decrease and then increase. For PVC < CPVC, this decrease is mostly due to the relaxation process, but for PVC > CPVC is mostly due to relief processes such as filler/binder dislocations and/or formation of microfissures.

DETERMINATION OF THE CPVC

The plot of the maximum internal stress (*Sm*) as a function of PVC enables one to determine the CPVC of a coating. Some examples are presented in Figs. 18 and 19.

These figures, as well as other results presented in Refs. [66,67], clearly indicate that *Sm* is a function of PVC. *Sm* increases with PVC up to a certain PVC and then decreases. This PVC corresponds to the CPVC, indicating the possibility of accurately determining this characteristic [69,70] from stress measurements, and agrees well with the CPVCs calculated or determined by other methods (density, various mechanical properties).

The dependence of *Sm* on PVC can be understood if one considers Eq (1) and the way E, ε, and ν are affected by the PVC.

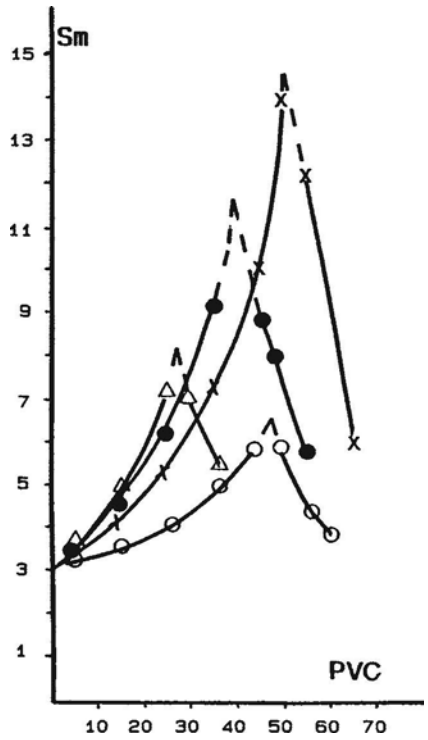

Fig. 18—Maximum internal stress (*Sm*) as a function of PVC (%) for a solvent-based thermoplastic binder filled with a TiO_2 (X),a red iron oxide (■), a yellow iron oxide (Δ), and a talc (○).

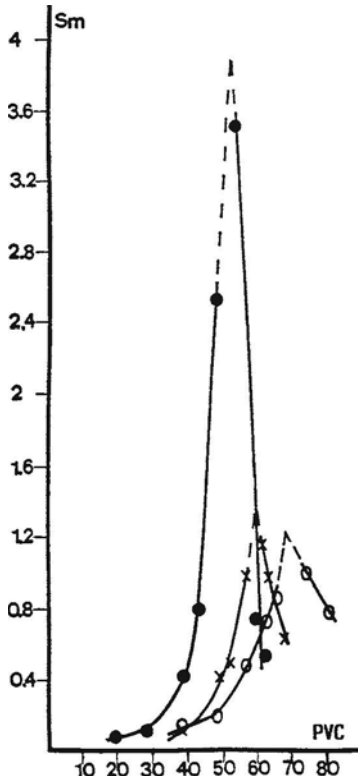

Fig. 19—*Sm* as a function of PVC (%) for a styrene acrylic copolymer filled with a TiO_2 (■), a calcium carbonate (X), and talc (□).

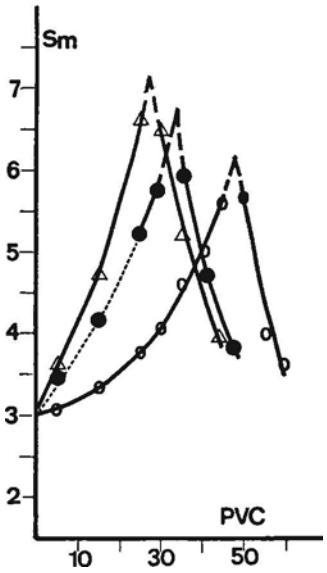

Fig. 20—*Sm* (MPa) as a function of PVC (%) for a thermoplastic binder in solution containing a yellow iron oxide (Δ), a talc (□), and their mixture (n = 0.5) (●); *n* = pigment volume fraction.

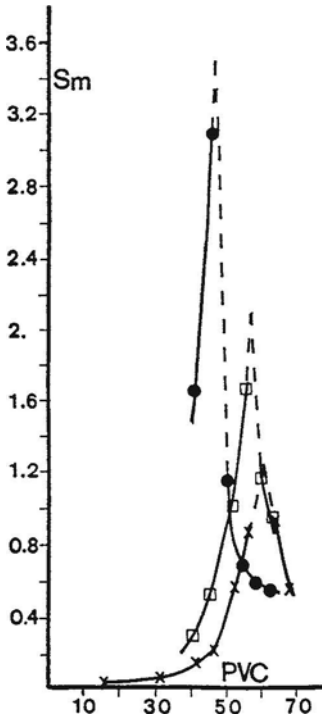

Fig. 21—*Sm* (MPa) as a function of PVC (%) for a latex binder containing a TiO_2 (●), calcium carbonate (X), and their mixture: TiO_2 (n = 0.4)/$CaCl_3$ (n = 0.6) (□).

For PVC < CPVC, E increases with increasing PVC because the E of an inorganic filler is in general higher than that of an organic binder [71]. For PVC > CPVC, E decreases as a result of the increasing film discontinuity [23,72]. Since in general ε and v are decreased (or are little affected) by the PVC, it follows that the increase of Sm with PVC is mainly due to the effect of PVC on E.

Figs. 18 and 19 also show that the magnitude of Sm is dependent on the type of filler. There are fillers which induce a higher stress (e.g., TiO_2, red iron oxide) than others (e.g., $CaCO_3$, talc). This is due to the filler/binder interaction (reinforcing effect), which is determined by the nature and, in particular, by the surface area and the acid/base character of the binder [73].

Examples of $Sm = f(\text{PVC})$ for coatings containing a mixture of fillers are presented in Figs. 20 and 21.

An examination of the results obtained with binary and ternary filler coating systems indicates that the stress Sm_t can be calculated approximately by means of an additive rule

$$Sm_t \approx n_1 Sm_1 + n_2 Sm_2 + \cdots + n_i Sm \approx \sum_{x=1}^{x=i} n_x Sm_x \qquad (20)$$

where

n_1, n_2, n_i = volume fraction of different fillers present in the mixtures, and

Sm_1, Sm_2, Sm_I = maximum stress of different single filler systems at a given A below or equal to 1 (A = reduced PVC, PVC/CPVC).

For organic coatings cured at high temperatures, such as baking paints, the CPVC can be determined by measuring the stress as a function of temperature of paints formulated at different PVCs. The representation of stress arising at a temperature (in the glassy or rubbery regions) as a function of PVC enables one to determine the CPVC (Fig. 22). As in the case of coatings formed at room temperature, the CPVC corresponds to the PVC that develops the highest stress.

In the literature one can also find simplified methods to determine the CPVC of latex coatings based on the same principle. They simply compare the force [74] or the deflection induced by the internal stress for flexible plastic substrates [75](Fig. 23) coated with paints of different PVCs.

These methods can be useful, but one has to be aware that they are valid only if both the thickness of the various paints and the time necessary to reach the maximum stress are the same.

Solvents

The presence of solvents in a coating can affect the magnitude and especially the rate of development of internal stress. This is illustrated in Fig. 24.

For thermoplastic binders in solution, the slower the evaporation of a solvent from a coating, the slower is the development of internal stress. The converse also is true. One should note that the coating cast from fast-evaporating solvents (Curve 1, Fig. 24) produces slightly higher stress values than those cast from more slowly evaporating ones (Curves 3 and 4, Fig. 24).

The results obtained were explained by using Eq (1), the principle of plasticizing effectiveness of solvents and the stress relaxation favored by the presence in the coating of the slower evaporating solvent [16].

For coatings containing a mixture of solvents (Fig. 25), both the development rate and the stress magnitude are mainly determined by the presence in the film of the less volatile solvent(s).

The situation may be different if the film formation is a result of solvent evaporation and cross-linking

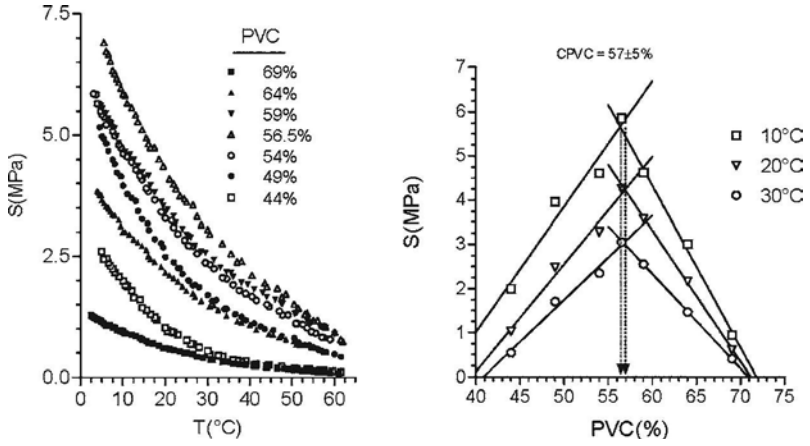

Fig. 22—A polyester/melamine system filled with a mixture of pigments cured at 150°C for 30 min. Left: Stress (*S*) as a function of temperature (*T*) at 0 % RH of 7 PVC formulations. Right: Stress (*S*) as a function of PVC at different temperatures determined during heating or cooling. CPVC (%) = 57±0.5.

processes (e.g., epoxy and polyurethane coatings). Under such circumstances the coating containing faster evaporating solvents can develop smaller stress values [76]. For such coatings, the volume of solvent present in the film after most of the cross-linking has occurred (Eq (2)) and which determines the magnitude of ε^F will increase the slower the solvent evaporates. If the stress relaxation process is negligible, it follows that for such coating systems the faster the solvent evaporates the smaller the internal stress.

The influence of solvents on internal stress is also evident for latex coatings where certain solvents, for example the coalescing agents, play an important role in the film formation process [15,52,77].

Examples of how the level and the type of coalescent affect internal stress are presented in Figs. 26 and 27, respectively.

Fig. 26 shows that: (1) the coalescent level affects the time necessary to reach the maximum stress, and (2) for each formulation, there is an optimal coalescent level to obtain a tight continuous coating developing the lowest internal stress.

In Fig. 27, the results obtained with three solvents used in latex coatings are given. One can see that the type of solvent influences both the value and the development rate of the internal stress.

As in the case of thermoplastic coatings, the influence of solvents on internal stress development in latex coatings was explained [15,68,75] by taking into consideration the plasticizing effectiveness [18,78], the molar volume, and the steric hindrance of solvents. The plasticizing effectiveness affects the internal stress magnitude, while the molecular dimensions affect the evaporation kinetics and consequently the rate of the stress development.

Binder

The binder is a key component of an organic coating with regard to stress development. To understand the role of the binder, one must consider the general Eq (1) (see also Eqs (3), (5), and (10)) and/or the T_g of a coating with respect to the experimental temperature.

Equation (1) indicates that the stress is directly affected by the magnitude of E, ε, and ν of the binder. The smaller the values of E, ε, and ν, the smaller the magnitude of stress.

With respect to T_g, it should be remembered that the binders having their T_g below or close to the film formation temperature (T) develop a negligible internal stress, while those having their $T_g > T$ develop a significant one. This is due to the fact that at $T > T_g$, the mobility of the binder molecular segments is high and the stress arising during film formation can partially or totally relax. Moreover, it can be shown that for a thermoplastic binder in solution

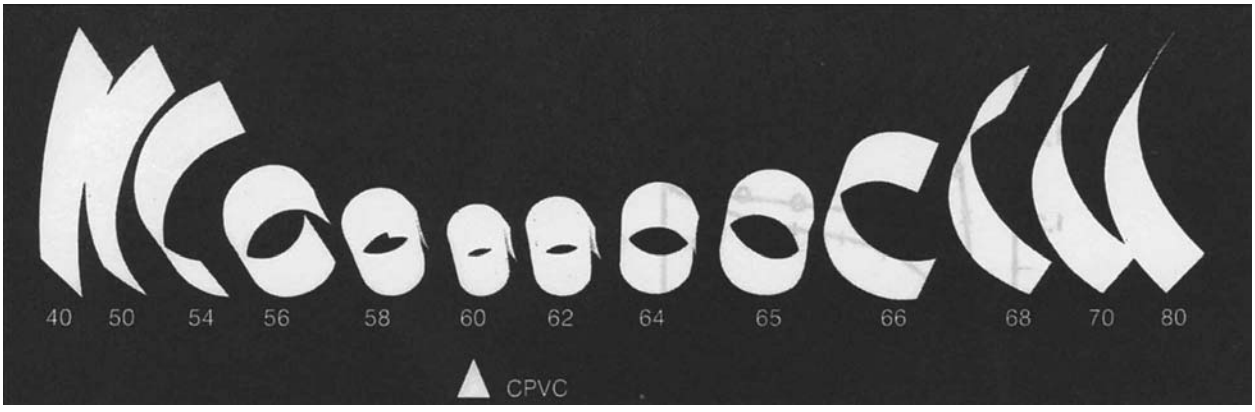

Fig. 23—Determination of the CPVC by comparing the curvature of painted plastic substrates.

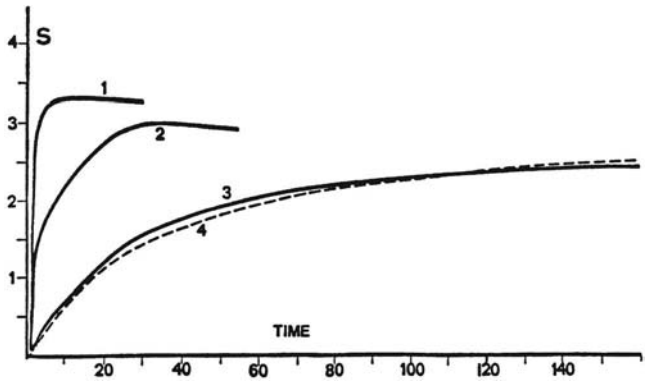

Fig. 24—Stress (*S*) as a function of time in a thermoplastic varnish cast from methyl ethyl ketone and ethyl acetate (1); toluene (2); xylene (3), methyl isobutyl ketone and isobutyl acetate (4), at 52 % RH and 21°C.

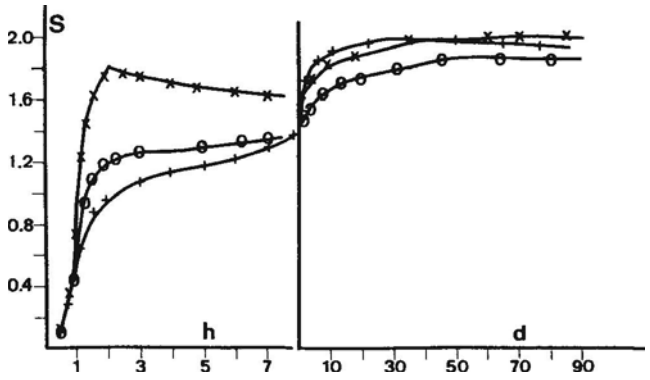

Fig. 26—Stress (*S*, MPa) as a function of time (h, hour; d, day) for a styrene acrylic latex paint containing different amounts of Texanol 5 % (X);10 % (○);15 % (+); percent of Texanol calculated by weight of binder solids.

having a $T_g > T$, the lower the T_g of the binder, the less will be the solvent in the film after its formation (see Eqs (2) and (3)) and therefore the smaller the internal strain and stress in the dry coating [16].

Studies carried out with polyimide coatings, materials usually developing high stresses, indicated that the stress level is determined by morphological and backbone structure [82], polymer chain rigidity and molecular orientation [79]. Ultraviolet-cured coatings, materials that also develop high stresses, were also investigated. It was found that the stress magnitude is mainly affected by photo-initiator concentration, light intensity [80], monomer functionality, monomer chain length [47,83], degree and distribution of cross-linking, and temperature at solidification point [81]. For multifunctional methacrylate coatings a lower stress can develop through lowering light intensity, lowering monomer functionality, [82] raising monomer chain length and plasticizer concentration, and using acrylate monomer instead of methacrylate [83]. Stress development in thermosetting coatings, below and above T_g, is discussed in Ref. [84]. Investigations designed to decrease the stress magnitude by forming low T_g polymer domains [85] or introducing soft polymeric inclusions [86] in the film have been performed.

In brief, any change occurring in the molecular structure of a binder (e.g., cross-linking, crystallinity, molecular weight, steric hindrance) may induce a change in E, ε, ν, and T_g and thus affect stress development.

STRESS VERSUS ADHESION AND COHESION

It is accepted that the stress arising in a coating can reduce the adhesion and cohesion, two crucial properties of an organic coating for obtaining durable coatings [1–10,87–91].

The way the stress affects adhesion is described in detail in Refs. [87,88].

Equation (21) will be used to demonstrate how the stress affects adhesion. This relation describes the factors affecting a measurement of adhesion regardless of the method used (pull-off, peel, torsion, etc.)[91].

$$W_T \approx \gamma_{adh} + W_P - \beta \tag{21}$$

where:

W_T = total measured work (energy) used to separate the coating from the substrate, where the substrate can be another coating. In the literature W_T is also known as *adherence* and the *measured* or *practical adhesion*;

γ_{adh} = the interfacial work of adhesion, a consequence of a variety of chemical and/ or physical interactions between the coating and the substrate. It represents the actual physical strength of adhesive bonds, and is known in the literature also as the *adhesion* or *basic and fundamental adhesion*;

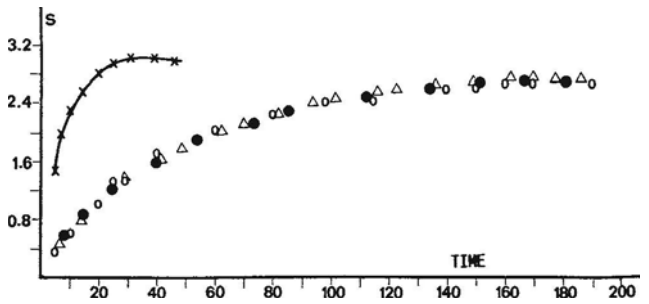

Fig. 25—Stress (*S*, MPa) as a function of time (day) for a thermoplastic varnish cast from toluene (X); isobutyl acetate (○), and their mixtures [1/1 (W/W) (●) and 1/3 (W/W) (Δ)].

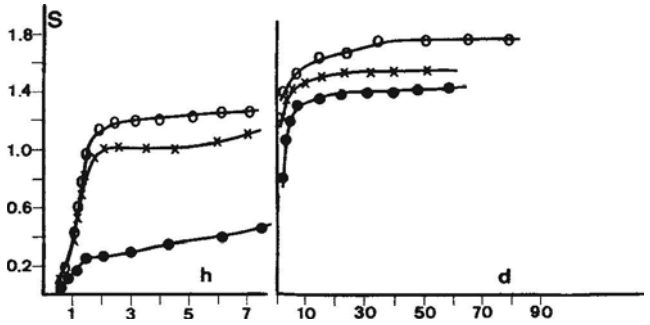

Fig. 27—Stress (*S*) as a function of time (h, hour; d, day) for a styrene acrylic latex paint containing Texanol (○); Dalpad A (X); Dalpad A + propylene glycol (●).

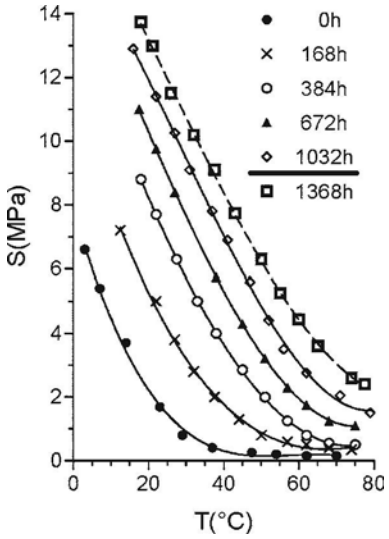

Fig. 28—Stress (*S*) as a function of temperature (*T*, °C) for a primer/clearcoat system after different periods of weathering (4 h UV-B at 60°C and 4 h condensation at 50°C) [100].

W_P = work (energy) expanded in plastic deformation and viscous dissipation occurring during the adhesion measurement. Depending on the viscoelastic character of the coating this work might be important;

β = elastic energy acting against adhesion.

It is shown that the application of an energy balance analysis [92] leads to the factor β

$$\beta = cU_r = \frac{cE\varepsilon^2}{1-\nu} \tag{22}$$

where U_r, c, and ε are the recoverable strain energy, the film thickness, and the strain.

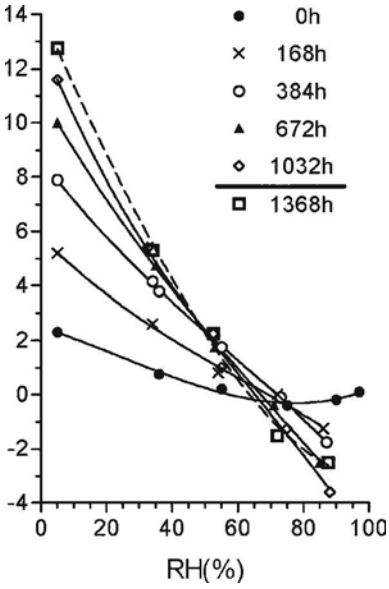

Fig. 29—Stress (*S*, MPa) as a function of RH (%) for a primer/clearcoat system after different periods of weathering (4 h UV-B at 60°C and 4 h condensation at 50°C) [100].

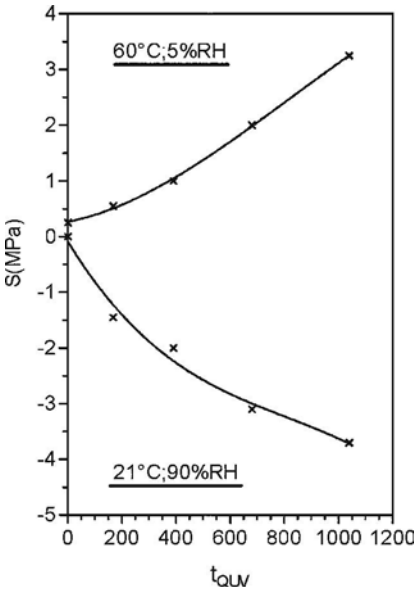

Fig. 30—Stress (*S*) as a function of time of weathering (t_{QUV}, hour) for a primer/clearcoat system at two climatic conditions [100].

To accommodate the effect of stress [19,28,93], Eqs (1) and (22) are combined to give:

$$\beta = cS\varepsilon \tag{23}$$

and the combination of Eqs (21) and (23) leads to

$$W_T \approx \gamma_{adh} + W_P - cS\varepsilon \tag{24}$$

Equation (24) shows, among others that: (1) that in most cases the measured adhesion (W_T) is not identical with inter-facial work of adhesion (γ_{adh}) one normally expects to measure, and (2) when the product "$c\ S\ \varepsilon$" overcomes γ_{adh} the coating will spontaneously detach from the substrate; thus, if a high stress arises in a coating, in order to prevent its detachment, it should be applied in a thinner layer.

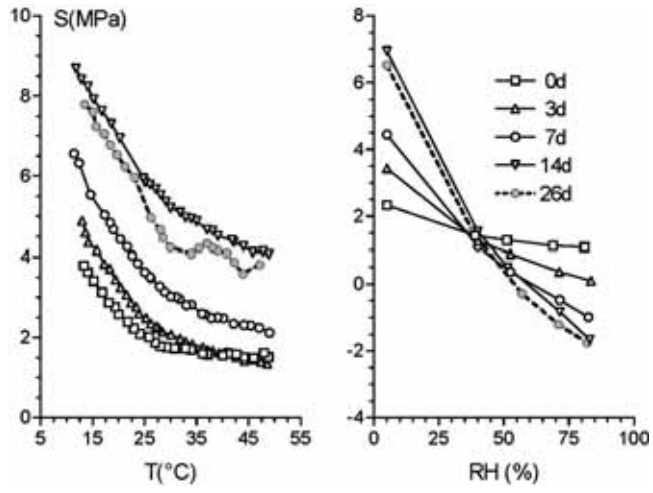

Fig. 31—Stress (*S*) as a function of temperature (*T*) at 5 % (left) and of RH at 21°C (right) for a polyester/melamine system after different periods of weathering (d, day) (4 h UV-B at 60°C and 4 h condensation at 50°C) [100].

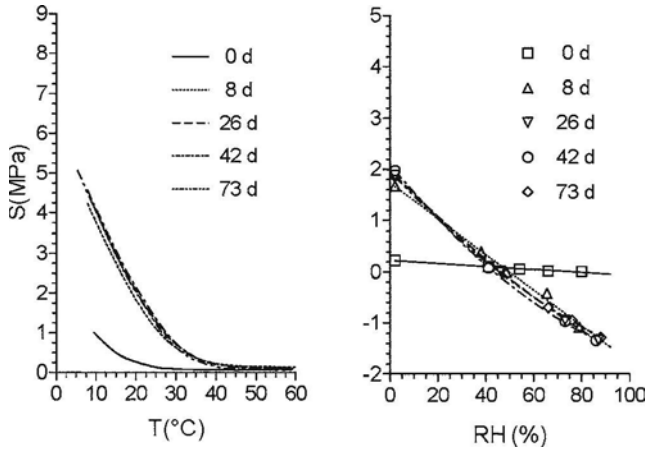

Fig. 32—Stress (*S*) as a function of temperature (*T*, °C) at 5 % (left) and of RH at 21°C (right) for an acrylic latex paint containing coalescing agents after different periods of weathering (d, day) (4 h UV-B at 60°C and 4 h condensation at 50°C).

Because it is energy that expresses the effect of e, tensile or compressive strains are identical in their effect [87].

Since stress develops in most organic coatings, the product "$c\ S\ \varepsilon$" should also be considered in adhesion tests performed in laboratories. This fact is taken into consideration in mathematical equations (25) and (26) for pull off and peeling at 90°, respectively [87].

$$\sigma \approx \left[\frac{2K}{c}(\gamma - cS\varepsilon)\right]^{1/2} \tag{25}$$

$$\frac{F}{b} \approx \gamma - cS\varepsilon \tag{26}$$

where

σ = stress applied to pull the coating from the substrate,
K = bulk modulus of the coating,

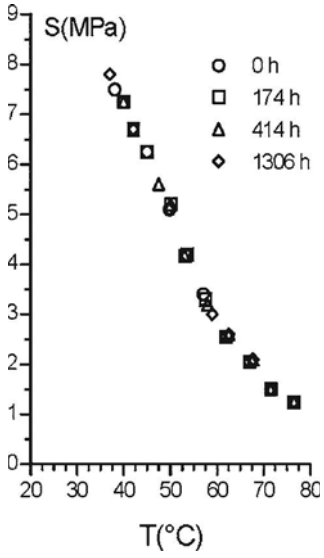

Fig. 33—Stress (*S*) as a function of temperature (*T*, °C) at 5 % for a polyester/TGIC powder coating after different periods of weathering (d, day) (4 h UV-B at 60°C and 4 h condensation at 50°C).

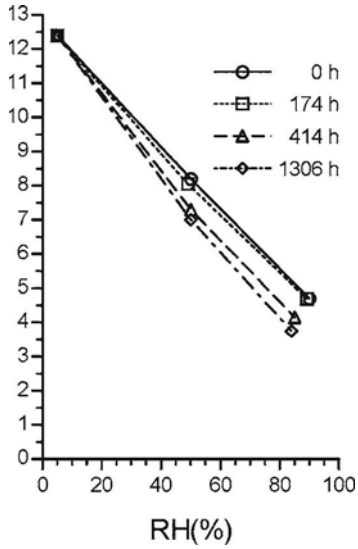

Fig. 34—Stress (*S*, MPa) as a function of RH at 21°C for a polyester/TGIC powder coating after different after different periods of weathering (d, day) (4 h UV-B at 60°C and 4 h condensation at 50°C).

γ = interfacial work of adhesion,
F = force applied to peel the coating, and
b = width of the coating.

Equation (27)(for pull-off measurements of coatings having $\nu = 0.4$) is interesting because it takes into consideration the work expanded in plastic deformation (W_p) [94].

$$\gamma = \frac{c}{4.286E}\left(\sigma^2 + 2.572S^2\right) \tag{27}$$

In addition, the study demonstrates the difference between adhesion and adherence [94] and the wrong interpretation of data that might result if only one of them is considered.

Equations (22)–(24) also indicate the possibility of determining the adhesion of a coating (i.e., factor γ) without applying any external force. This is due to the fact that at a particular film thickness a spontaneous detachment should occur [87]. Unfortunately, this method can only be used for badly adherent coatings. For all other coatings, extremely high film thicknesses, difficult to apply and cure, would be necessary. When necessary, the product "$c\ S\ \varepsilon$" can also be increased by submitting the coated substrate to high stresses, e.g., thermal stresses.

If the adhesion forces exceed the cohesive strength of a coating the stresses arising in the coating can provoke cracking, Assuring rather than loss of the coating from the substrate. Such damage can occur at low stress values due to stress concentration in the film, a consequence of the presence of heterogeneity in the coating (e.g., bad pigment/binder dispersion, presence of impurities, air voids, and variation in film thickness). The verification of this principle can be realized very approximately by determining the stress and the ultimate properties of a coating. Since most organic coatings are viscoelastic, it is essential that these properties be evaluated under the conditions (strain rate, temperature, RH) corresponding to the stress development in the coating. A more quantitative approach of the failure mechanism in organic coatings, but also more difficult to

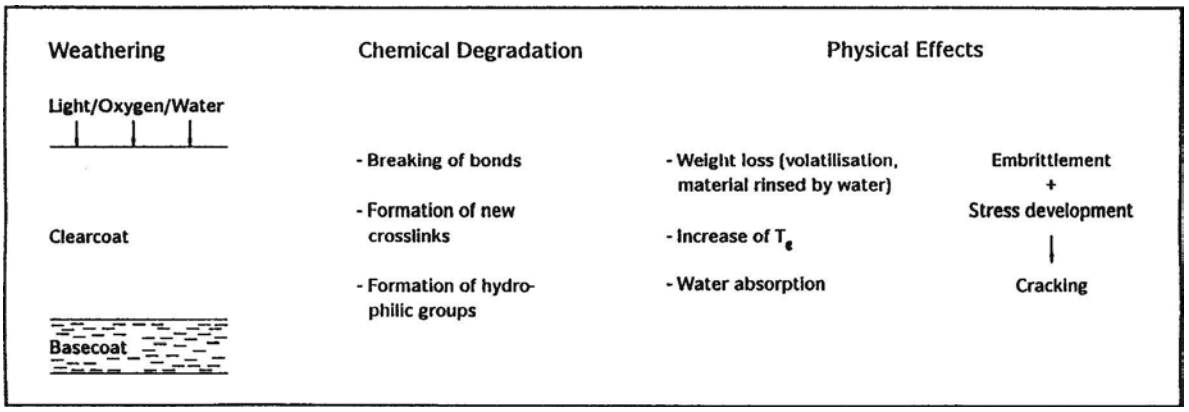

Fig. 35—Schematic representation of processes causing crack formation in a coating.

realize, mainly due to relatively low thickness of the films, is the application of fracture mechanics principles [95]. According to certain publications these difficulties are partially solved both theoretically [96,97] and experimentally [98,99].

It is important to add that fatigue processes (e.g., due to variation of temperature and RH) are factors decreasing the overall stress at which the coatings are damaged (delaminates and/or cracks).

DURABILITY AND STRESS DEVELOPMENT

Weathering

In most cases when organic coatings are exposed to weathering (accelerated or natural), they undergo chemical and physical modifications which are expressed in the change of T_g, E, α, ν, and cross-link density. Under such circumstances and according to Eqs (1), (3), (5), and (10), one can also expect to see changes in stress development.

A more detailed discussion of the role played by stress in the coating deterioration is given in Refs. [9,100]. It is shown that depending on the type of coating the weathering can affect the stress development in different ways.

In one case weathering provokes: (1) a shift of the curves $S = f(T)$ to higher temperatures indicating an increase of T_g, which in turn induced higher thermal stresses (Fig. 28), and (2) an increase of the slope of the curves $S = f(\text{RH})$ due to an increase of the coating sensitivity to moisture, which induced higher hygroscopic stresses (Fig. 29).

The representation of the stress as a function of time of weathering for two experimental conditions similar to those present in the accelerating apparatus (Fig. 30) indicates that every time the experimental conditions changed (every 4 h) the coating was exposed to an increasing hygrothermal stress (tensile thermal stresses under dry conditions and compressive hygroscopic stresses under wet conditions).

Another case often met in practice is represented in Fig. 31. In this case weathering induced a relatively small increase of T_g and a significant upward shift of the curves $S = f(T)$ to higher stress values. This upward shift is a consequence of oxidative cross-link reactions the coating undergoes, a fact confirmed by infra red spectra measurements and the stress increase in the rubbery region (Eq (8)). The $S = f(\text{RH})$ curves are similar to the case described above, showing an increase of coating hydrophylicity with weathering.

Fig. 32 is often observed with (acrylic) latex paints containing coalescent solvents. The shift of the curve $S = f(T)$ to higher temperatures, observed during the first days of weathering, is mainly due to loss of coalescent solvents present in the coating. The stress dependence on RH of the unweathered coating is negligible. This is due to its T_g (about 21°C at 0 % RH), close to the experimental temperature (21 ± 1.5°C), a fact that enables a fast relaxation of hygroscopic stresses induced by variation of RH. With coalescing solvents departing from the coating, T_g increases (to about 31°C at 0 % RH) and the hygroscopic stresses become measurable.

For organic coatings possessing a good durability it is expected that $S = f(T)$ and $S = f(\text{RH})$ to be little, or not at all affected by weathering. This is illustrated in Figs. 33 and 34. Contrary to other coatings, for this one (a polyester/triglycidyl isocyanurate (TGIC) powder coating), the dependencies $S= f(T)$ and $S = f(\text{RH})$ are not changing or changing very little with weathering. These results are in agreement with the behavior of the coatings mentioned above under tropical conditions. While the acrylic/polyurethane and the polyester/melamine coatings are cracking after a few years, for the same period, the powder coating is still undamaged.

The processes thought to lead to fissuring of the clearcoat are described in Fig. 35. Briefly, the chemical degradations induced by UV, water, and oxygen, which decrease the coating cohesion, combined with the fatigue process at steadily increasing hygrothermal stress levels are the causes of the coating degradation.

Hygroscopic Stress and Corrosion

Due to the heterogeneous nature of most of organic coatings, which possess regions of different hydrophilicity [101], hygroscopic stresses are arising in a coating exposed to a high RH or immersed in water [102]. They participate in formation and/or enlargement of pathways through which water and electrolyte can reach the metallic substrate and thus provoke corrosion. This affirmation is based on the observation that the coatings developing low hygroscopic (compressive) stresses or able to relax them fast, protect well the substrate against corrosion. Among the coatings investigated in one study (Fig. 36), the powder coating and Plexigum developed the lowest hygroscopic compressive stresses and protected well the substrate against the aggressive action of 0.5M NaCl electrolyte. The polyurethane,

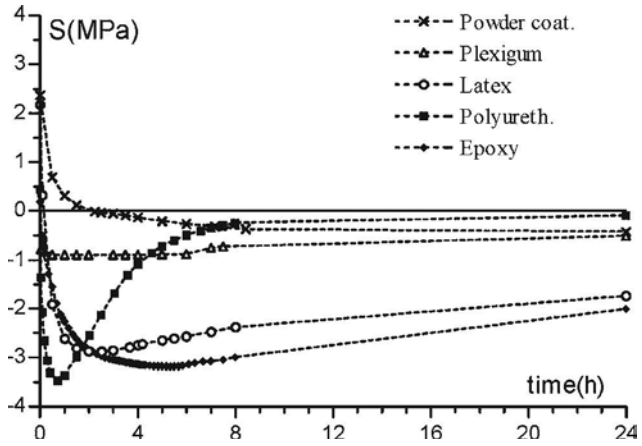

Fig. 36—Stress (S) as a function of immersion time in water at 21°C for five organic coatings [102]. (With permission from Marie-Odile Barkallah, AFTPVA-EUROCOAT.)

a system which developed high hygroscopic compressive stresses but which relaxed relatively fast, provided only an average protection.

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Friction and Slip Resistance

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PREFACE

In preparation of this chapter, the contents of Chapter 50 Slip Resistance in the fourteenth edition were drawn upon. The author acknowledges the author of the chapter in the fourteenth edition, Paul R. Guévin, Jr. The current edition will review and update the topics as addressed by the previous author, introduce new technology, and include up-to-date references.

INTRODUCTION

FRICTION IS AN INTERESTING PROPERTY THAT IS often taken for granted. For example, it would not be possible to walk if there were no friction between shoe soles and the ground or other surfaces. There is also an awareness that friction varies with the nature of the shoe bottoms—rubber, plastic, leather, etc.—and of the surface—ground, concrete, painted concrete, ice, wood floor, polished floor, steel, etc. Automobiles would not move if it were not for the friction between tires and road surface, would not slow down if it were not for the friction between brake discs or drums, and would not stop if it were not for the friction between tires and road surface. Without friction, dishes would not stay on a table and the slightest jostling would cause items to slide. Many other examples could be given of friction and slip.

At times, conditions of high friction are desirable and other times low friction is needed. If a heavy object is to be slid, low friction is useful. Skiers want low friction between their skis and snow or ice and use waxes as a lubrication to decrease friction. In the cases of polished, wet, or icy surfaces, frictional forces are quite small and automobiles, people, and animals have a tendency to slip. In the case of dry concrete, neat or painted, or wood, the frictional forces are quite high and the surface is stable and with it less chance for slipping. It should be kept in mind that there is a need for material combinations that result in high friction, as in a painted or otherwise coated walkway area where a person walking or running on the surface does not want to slip and fall, and in low friction, as when an object is to move smoothly and evenly by another object of similar or different composition, as when sheets of paper move by one another in a copy machine. Friction can be increased by use of additives such as sand on an icy surface and decreased by the use of lubricants such as oil, water, graphite, and the like.

Slip is a word that has many meanings [1–3], but it is obvious that slip occurs when friction is low. In certain areas of the coating industry, slip is considered to be the ability of an object to move in a relatively free or unencumbered but controlled manner as when one sheet of coated or uncoated metal passes over another in a coating-line feeding operation, when such sheets move along a conveyor system in coating, printing, fabrication, or packaging operations, and the like. The material or coated material must have proper "slip" or "lubricity" to allow passage through various sections of the coating fabrication or packaging section of the line. Slip is also important in fabricating operations wherein the coated object is in contact with a tooling system as in fabrication of bottle caps, in bending or forming operations, and so on. In various textile lines, proper slip is need for threads to flow smoothly and uniformly through fabrication systems and not cause thread or yarn breaks and defective final products or lost production.

CONCEPTS OF FRICTION

In a technical sense, *friction* is the force between contacting objects that resists the relative motion of the objects. Starting or static friction is the frictional force between stationary objects, and dynamic, kinetic, or sliding friction is the frictional force between objects that are sliding with respect to one another. Consider a block resting on a solid surface as in Fig. 1. The upward force, F_U, of the solid surface, counterbalances the weight or mass of the block, F_N, and the block is at rest. F_N is usually referred to as the perpendicular or normal force. If a force, F_A, is applied to the block and parallel to the solid surface, the force of friction, F_F, resists it. If F_A is slowly increased, at some point the block will begin to move and slide along the solid surface without further increase in F_A and actually with a small decrease in it [4,5]. Thus, the force required to move an object from rest is greater than the force required to continue the movement at constant velocity. At this point,

$$F_A = F_F \tag{1}$$

By sliding blocks of the same material with equally smooth surfaces but different sizes (i.e., different contact areas) across the same surface, it has been found that the ratio of the frictional force to the mass of the block or F_N is constant. The proportionality factor between the frictional resistance force and the normal force is known as the *coefficient of friction,* μ, with a distinction made between the coefficient of static friction, μ_S, and coefficient of kinetic friction, μ_K, as indicated in the following relationships:

$$F_F = \mu_S F_N \quad \text{stationary} \tag{2}$$

$$F_F = \mu_k F_N \quad \text{sliding} \tag{3}$$

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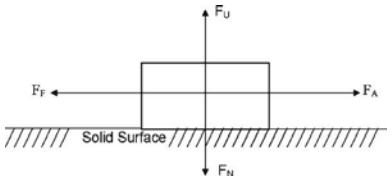

Fig. 1—A solid block resting on a solid surface with an upward force, F_U, and a normal or downward force, F_N, acting on it. A force, F_A, acting parallel to the solid surface is applied to the block and a friction force, F_F, opposes the force F_A.

This points out that it should be stated whether a measured or cited coefficient of friction is for the static or the kinetic condition, however, quite often this is not done in the literature as will be illustrated below.

The friction force is often discussed in terms of an object sliding down a solid inclined surface as indicated in Fig. 2. When the angle of incline, θ, is 0°, the situation is that of Fig. 1, which becomes Fig. 2 as the angle of incline is increased from zero to some finite value less than 90°. As the angle of the incline increases, the force component tending to move the object down the incline, F_A, also increases. At some point, the slightest increase in the angle will sufficiently increase the force component parallel to the plane of the incline, F_A, to a value such that F_F is overcome and, if unrestrained, the object begins to move down the incline at constant speed. Thus, the object does not slide until the force parallel to the incline, F_A, reaches a certain value that is equal to the frictional force, F_F. The mass of the object represented by vector F_M can be resolved into vectors F_A and F_N parallel and normal to the plane of the incline, respectively. At the described condition of sliding at constant speed, $F_A = F_F$. Since $F_F = \mu_K F_N$, substitution leads to $F_A = \mu_K F_N$ or

$$\mu_K = F_A/F_N \tag{4}$$

From the vector diagram in Fig. 2, it is apparent that

$$F_A/F_N = \tan \theta = \mu_K \tag{5}$$

and

$$\theta = \text{arc}\tan \mu_K \tag{6}$$

Thus, if μ_K is known, the angle of incline, at which a block placed on the incline will slide regardless of the weight or mass of the block, can be determined. Note that the coefficient of friction can take on values from zero to extremely high values, but usually it has a value of between zero and one unless special conditions are involved as, for example, in the case of gage blocks, which are ultrasmooth, and in contacting spectroscopically pure metals such as copper that were outgassed in a vacuum prior to admitting other gases such as nitrogen, oxygen, or hydrogen.

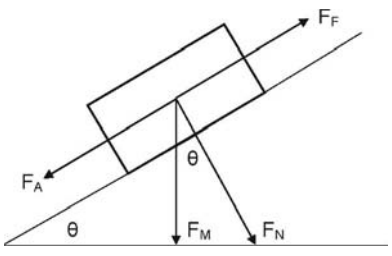

Fig. 2—A solid block resting on an incline. As the angle θ increases, the force, F_A, increases until the friction force, F_F, is overcome and the block will begin to slide.

In physics, the study of friction is called *tribology*. In a physics sense, friction is the resisting force that takes place when two surfaces contact and rub against each other. When investigating the causes of friction, it should be accepted that the surface of materials is microscopically irregular and is not flat on an atomic scale. Although surfaces may appear to be smooth, on a microscopic scale they are covered with asperities and are jagged and rough. The uneven or rough surfaces of the touching objects are thought to be one of the main causes of friction. As the surfaces move or tend to move, the rough surfaces interlock and offer resistance to being moved over one another until a certain value of applied force is reached.

From this model of rough surfaces interlocking, friction would be expected to decrease as the surfaces are smoothened. This is the actual state of affairs—up to a point. If the surfaces are made increasingly smoother, at some point friction will increase.[2] This phenomenon, which is another of the main causes of friction, is thought to be due to the bonding or interaction between surface atoms and these bonds must be broken before friction is overcome and sliding can take place. Such bonding will only take place where the surface atoms can come sufficiently close so as to be within each other's force fields. Thus with usual surfaces, it is only asperities on one surface that make contact with asperities on the other surface that can "bond" and interact through van der Waals or other chemical forces with adhesion bonds. The entire normal force is carried on the tips of the asperities and the true or actual area of contact is much less than the apparent or measured area. Local stress on the contacting asperities may result in a flattening of the asperities and produce an area of minute but intimate contact. With metals, the deformation may be within the elastic limit, but with plastics the viscoelastic deformation may be permanent or a hysteresis effect may be involved. As the surfaces are made increasingly smoother, at some point the overall contact area between them increases and as a result, bonding and resultant friction forces will increase. To move a surface over another surface, the adhesive bonds at the interface must be broken in a shear plane near the surface of one of the materials.

The shear fracture at the minute interaction areas or area of true contact between the dry contacting surfaces is a part of the mechanism of dry friction theory. If it is assumed that the interaction areas are more or less randomly distributed over the apparent contact area, the friction force can be expressed as

[2] Gage blocks are probably the best example of smooth surfaces that have high friction. These devices are used to provide linear dimensions to within given and very small tolerances—reference blocks that can have a high tolerance of ±0.000 002 in. or ±0.000 05 mm are built up to make the desired linear dimension. To develop a particular length, the appropriate blocks are slid together and held together by "forces" akin to the forces between molecules or atoms. Assembled blocks cannot be left together for long periods of time or they will become permanently joined through the forces. See www.claymore.engineer.gvsu.edu or www.ptb.de/en/org/5/54/543/parendm_e.htm as well as other sites for detailed information.

$$F_F = \sigma_G \cdot A \quad (7)$$

where A is the actual area of contact and σ_G is the average shear strength of the interaction areas. Since it is the interaction areas that actually carry the normal force, F_N, between the surfaces, the following relationship also exists.

$$F_N = \rho_m \cdot A \quad (8)$$

where ρ_m is defined as the flow pressure or shear stress of the softer material in the vicinity of local areas of actual contact. If the last two equations are combined, the coefficient of friction is obtained as

$$\mu = F_F/F_N = \sigma_G/\rho_m \quad (9)$$

and the coefficient is independent of the contact area.

Friction coefficients involving true area of contact have also been expressed in accord with the following relationships [6]. For metals, the deformation of asperities to form the true area of contact is approximately proportional to the normal force, F_N. In the case of polymeric materials, rubbers undergo an essentially elastic deformation and the area of contact increases with $(F_N)^{2/3}$ indicating that the coefficient of friction decreases with increasing F_N. When polymers that deform in a viscoelastic manner, the friction force follows a relationship that has the form

$$F_F = k(F_N)^X \quad (10)$$

with k a constant. Since $F_F = \mu/F_N$, the coefficient of friction may be expressed as

$$\mu = k(F_N)^{X-1} \quad (11)$$

with $2/3 < X < 1$. In the case of polytetrafluoroethylene, ithas been found that X has a value of 0.85 for over ten orders of magnitude change in F_N.

In a general sense, both mechanisms, the interlocking and the bonding mechanisms, play a major role in causing friction. Other mechanisms that may be involved in friction forces include, a gouging effect in which asperities on a hard material may gouge a grove in a softer material as moving objects drag and grind against each other; a roughness effect wherein the asperities interlock and there is a need to lift some asperities over other asperities; electrostatic effects in which work must be done to separate charged regions on the sliding surfaces—an effect that may be seen with electric insulators; and hysteresis effects in elastic and plastic deformations at the touching points or near them that take place with not all of the deformation work recoverable. Heat generation and dissipation account for the non-recoverable work.

Values for the coefficient of friction for plastics will depend on test conditions such as humidity, material degree of cure, moisture content, and temperature. For example, the coefficient of friction for nylon will vary from 0.91 to 1.19 when the moisture content is varied from 0.2 to 10 % [7]. Table 1 has coefficients of static friction, μ_S for various synthetic and natural polymers when in contact with the same polymer and with steel. In general, μ_S is greater for these polymers when sliding on the same polymer than when sliding on steel. The values are abstracted from a handbook [8] that contains many more values of the coefficients of friction including the static coefficients for a variety of polymers when in contact with wet and dry snow at 0°C as given in Table 2. In general, the coefficients are lower on dry snow indicating that it should be easier to move an object on dry snow than on wet snow. As the temperature of dry snow decreases from 0°C to –32°C, Table 2, μ_S increases with the effect dependent on the nature of the polymer. A range of values for the coefficient of sliding friction for a number of polymers sliding on a variety of unnamed substrates is given in Table 3.

TABLE 1—Coefficient of Static Friction, μ_S, for various synthetic and natural polymers on self and on steel [8]

Materials in Contact	Condition	μ_S
Poly(methyl methacrylate) on poly(methyl methacrylate)	Clean	0.8
Poly(methyl methacrylate) on steel	Clean	0.4–0.5
Polystyrene on polystyrene	Clean	0.5
Polystyrene on steel	Clean	0.3–0.35
Polyethylene on polyethylene	Clean	0.2
Polyethylene on steel	Clean	0.2
Polytetrafluoroethylene on polytetrafluoroethylene	Clean	0.04
Polytetrafluoroethylene on steel	Clean	0.04
Nylon on nylon[a]	Clean	0.15–0.25
Silk on silk	Clean[b]	0.2–0.3
Cotton thread on cotton thread	Clean[b]	0.3

[a]Type nylon not specified.
[b]Commercially clean.

Examination of the data in Tables 1–3 indicates that polytetrafluoroethylene has a very low coefficient of friction, and it is widely used to make slippery or low friction surfaces. But, the polymer can quite easily erode and wear when used in systems that have repetitious operation. The wear factor can be improved without compromising its frictional properties when it is filled with certain hard particulate solids. However, hard fillers can have a deleterious effect on an opposing surface. It has been found the improved wear while maintaining low friction or a high degree of slipperiness can be obtained without affecting the opposing surface if the polymer is irradiated with an electron beam [9].

Table 4 has values of the coefficients of kinetic friction for Nylon 6-6 in two states of smoothness (molded or machined surface) sliding against the same surface, against the opposite surface, or against mild steel as well as mild steel sliding against itself or the two nylon surfaces. The data indicate the machined nylon surface, $\mu_K = 0.46$, is smoother than the molded nylon surface, $\mu_K = 0.63$. It also appears that friction is less when the smoother machined nylon surface is moving on the rougher molded nylon surface than vice versa. There is very little, if any, difference in friction when either nylon surface is moving on mild steel, $\mu_K = 0.31$ and 0.33, or when a mild steel surface in moving on either nylon surface, $\mu_K = 0.41$. The strong effect of

TABLE 2—Coefficient of static friction, μ_s, for natural polymers under various conditions and for synthetic polymers at certain temperatures on wet and dry snow [8].

Material	Condition	Temperature, °C	μ_s
Leather on	Metal[a]	. . .	0.6
Leather on	Greasy metal[a]	. . .	0.2
Leather on	Wet metal[a]	. . .	0.4
Leather on	Wood	. . .	0.3–0.4
Nylon[b] on	Wet snow	0	0.4
Nylon[b] on	Dry snow	0	0.3
Nylon[b] on	Dry snow	–10	0.3
Paraffin wax on	Wet snow	0	0.06
Paraffin wax on	Dry snow	0	0.06
Paraffin wax on	Dry snow	–10	0.35
Paraffin wax on	Dry snow	–32	0.4
Polyethylene terephthalate on	Wet snow	0	0.5
Polyethylene terephthalate on	Dry snow	0	0.35
Polyethylene terephthalate on	Dry snow	–10	0.38
Poly(methyl methacrylate) on	Wet snow	0	0.5
Poly(methyl methacrylate) on	Dry snow	0	0.3
Poly(methyl methacrylate) on	Dry snow	–10	0.34
Poly(methyl methacrylate) on	Dry snow	–32	0.4
Polytetrafluoroethylene on	Wet snow	0	0.05
Polytetrafluoroethylene on	Dry snow	0	0.02
Polytetrafluoroethylene on	Dry snow	–10	0.08
Polytetrafluoroethylene on	Dry snow	–32	0.1
Ski lacquer on	Wet snow	0	0.2
Ski lacquer on	Dry snow	0	0.1
Ski lacquer on	Dry snow	–10	0.4
Ski lacquer on	Dry snow	–32	0.4

[a]Commercially clean, unspecified metal.
[b]Type nylon not specified.

lubricants, which will be discussed later in this chapter, is apparent from certain data in Table 4.

Shearing processes as described above depend on the viscoelastic nature of polymers and therefore are a function of strain rate (sliding speed) and temperature. It has been demonstrated that the coefficient of friction for crystalline polymers such as polyethylene, polypropylene, and Nylon 6-6 depends markedly on sliding speed and passes through a maximum [6,11]. Amorphous polymers such as poly(methyl methacrylate) and polystyrene only show moderate increases in μ_K and only a slight maximum as strain rate increases. As the temperature is increased, the dependency of friction coefficient curves is shifted to the right or to higher sliding speeds. Grosch [12] found similar effects for μ_K when a variety of rubbers (natural, butyl, styrene-butadiene, and acrylonitrile-butadiene elastomers) sliding on glass was examined as a function of sliding speed over a broad range of temperatures. The viscoelastic nature of friction is further demonstrated by subjecting the μ_K, sliding speed, temperature data to the Williams–Landel–Ferry reduced variables analysis [13]. The shift factor, log a_T, fits a continuous master curve when reduced to a reference temperature. Others [14–16] have obtained similar results that demonstrate the frictional characteristics of elastomeric materials behave in a viscoelastic manner.

Polymers are used in many facets of the electronics industry, and frictional characteristics can play an important role in their usage. Coefficients of friction for some polymers used in this industry and for two lubricants used are given in Table 5 [17]. Friction can cause tribolelectric charging of polymers by contact and rubbing. Since polymers have high resistivity, electrostatic charge can accu-

TABLE 3—Ranges of coefficients of sliding friction, μ_K, for various materials sliding on various unnamed surfaces [6].

Material	μ_K
Natural rubber	0.5–3.0
Nylon 6-6	0.15–0.40
Poly(ethylene terephthalate)	0.20–0.30
Poly(methyl methacrylate)	0.25–0.50
Poly(vinyl chloride)	0.20–0.90
Poly(vinyl fluoride)	0.10–0.30
Poly(vinylidine chloride)	0.68–1.80
Polybutadiene	0.4–1.5
Polyethylene—High Density	0.08–0.20
Polyethylene—Low Density	0.30–0.80
Polypropylene	0.67
Polystyrene	0.33–0.5
Polytetrafluoroethylene	0.04–0.15
Styrene-butadiene copolymer	0.5–3.0

mulate in large amounts and represent serious, hazardous consequences. For example, discharge between dissimilar pairs can cause a spark and a resultant fire or destruction of electronic equipment. A tribolelectric series for a number of widely used polymers is given in Table 6 [6]. Antistatic additives can decrease resistivity, and leakage currents can be used to dissipate an accumulation of electrostatic charge from friction.

ASTM DEFINITIONS/TERMINOLOGY

Table 7 contains a number of specific definitions or terminology that can be found in the ASTM publications indicated in the table. Although the definitions may differ in the exact wording, they are in basic agreement with each other and with the information given above. Terminology related to that in Table 7 may be found in ASTM D1436 Test Method for Application of Emulsion Floor Polishes to Substrates for Testing Purposes in ASTM D2825 Terminology Relating to Polishes and Related Materials, as well as in ASTM and other standards.

ASTM G115-10 Standard Guide for Measuring and Reporting Friction Coefficients contains schematic diagrams for more than 20 device/test configurations for friction testing, the applicable materials for the particular test, and the measured parameters for the standards listed in Table 8. It is a useful guide for those involved in a friction and its measurement. Two other definitions included in this standard are:

triboelement—one of two or more solid bodies that comprise a sliding, rolling, or abrasive contact, or a body subjected to impingement or cavitation. Each triboelement contains one or more tribosurfaces; and

tribosystem—any system that contains one or more triboelements, including all mechanical, chemical, and environmental factors relevant to tribological behavior.

SLIPPERINESS

In a general sense, slipperiness can be defined as the tendency of something to suddenly or involuntarily slide. In many cases, an organic polymer surface such as a coating is involved when slipperiness in considered. In terms of the flooring market area, for which the above definition was written, the flooring surface could be an alkyd or polyurethane enamel on a porch or deck, a vinyl- or polyurethane-coated gymnasium floor, a waxed vinyl composition floor, an epoxy-coated concrete floor, structural steel and coated structural steel, and so on. Slipperiness can be considered as involving of two factors—skid resistance and slip resistance. Skid may be defined as an act of sliding without rota-

TABLE 4—Coefficients of kinetic friction, μ_K, for Nylon 6-6 with various degrees of surface smoothness in contact with same material or steel with and without lubricants [10].

Moving Surface	Stationary Surface	Lubricant	μ_K
Nylon—molded surface	Nylon—molded surface	None	0.63
Nylon—molded surface	Nylon—machined surface	None	0.52
Nylon—molded surface	Mild steel	None	0.31
Nylon—machined surface	Nylon—molded surface	None	0.45
Nylon—machined surface	Nylon—machined surface	None	0.46
Nylon—machined surface	Mild steel	None	0.33
Mild steel	Nylon—molded surface	None	0.41
Mild steel	Nylon—machined surface	None	0.41
Mild steel	Mild steel	None	0.6–1.0
Nylon—machined surface	Nylon—machined surface	Graphite	0.28
Nylon—machined surface	Nylon—machined surface	Liquid paraffin	0.13
Nylon—machined surface	Nylon—machined surface	Water	0.24

TABLE 5—Coefficients of friction for various coatings used in the electronics industry and elsewhere [17].

Coating Material	Coefficient of Sliding Friction[a]
Epoxy coating with Teflon™ fiber	0.15
Nylon	0.3
Polyethylene	0.6–0.8
Polyimide	0.17
Poly(methyl methacrylate)	0.4–0.5
Polystyrene	0.4–0.5
Polytetrafluoroethylene (Teflon™ TFE)[b]	0.05–0.1; 0.04; 0.016
Poly(vinyl chloride)	0.4–0.5
Polyxylylene	
Parylene N	0.25
Parylene C	0.29
Parylene D	0.31–0.33
Lubricants for comparison	
Graphite	0.18
Molybdenum disulfide	0.12

[a]Not designated as static or kinetic coefficients.
[b]Values from different sources.

tion, and slip can be defined as a slide that occurs suddenly or involuntarily. The coefficient of friction is a measure of slip with a high coefficient of friction denoting poor slip and a low coefficient of friction denoting good slip [5]. Slip resistance is something that is not really measurable in common terms and is often defined by different people in different ways— but everyone realizes that it does exist and the importance of testing for it remains regardless of the difficulty in defining the term [18].

TABLE 6—Tribolelectric series for a number of widely used polymers [6].

Most Negative End of Series	Polytetrafluoroethylene
	Polyethylene
	Poly(vinylidine chloride)
	Poly(vinyl chloride)
	Polyacrylonitrile
	Poly(ethylene terephthalate)
Decreasing Negativity ↓	Poly(vinyl alcohol)
	Poly(methyl methacrylate)
	Cellulose acetate
	Silk
	Cotton
	Cellulose
	Polyamide (nylons)
Most Positive End of Series	Wool

The importance of slip and slipperiness is evidenced by a recent scientific symposium that was entitled "The Measurement of Slipperiness—an International Scientific Symposium" [19]. The seven papers in this symposium dealt with concepts and definitions [20], occupational slip injuries [21], biomechanics [22], human-centered approaches to slipperiness measurement [23], the role of surface roughness [24], and the role of friction in slipperiness [25,26]. For example, Chang and coworkers [26] studied friction mechanisms at the shoe-floor interface under a variety of conditions that included dry surfaces, liquid- and solid-contaminated surfaces, and icy surfaces. They concluded that static friction measurements determined by the traditional use of a drag-type device are only suitable for dry, clean surfaces. Dynamic and stick-slip measurements are needed to properly evaluate contaminated and icy surfaces and to estimate potential risk on such surfaces. Miller [27,28] has presented interesting discussions related to the measurement of slip resistance and to slip resistance standards. These discussions are readily available on the Internet. Di Pilla [29] has also discussed the measurement of slip resistance and the state of the technology, as it existed in late 2001.

DETERMINATION OF THE COEFFICIENT OF FRICTION (COF)

Three types of instruments are used to measure the COF, and these are illustrated in Fig. 3 [30]. These devices are drag-type meters that are based on $\mu = F_F/F_N$, pendulum-type meters that measure the energy loss of the pendulum as an indirect indication of dynamic friction, and articulated-strut devices that are based on the direct and fundamental principle of the resolution of forces that take place when as object slides down an incline as described above wherein $\mu_K = \tan \theta$.[3] Other instruments include torque (ASTM E510 and G99), ball-rolling (ASTM G123), roller (ASTM D3412 and G143), and other devices (see Table 8 for Standard titles). Short descriptions of various devices for studying friction and related properties that are available nationally and internationally can be found on the Internet [18].

Recently [31], sliding experiments were performed on amorphous polystyrene of various molecular weights using an atomic force microscope equipped with a nanotip probe. Friction coefficients were found to range between 0.2 and 0.45 and were similar to those found with other devices. Velocity effects on the dynamic coefficients were slight to nil, but there were marked effects involving the force at which the tip is unstuck as a function of polystyrene molecular weight. As molecular weight decreases, the applied force to overcome friction increases. Overall the results suggest that untangling of polymer molecules plays a role in describing breakage of the contact between interacting

[3] Although the COF from inclined plane testing is often referred to as a dynamic COF, μ_K, Section 10.1 of ASTM G115, Standard Guide for Measuring and Reporting Friction Coefficients, indicates that such testing only yields the static coefficient of friction. The standard recommends that the term static friction coefficient, μ_S, be used to describe a coefficient calculated using a breakaway force in a friction test rig that moves a specimen with a mechanism other than gravity.

TABLE 7—Definitions/Terminology for friction and slip properties taken from two ASTM publications.

ASTM G115-10 Standard Guide for Measuring and Reporting Friction Coefficients	ASTM D2047 Test Method for Static Coefficient of Friction of Polish-Coated Floor Surfaces as Measured by the James Machine
Coefficient of friction—The dimensionless ratio of the friction force between two bodies to the normal force pressing these bodies together.	*Coefficient of friction*—The ratio of the horizontal (shear) component of force required to overcome friction, to the vertical (normal) component of the force applied.
Kinetic coefficient of friction—The coefficient of friction under conditions of macroscopic relative motion between two bodies.	*Dynamic coefficient of friction*—The ratio of the horizontal component of force required to cause a body to continue to slide at a constant velocity, to the vertical component of the force applied.
Friction force—The resisting force tangential to the interface between two bodies when, under the action of external force, one body moves or tends to move relative to the other.	*Friction*—The resistance to relative motion developed between two solid contacting bodies at, and parallel to, the sliding plane.
Static coefficient of friction—The coefficient of friction corresponding to the maximum friction force that must be overcome to initiate macroscopic motion between two bodies.	*Static coefficient of friction*—The ratio of the horizontal component of force required to a body that just overcomes the friction or resistance to sliding, to the vertical component of the force applied.
. . .	*Slip resistance*—The frictional force opposing movement of an object across its surface, usually with reference to the sole or heel of a shoe on a floor. A surface having a static coefficient of friction of 0.5 or greater as measured by this test method is considered to have adequate slip resistance. That is, it will provide the required traction for preventing or markedly reducing the probability of slipping while walking.
Stick-slip—A relaxation oscillation usually associated with decrease in coefficient of friction as the relative velocity increases	. . .

bodies. Scratch testing with a spherical indenter has been used to measure the friction coefficient of polydimethylsiloxane on stainless steel [15]. These results indicated that the dynamic friction coefficient decreased with increasing normal load suggesting that the viscoelastic character of the coating influenced its frictional behavior.

Another technique involving scanning-probe microscopy and known as friction-force microscopy measures the lateral force on a sliding probe caused by sliding friction [32]. The technique allows frictional processes to be examined on a nanometer scale. It has been found that the velocity dependence of friction has a maximum in the friction-velocity interaction and this is related to the glass transition temperature, T_g. Hammerschmidt and coworkers [33] have summarized some of these studies when they used temperature-controlled friction-force microscopy to investigate viscoelastic relaxations of polystyrene, poly(methyl methacrylate), and poly(ethylene terephthalate) and their effect on friction. They concluded that for polymer films the main contribution to friction was viscoelastic mechanical loss.

SLIP RESISTANCE

One may think of slip as the antithesis of friction. While both high and low friction are important, in the sense of walkways, working surfaces, sidewalks, swimming pool, bathing, and other tiled areas, and similar surfaces, there must be sufficient friction to ensure that slipping and/or tripping with subsequent falling and potential injury will not occur. There are many different slip resistance testing specifications and standards. OSHA (Occupational Safety and Health Administration) has a standard [34] that deals with the slip resistance of skeletal structural steel. A subpart of this standard, Standard Number 1926.754(c)(3), indicates that after July 18, 2006, workers will not be permitted to walk on the top surface of structural steel that has been coated with paint or similar material unless documentation or certification indicates that the coating has achieved a minimum average slip resistance of 0.5. This value must be achieved when measured with an English XL tribometer [35] or equivalent tester on a wetted surface at a testing laboratory. The certification or documentation is to be based on the appropriate ASTM standard test method in a laboratory that is capable of performing the test. The cited ASTM test methods [36] are:

ASTM F1677-96 Standard Test Method for using a Portable Inclinable Articulated Strut Slip Tester (PIAST). This method is approved for dry and wet testing. The method, which simultaneously applied the horizontal and vertical forces, can be used on nearly all surfaces. The device used with this method is the Brungraber Mark II.

ASTM F1679-00 Standard Test Method for using a Variable Incidence Tribometer (VIT). The literature suggests that this is an excellent testing method that is approved for both dry and wet testing on essentially all surfaces. As in the previous method, the horizontal and vertical forces are applied in a simultaneous manner. The device used with this method is the English XL tribometer [35], and operators using this equipment should be certified for such use.

With the above said, it must be pointed out that ASTM has found that these methods lack a precision and bias statement and have a reference to proprietary apparatus

TABLE 8—ASTM Standards for measuring friction coefficients and related technology (other standards exist).

ASTM	Title
C808-75(2010e)	Guideline for Reporting Friction and Wear Test Results of Manufactured Carbon and Graphite Bearing and Seal Materials
C1028-07e1[a]	Test Method for Determining the Static Coefficient of Friction of Ceramic Tile and Other Like Surfaces by the Horizontal Dynamometer Pull-Meter Method
D1894-08	Test Method for Static and Kinetic Coefficients of Friction of Plastic Film and Sheeting
D2047-99	Test Method for Static Coefficient of Friction of Polish-Coated Flooring Surfaces as Measured by the James Machine
D2394-83	Methods for Simulated Service Testing of Wood and Wood-Base Finish Flooring
D2714—94	Test Method for Calibration and Operation of the Falex Block-on-Ring Friction and Wear Testing Machine
D3108-07	Test Method for Coefficient of Friction, Yarn to Solid Material
D3412-07	Test Method for Coefficient of Friction, Yarn-to-Yarn
D4103-90(2009)	Practice for Preparation of Substrate Surfaces for Coefficient of Friction Testing
E303-93(2008)	Test Method for Measuring Surface Frictional Properties Using the British Pendulum Tester
E670-09	Test Method for Side Force Friction on Paved Surfaces Using the Mu-Meter
E707-90(1996)	Test Method for Skid Resistance Measurements Using the North Carolina State University Variable-Speed Friction Tester
F609-05	Test Method for Using a Horizontal Pull Slipmeter (HPS)
F695-01(2009)	Practice for Ranking of Test Data Obtained for Measurement of Slip Resistance of Footwear, Sole, Heel, or Related Materials
F732-00(2006)	Test Method for Wear Testing of Polymeric Materials Used in Total Joint Prosthesis
G40-99	Terminology Relating to Wear and Erosion
G65-04(2010)	Test Method for Measuring Abrasion Using the Dry Sand/Rubber Wheel Apparatus
G77-98	Standard Test Method for Ranking Resistance of Materials to Sliding Wear Using Block-on-Ring Test
G99-05(2010)	Test Method for Wear Testing with a Pin-on-Disk Apparatus
G115-10	Standard Guide for Measuring and Reporting Friction Coefficients
G133-05(2010)	Test Method for Linearly Reciprocating Ball-on-Flat Sliding Wear
G143-03(2009)	Test Method for Measurement of Web/Roller Friction Characteristics

[a]Withdrawn, but these standards are referenced and therefore included in above listing.

that violates certain ASTM requirements [37]. A deadline of September 30, 2006 had been set for correcting the deficiencies, but it was felt that this deadline would not be met. As a result, a decision was made to withdraw ASTM F1677 and ASTM F1679 as well as two related test methods.[4] At the same time the above was taking place, OSHA [38] reopened and sought comments and information regarding its Standard Number 1926.754(c)(3) and attendant Appendix B [34,36]. OSHA's purpose of reopening this matter was to consider whether to retain, amend or revoke the provision regarding test methods for slip resistance on skeletal structural steel and whether slip-resistant coatings meeting the requirements could be available by July 18, 2006. Since OSHA ascertained that no progress would be made toward meeting these goals[5] by the "to-be-effective" date, the group decided in early 2006 to revoke a provision within the Steel Erection Standard that addresses slip resistance of skeletal structural steel [39]. Readers interested in this matter would do well to follow proceedings that probably will be found in the Federal Register and/or ASTM literature.

English [40] has a listing of slip resistance standards that are in wide use. Included in the compilation are the above test methods as well as other standards from ASTM, American National Standards Institute (ANSI), National Fire Protection Association (NFPA), and Underwriters Laboratories. The standards are separated by their suitability for wet or dry testing. English also has a description of other tribometers based on pendulum and drag-sled principles.

SENSOR MATERIALS

Materials that may be used as sensors or test pads include a broad range of known items [41]. Of course, sensors are used in context with the tests being conducted. For friction testing, two surfaces are required for any measurement—one is the surface of the specified material to be tested and the other is a sensor material or the surface against which the specified material is to be tested. The specified material and sensor material may be the same or different, but both must be defined and specified.

To obtain meaningful and reproducible results, it is essential that the sensor material be selected to represent use conditions and be well defined. Properties such as uniformity (surface character including flatness, roughness, chemical composition, resilience, and shear modulus), permanence in that chemical and physical characteristics do not change with time, and availability in a usable form that does not require excessive preparation should be considered when selecting a sensor. Many feel that a major concern in sensor selection is choosing a material that will not change as a function of time. Both sensor material and

[4] The "other two" test methods are ASTM F1678-96 Test Method for Using a Portable Articulated Strut Slip Tester and ASTM D5859 Test Method for Determining the Traction of Footwear on Painted Surfaces Using the Variable Incidence Tester.

[5] Comments received by OSHA prior to the deadline suggested that no significant progress had been made regarding the suitability of the test methods referenced in the provision for testing slip resistance or the availability of coatings that would need the slip resistance requirements of the provision [39]. The final revocation rule was effective January 18, 2006.

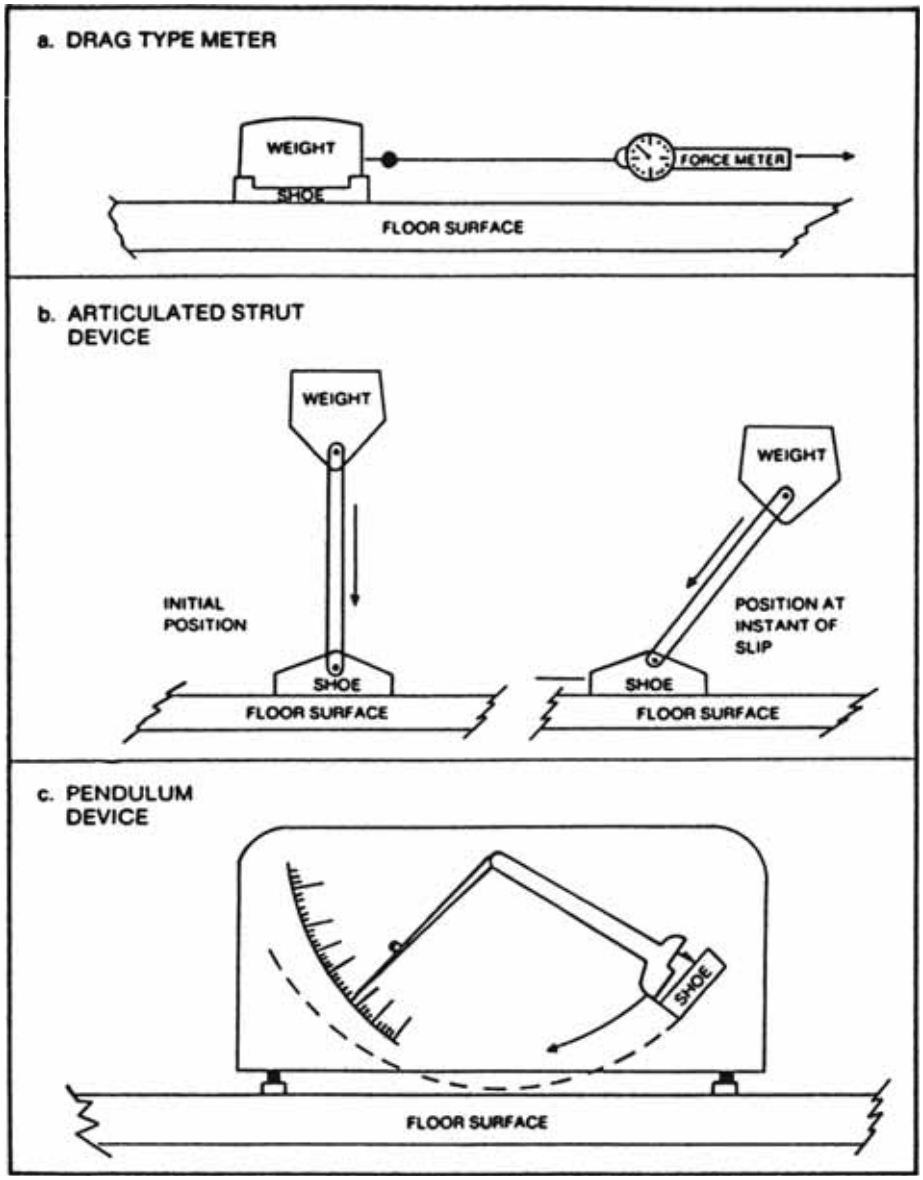

Fig. 3—Schematics of different friction measurement devices (courtesy of the National Institute of Standards and Technology).

test material may be the same or different and both should be reported when the coefficient of friction is stated.

Sensors might be exemplified by leather that is used as a primary source material when friction of flooring is studied. For interlaboratory and specification testing, shoe materials such as leather conforming to Federal Specification KK-L-165C[6] [42] are used. When leather is used as a sensor or as a test material, it should be kept in mind that leather soaks up water and becomes somewhat sticky which will result in high coefficients of friction being measured. Also, leather is not homogeneous in character and can vary from piece to piece. It is important that the appropriate materials are used when specific testing is done. In the case of rubber, it is recommended that a rubber conforming to Section 7.1 of ASTM D1630-06 Test Method for Rubber Property—Abrasion Resistance (Footwear Abrader) be used. Neoprene, nitrile, and styrene-butadiene rubbers have been used in many investigations. In another study [43], three leathers with three levels of oil content, two Kraton® thermoplastic elastomers, and 15 different rubbers were used to generate statistical data for ASTM F609-05 Test Method for Using a Horizontal Pull Slipmeter (HPS). Neolite® is also used as a test pad material that does not change regardless of moisture or wear conditions.

LUBRICANTS

For those instances where friction is to be decreased (slip increased), a variety of lubricants, slip agents, or slip additives are available. These compounds include micronized polyethylene, polytetrafluoroethylene as well as various waxes, oils, and silicones. Water can also act as a lubricant when it is present on many solids. Persson [44] and coworkers have studied the effect of water on the loss of braking power and rubber skidding on a wet highway (tire asphalt). They reported that rubber can seal water-filled pools or

[6] Available from Standardization Documents Order Desk, Attn: NPODS, Bldg. 4 Section D, 700 Robbins Ave., Philadelphia, PA 19111-5094.

TABLE 9—Examples of lubricants
Esters
Fatty alcohol esters
Fatty esters
Glycerol esters
Wax esters
Fatty acid amides
Alkanolamides
Monoamides
Bisamides
Metallic compounds
Aluminum stearate
Barium stearate
Calcium stearate
Graphite
Molybdenum sulfide and disulfide
Oils and greases
Conventional and synthetic
Polymeric and oligomeric materials
Fluoropolymers
Micronized polyethylene
Micronized polytetrafluoroethylene
Montan waxes
Oxidized polyethylene waxes
Paraffins, low melting
Polyolefin waxes
Silicones

pockets and effectively smooth the rubber surface. This effect reduces the viscoelastic dissipation that surface asperities induce in bulk rubber, and decreases friction. High molecular weight polyoxyethylene has remarkable properties for reducing the friction or drag characteristics of water [45] on objects such as pleasure/racing boats, naval craft, and torpedoes when used in various forms, for reducing the friction of ski waxes on snow when compounded into the wax, and increasing volume output of water under constant pressure through hoses and ducts.

In some instances, a material of construction can have an internal lubricant as is the case with the acid- and chemical-resistant wood from the tree *lignum vitae*[7] (*Guai-acum Officinale*), an extremely hard wood that find use in noiseless underwater bearings and as saw guides. McLaren and Tabor [46] found that in the dry state this self-lubricating wood has friction characteristics comparable to those of polytetrafluoroethylene. Experimental evidence indicated that the lubricity is due to wood waxes that exude from the wood during sliding operations. Formulation with solid lubricants has made great strides in recent years for industrial operations that impose severe sliding conditions [47]. Nanostructured or nano-composite forms are coupled with micro-texturing, micro-patterning, or other smart surface engineering strategies [48] to achieve very high levels or durability and performance.

Many lubricants also function as abrasion resistance and mar-reduction agents. In certain instances, they can be used as antiblocking agents. They are often used in the plastics processing industry where they function as melt viscosity reducers and flow agents to improve flow onto metal surfaces and, at times, as co-stabilizers. The use of lubricants to reduce wear and power consumption is well known.

Factors that should be considered in selecting a lubricant include absorptivity, melting point, polarity, solubility, effect on adhesion, potential reactivity from friction thermal energy developed, volatility, and similar characteristics. Common lubricant families as well as selected specific lubricants are listed in Table 9. Polyethylene and polytetrafluoroethylene are available in powdered or micronized form in a variety of particle sizes [49]. Silicones are available as formulated products designated for use in the coating industry [50,51]. The powdered and micronized products are incompatible and function as filler when incorporated into the coating where they act as tiny "ball bearings" that decrease friction and often improve abrasion and mar resistance.

[7] A small tree that is native to the Netherlands Antilles and St. Johns in the Virgin Islands and that has been cultivated in Argentina. The wood from this tree is very dense and will sink in water. In addition to its self-lubricating frictional properties, the tree s sap and bark are said to have medicinal properties.

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Part 12: Environmental Resistance

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Prevention of Metal Corrosion with Protective Overlayers

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THE PREVENTION OF CORROSION BY SURFACE processing enjoys significant economic leverage, and, as evidence, one may cite the widespread use of coatings, films, and inhibitors for metals and semiconductors in many service environments. All engineering metals used in modern technological societies are unstable with respect to corrosion, and the result is a loss of properties. Natural oxide films provide protection against continued attack for some metals, and alloying extends the life of other metals by developing highly stable passive films. Where metals may not be protected by oxide films, other modification methods have been developed to reduce corrosive attack. In reality, the improvement of corrosion resistance of metals by modification of the surface has been practiced since the invention of metal tools. Some of the earliest techniques to prevent corrosion involved coating with greases or natural oils. More modern methods were developed in the 19th and 20th centuries and include multiple coatings, zinc galvanizing, electroplating of other pure metals, and vacuum physical vapor deposition of mostly pure metal coatings by electron beam and sputtering techniques. The metal coatings are better barriers than organic films because of the lower permeability of the former to moisture, oxygen, and ions. Inhibitors or conversion coatings and primers for paints are cheaper than metal coatings and are used widely by paint manufacturers even though they remain highly proprietary in nature.

The use of organic coatings to protect metal surfaces is practiced widely. Much of the use is for atmospheric exposure of motor vehicles as well as for structural units such as bridges and buildings. The successful implementation of existing technologies has greatly reduced the effects of corrosion of automobiles, for example, in the past decade in response to consumer demand. Despite many recent advances, coating technologists and scientists acknowledge that much is unknown and that new processes and understanding are the keys for further progress [1]. Defects in the metal substrate and in the overlayers are among the primary concerns because they are the source of localized corrosion phenomena. Defects may occur on length scales from atomic-level lattice vacancies to arrays of defects at grain boundaries (for crystalline materials) or to random pores or cracks (for example, in noncrystalline films). Avoiding such defects by proper quality control is a major concern in coatings science and technology.

In the discussion that follows, aspects of corrosion that involve thermodynamics and kinetics will be developed as a basis for the description of the specific nature of corrosion of metals under protective films and overlayers. Some emphasis will be given to protection of thin metal films and micro-structures that are particularly sensitive to corrosion and whose successful protection provides a basis for advancing protection technology in general.

CORROSION IN AQUEOUS SOLUTIONS

The driving force for a reaction is the change in Gibbs free energy, AG, for reactants to products. Mathematically, this may be expressed by

$$\Delta G = \sum_{\text{products}} G - \sum_{\text{reactants}} G \qquad (1)$$

The summation signs are used as a general notation to indicate that all reactants and products are included in the calculation. From the nature of the free energy function, this calculation applies to initial (reactants) and final (product) states and is independent of intervening states. The reaction may be investigated under controlled reversible conditions such as in an electrochemical cell or under irreversible conditions such as in corrosion, and the same total free energy change (ΔG) will be appropriate. A quite general predictive capability may be applied to specific corrosion reactions since all the available thermodynamic data may be used for corrosion calculations directly. This enables the position of final equilibrium of the corrosion system to be established. The thermodynamic calculations have the limitation that no information concerning the *rate* of the reaction is provided, only what the final state will be for the process.

The value of ΔG for reactions of elements to form a compound, all in their standard states at a particular temperature, is the standard free energy of formation of the compound, $\Delta G^0_{f,T}$. Here, the subscript T denotes the temperature. Description of the detailed calculations are beyond the scope of this discussion, but several excellent textbooks are available [2,3].

The most extensive tabulations of thermochemical data for chemical compounds in their standard state at 25°C are in a series of National Bureau of Standards publications [4]. These are NBS Technical Notes 270-3, 270-4, and 270-5, which supersede the older NBS Circular 500 for the elements they cover. These tabulations also update the older

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data of Latimer [5]. The book by Latimer [5] remains a valuable reference because of the description of techniques to estimate thermodynamic quantities where reliable data are sparse. Lewis and Randall [3] tabulated thermodynamic data, including data for aqueous solutions of a number of electrolytic solutions that are valuable for corrosion calculations. There is overlap between this tabulation and the JANAF thermochemical tables [6], but the latter also tabulate the standard enthalpy and free energy of formation of chemical compounds at several temperatures along with $-(G^0 - H^0_{298})/T$.

Oxide and hydroxide solubility are strongly influenced by the pH of the aqueous phase. Pourbaix recognized this and summarized the thermodynamic stability of metal-aqueous systems by the use of potential-pH diagrams. The thermodynamic data tabulations already quoted [3–6] should be utilized for detailed calculations, however.

Usually when studying corrosion, one is not concerned with the conditions for thermodynamic stability, but rather with the rate of attack and how it may be altered in basically unstable conditions because only a limited number of systems have absolute or *thermodynamic stability*. As a practical matter it is necessary to accept some rate of corrosion and/or to control or mitigate the rate of attack. Thus *kinetic stability* is always relative and subject to interruption if control is not maintained. Controlling the rate of degradation may be accomplished, for example, by the use of cathodic or anodic protection, the use of inhibitors, the maintenance of protective surface films, or buffering the composition of an otherwise aggressive solution. All these techniques are used widely to extend the life of metallic structures with continuing improvement.

Corrosion reactions are electrochemical in nature. The kinetics of the corrosion reactions are then related to the kinetics of the electrochemical reactions that occur during the corrosion process. The reactions involve not one but at least two electron transfer reactions, and the reactions are not in series but are in parallel. Coupling of parallel or simultaneous reactions is a fundamental feature of the corrosion process. Each of the simultaneous reactions may consist of multiple steps, respectively, as described above, but the simultaneous, independent reactions are coupled electrically. The independent reactions occur on the same surface at the same time, but also at the same potential. The reactions may be coupled chemically as well, e.g., through pH effects, but this is not essential. The specific relation that defines the coupling of simultaneous corrosion reactions on an isolated metal surface is

$$\sum_{\text{anodic}} I_a = -\sum_{\text{cathodic}} I_c \tag{2}$$

There will then be zero net current to the corroding metal electrode. The relationship is written in terms of currents (I_a and I_c) rather than current densities for reasons which will be discussed. The potential at which the balance is satisfied is the mixed or corrosion potential. It is determined by the rates of the simultaneous reactions and is not defined by the state of the system in a thermodynamic sense. The corrosion potential always lies between the equilibrium potentials of the anodic and cathodic processes, respectively.

As a summary, the general corrosion of metallic materials in aqueous solutions is well understood. The anodic or oxidation reaction of the metal is superimposed on a cathodic reaction, and the two are balanced locally on a homogeneous surface. The rate of the reaction is a function of both the rate of metal dissolution and the rate of the cathodic (reduction) reaction. Each reaction may be influenced in general by the composition of the solution, especially the pH and the electrolyte anion, and by the nature of the (oxide) films, if any, which may be formed at the metal/electrolyte interface. If several oxidizing species are present in the solution, each may act in parallel so that the total rate of metal dissolution is increased. For example, most metals will react directly to displace hydrogen from water and to produce an oxide of the metal or some other corrosion process. The addition of oxygen will increase the rate of corrosion of the metal, usually in direct proportion to the concentration of the oxygen added. The specific details will vary with each metal to reflect the thermodynamic, kinetic, and mass transfer driving forces that are acting [7].

Heterogeneous surfaces are commonly observed in corrosion situations and are of the three general classes: (1) the inclusion of foreign metal impurities on the metal surface, (2) the nonuniform coverage of the surface by a film, either an oxide film or an artificial coating in aqueous solutions, and (3) nonuniform conditions in the electrolyte environment. All these are of great importance because localized, or nonuniform, corrosion of metals may be caused by any of the three. A form of galvanic corrosion and pitting corrosion is caused by the first type of heterogeneity, while crevice and pitting corrosion are produced by both (2) and (3).

Restrictions of geometry, e.g., in crevices and corners, prevent mixing of solutions everywhere, and local buildup of reaction products or the exhaustion of an oxidant may occur. The local kinetics will be relatively independent of that in other regions except that there may be coupling through the electric field and electrical current may flow between a localized corrosion site and the surrounding surface. This may lead to nonuniform corrosion, particularly where the buildup of products increases the aggressiveness of the local solution. In this case, corrosion will be most severe, not where the concentration or flux of the bulk solution oxidant is highest but where it is lowest. Crevice corrosion is considered to be an example of this type of attack, and the aggressive solution within a crevice or pit is one which is more acidic than the external solution.

Anodic dissolution, plus hydrolysis of the product metal ion, causes an increase of hydrogen ion concentration. On the other hand, reduction of either hydrogen ions or dissolved oxygen reduces the hydrogen ion concentration. If the net corrosion reaction plus hydrolysis would lead to an increase of hydrogen ion concentration, the process may occur independently of any other process and would accelerate with time to some steady state where diffusion out of the occluded region would limit the buildup. If the corrosion reaction plus hydrolysis leads to no net change in H^+ concentration, an acid solution in a crevice or pit could only be created by separation of the anodic and cathodic regions. Concentrating the cathodic reaction on the outer surface would occur naturally if dissolved oxygen, for example, were the primary bulk oxidant. Coupling this with a net anodic reaction (plus hydrolysis) in the inner region for an overall current balance would lead to a steady state crevice or pit.

For separation to occur as described above, a quite general condition imposed on the corrosion kinetics must be

obeyed. The outside surface must support a cathodic reaction, and it must be supported at a potential that is positive of the potential of the anodic reaction in the crevice. The direction of current flow through the solution establishes this criterion. A qualitative laboratory test may be used to identify metal solution combinations that could cause localized attack by the mechanism described above. The test involves the corrosion kinetics on the metal of interest. Cathodic currents must be observed on the metal in the exterior solution at potentials that are positive of the anodic region for the crevice conditions or the separated reactions will not support increased anodic dissolution in the isolated region. This is a very definitive test, and very few metal-environment combinations match the criterion.

Ohmic drop restricts the penetration of current into a small-gap, occluded region [8]. This causes the anodic reaction to be distributed over a relatively small region, which concentrates the attack. At greater depths in the gap, the metal is isolated from the external surface reactions. Newman [9] calculated the limited depth to which a reaction may penetrate inside a circular geometry, in this case a cathodic protection reaction. The reaction is concentrated near the opening.

Composition gradients are considered to be important for pitting and differential aeration corrosion as well. For pitting corrosion, similar conditions to those for crevice corrosion are considered important. Pits may be initiated in ways that are different from crevice corrosion, e.g., at foreign metal inclusions. However, the propagation of pits depends largely on a locally aggressive solution. Stirring to eliminate concentration effects will stop the growth of pits. Differential aeration could also drive corrosion at locally variable rates under an electrolyte film of nonuniform thickness. The diffusion-limited flux of oxygen through the film would be directly proportional to the film thickness. If the local corrosion rate is limited by the oxygen flux, the attack will be most severe at low film thicknesses. For active/passive metals, increase of the oxygen flux may exceed the peak current for active dissolution and cause the metal to adopt the passive state. In this case, then, thin films of electrolyte will *reduce* the corrosion rate.

ATMOSPHERIC CORROSION OF METALS

Most atmospheric corrosion tests have been conducted in environments such as indoor atmosphere, outdoor atmosphere, and laboratory tests under simulated conditions. Indoor corrosion studies have been performed for the electronics, computer, and communication industries for the development of more durable materials with desirable structural, magnetic, and electrical properties. On the other hand, outdoor studies aimed at understanding corrosion behavior are highly dependent on atmospheric weather factors, especially in marine and urban areas. The latter studies have been performed in the automobile, marine, and aircraft industries. Laboratory tests attempt to use accelerated methods under simulated atmosphere or aqueous conditions. Electrochemical methods have been used extensively in such tests to analyze and monitor the corrosion behavior of metals.

Several weather factors are known to influence outdoor corrosion [10–13]. Precipitation, ambient and dew-point temperatures, atmospheric pollutants, wind direction and wind velocity, and solar radiation can be considered as weather factors in outdoor and/or urban corrosion tests. Among these factors, moisture or relative humidity, temperature, and pollutants such as sulfur dioxide and chlorides are the most important variables.

Relative humidity is known to be the most important factor in determining the atmospheric corrosion rate. It has been reported that rapid acceleration of corrosion occurs beyond a certain value of relative humidity, defined as the critical humidity [14,15]. The period in which the relative humidity exceeds the critical humidity is called the time-of-wetness, and this factor is quite significant in determining atmospheric corrosion rate of metals [16]. In addition, in the presence of a pollutant such as sulfur dioxide, the critical humidity at which corrosion is enhanced to a significant extent will decrease with increasing pollutant concentration [17,18].

It has been reported that comparatively large aggregates of water are present on oxyhydroxide surfaces at humidities below 40 % [19]. Even on clean metal surfaces obtained under ultrahigh vacuum or reducing conditions, significant quantities of water are adsorbed on air-formed films when exposed to the environments containing only oxygen and water vapor for more than a microsecond [13]. As a result, monolayers of adsorbed water may provide the medium for electrochemical microcells that may drive a heterogeneous corrosion process. Water may also exist in the form of complex mixtures with oxides, hydroxides, and mixed oxyhydroxides [19,20].

The corrosion rate of metals is accelerated by the presence of air pollutants such as sulfur dioxide, nitrite, nitrate, hydrogen sulfide, chloride, and some kinds of salts [10,15]. These species may derive from gas-borne particles or from reactions at the surface. Reaction with adsorbed water monolayers yield electrolyte films that facilitate further corrosion processes. Among these pollutants, sulfur dioxide, chlorine gases, sulfur gases, and ozone are important species that promote corrosion in the presence of water [21].

The corrosion-accelerating effect of sulfur dioxide with humidity has been reported by many investigators [10,13,15]. Vernon [15] suggested that sulfur dioxide may change the pH in electrolyte films present on metal surfaces and enhance the corrosion rate. Rice et al. [13] also suggested that sulfur dioxide is readily soluble in water to form sulfurous acid; these local acidic regions accelerate oxide formation, and the corrosion rate is also enhanced by other electrochemical effects. It has been reported that wetting of the metal surface is promoted in the presence of ammonia, and the water droplets contain higher concentrations of sulfates than for the same concentration of sulfur dioxide with no ammonia [10,22].

The effect of chlorine gas or chloride on atmospheric corrosion has been reported [10,13]. In aqueous electrochemical corrosion studies, the chloride ions usually enhance pitting corrosion of many metals and also degrade the oxide surfaces. Rice et al. [13] reported that chlorine gases reduce the surface pH and yield hygroscopic corrosion products that influence the amount of adsorbed water. A direct relationship between the amount of chlorides in corrosion products and atmospheric corrosion rates was reported by Sereda [10].

The effect of ozone gas on copper and silver corrosion has been known to be significant, while cobalt, nickel, and iron are insensitive to ozone [13]. It has been reported that

ozone may enhance the corrosion rate of metals sensitive to H_2S.

The atmospheric corrosion rate can be measured either in field tests in different atmospheres or with accelerated tests in the laboratory. The field tests require long exposure times and yield complicated data that prevent detailed analysis. Accelerated tests are performed under simulated atmospheric conditions, and they are the easiest way to acquire more information with various setup conditions. However, it may not be possible to simulate practical service conditions.

There are several methods to monitor and control the corrosion rates by means of either field or laboratory tests. The conventional method is the weight loss determination, which requires long-term exposure unless a continuous method is used that involves the quartz crystal microbalance [23,24]. Another method is the electrical resistance method and measurement using electrochemical cells. Electrical resistance methods use the changes in the electric resistance of thin wires or foils to monitor failure, but they cannot be used for determination of the instantaneous corrosion behavior [25–27].

Electrochemical methods have been developed to take advantage of the electrochemical basis for atmospheric corrosion [28,29]. Corrosion currents can be monitored electrochemically, and the instantaneous value of current can be detected. One way to monitor atmospheric corrosion with an electrochemical method is to design a cell that will work under thin electrolyte layers (less than 500 μm) with consideration of the effects of corrosion products and dilute pollutants [30].

Electrochemical methods for monitoring atmospheric corrosion have been well reviewed by Mansfeld [30,31]. Most of the studies have been aimed at macroscopic measurement of time-of-wetness that is associated with electrochemical corrosion [10,12,16,17]. Galvanic cells with electrodes of different metals have been commonly used [16,32]. Sereda [10] has developed galvanic cells of platinum-iron and platinum-zinc couples to determine the time-of-wetness. Time-of-wetness was arbitrarily defined as the interval during which the external potential exceeded 0.2 V. This figure was the period during which the relative humidity was greater than 85 % [12,16]. Tomashov [33] has used sandwich-type galvanic cells of iron-copper, iron-zinc, iron-aluminum, and copper-aluminum. They concluded that the method was suitable for fast determination of the corrosivity of the atmosphere and that the direct measurement of corrosion rate for testing metals was possible.

Several investigators [17,34–36] have used galvanic cells consisting of steel-copper and electrolytic cells consisting of individual metals (steel, zinc, or copper) to which an external potential was applied. They concluded that the cell current gave qualitative agreement with the weight-loss data. Recently, extensive studies have been performed by Mansfeld and his coworkers [30,31,37–39]. They used galvanic cells and electrolytic cells which consisted of two electrodes and three electrodes. Galvanic cells such as copper-steel, copper-zinc, steel-zinc, steel-aluminum, and aluminum-zinc couples were used to study the effects of pollutants, relative humidity, and so on. They used the electrolytic cells such as two- and three-electrode cells for studies of the corrosion kinetics and for the measurement of corrosion currents. The polarization resistance method was used to determine atmospheric corrosion kinetics under thin electrolytic layers. Mazza et al. [40] have used a galvanic cell that consisted of a sandwich formed of bronze covered by its artificial corrosion products on which a high-porosity gold film was applied. They monitored the corrosion current with a zero resistance ammeter and obtained instantaneous and continuous information on the corrosion rate of the bronze. Tosto and Bruco [41] used galvanic cells of copper-steel to obtain the relation between the corrosion content and relative humidity. They found that the corrosion current depended on relative humidity (RH).

As a rapid electrochemical method for monitoring atmospheric corrosion, measurements of electrode potential using a suitable reference electrode have been developed by several investigators [42,43]. Although the method gives no absolute data on corrosion rates, it is a fast and easy method for on-site investigations. Thin film methods to measure corrosion rates were discussed by Howard [44]. Pourbaix and his coworkers [42,45] developed an accelerated electrochemical wet and dry method that was designed to use alternate immersion cycles in an electrolyte bath. The electrode potential was monitored when the steel electrode was in the wet part of the cycle. They concluded that their method was selective and yielded reproducible data.

Electrochemical cells designed to simulate thin electrolytic films formed during atmospheric corrosion have been developed by several investigators [46,47]. Fishman and Crowe [47] have studied the thin film of electrolyte with a potentiostatic polarization technique. The corrosion current increased with an increase of RH. They concluded that the resultant corrosion rates were consistent with those reported from long-term weight loss measurements. Fiaud [46] created a thin electrolytic film (80 μm thickness) using the device similar to one developed in the field of thin layer electrochemistry [48]. Platinum and nickel were used as electrodes and sodium sulfate (Na_2SO_4) solution was used as the electrolyte with change of pH by addition of sulfur dioxide (H_2SO_4). SO_2 gas was introduced into the electrolyte through a membrane. They observed the depolarization effect of SO_2, oxidation of SO_2, and reduction of SO_2 with use of cyclic voltammetry and linear polarization techniques.

CORROSION OF THIN METAL FILMS AND MICROSTRUCTURES

Corrosion of a metal occurs by the same fundamental reactions whether it is used in a large structure like an automobile, a bridge, or a heat exchanger, or in a small structure characteristic of magnetic, optical, or microelectronic devices, or under a protective layer [49]. The uniqueness of each application is tied up in the definition of the environment to which the metal is exposed or which develops with time, as well as the definition of a characteristic size of the corroding material. Since the time to failure of a material (i.e., its lifetime) is normally inversely proportional to the corrosion rate and directly proportional to the thickness of the corroding material (its characteristic size), small dimensions are more susceptible to corrosion failure and loss of properties. For example (see Fig. 1), a 50 nm cobalt magnetic film may be corroded completely in about 38 h at a corrosion rate of 1 $\mu A/cm^2$. The desired lifetime is about five years, so a protective film (e.g., diamond-like carbon) must be used to moderate the rate of attack. The protective layer

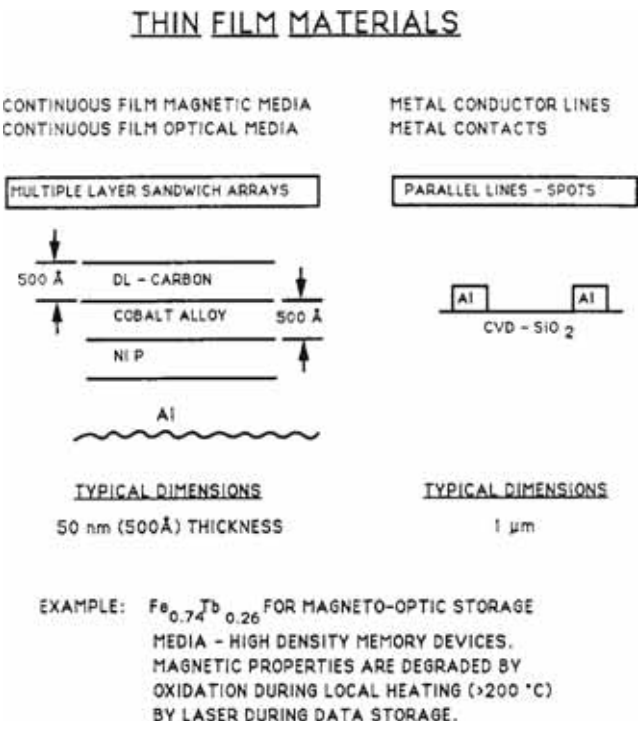

Fig. 1—Thin film materials for magnetic, optical, metal conductor lines and microelectronic contacts make them highly susceptible to have small dimensions that are highly susceptible to corrosion.

must be thin to read or write to the cobalt film with the magnetic head, and defects in the protective layer will lead to localized corrosion attack. Wear and friction are mechanical processes that result from the relative movement of the disk and head. The head is designed to fly very close to the disk to take advantage of the magnetic properties [50], but it comes to rest on the disk surface when the system is idle. Humidity and other factors affect wear and friction, and layers or films may be added to lubricate the magnetic film. Of more interest here, however, are the chemical effects that cause corrosion. Accelerated tests have been used to determine disk reliability [51], tests that measure the affects of wear, friction, atmospheric contaminants, humidity, oxygen diffusion, and galvanic corrosion. Also described by Antler and Dunbar et al. [51] is the comparison between field test experience and laboratory simulated corrosion test results. Earlier results on microelectronics failures are reviewed by Schnable et al. [52], Comizzoli et al. [53], Wood [54], and Stojadinovic et al. [55]. Whatever the mode, the result is a loss of information at the site of degradation and the loss of properties. Better preparation and processing, or better design, may reduce flaws and defects that cause mechanical failure, but they may not reduce corrosion that is the result of the natural instability of the metal in an aggressive environment. Rarely are the thin film metals stable in the environment, so techniques must be found to stabilize the structures and extend the lifetimes.

In the other example of Fig. 1, aluminum interconnects in microelectronic devices have characteristic widths of 1 μm or smaller. Ionic conduction along adsorbed water layers at the silicon dioxide (SiO_2) surface can lead to electrochemical corrosion and "breaks" in the Al conductor. If the corrosion rate were 1 $\mu A/cm^2$, the lifetime of the Al interconnects would be about 48 days, rather than the 10 to 20 year lifetime desired. A protective layer is required for this application as well.

The corrosion phenomena of thin films chosen for magnetic, optical, or electrical applications have unique characteristics, but they are often similar to those observed for bulk materials [35,50,56]. Thin films have bulk metallurgical properties in thicknesses larger than 1–3 nm and have the same chemical reactions as well. Both observations lead to the general conclusion that both bulk metals and films 30 nm or thicker will have similar corrosion behavior. On the other hand, thin film materials have small grain size and are prepared for magnetic disk applications in "tracked" or grooved geometries. The small grain size causes films to have more homogeneous properties, with fewer inclusions and smaller chemical segregation effects than ordinary bulk materials. The tracks have sharp edges and dimensions to generate unique morphologies in the films. The homogeneous properties would make the films less susceptible to corrosion, but the defects generated at edges could be sites for enhanced attack. The dimensions and geometry of the tracks may lead to nonuniform chemical composition in the recesses, which would produce localized corrosion effects as well. Atmospheric corrosion has been studied under simulated conditions for thin magnetic films [35], and, as in other cases, it was found that the affect of humidity and atmospheric pollutants was synergistic. The level of humidity may influence the condensation of thin moisture films on surfaces, which will facilitate transport across surfaces and may cause the accumulation of water in microscopic domains. In the latter, the concentrations of dissolved contaminants may approach saturation conditions. The contamination may come from dust or inclusions of other layers [49]. The conditions are difficult to simulate in the laboratory because of the lack of knowledge of local conditions in the microscopic regions that are relevant to the problem. In addition, it has been difficult to make in situ measurements for conditions that simulate atmospheric-corrosion measurements, which would give a direct indication of the processes responsible for corrosive attack. Several standard tests have been developed to assess atmospheric corrosion damage ASTM Practice for Conducting Atmospheric Corrosion Tests on Metals (G50–76 (1990)); ASTM Practice for Rating of Electroplated Panels Subjected to Atmospheric Exposure (B537-70 (1992)) without addressing the mechanism of the attack.

The second topic relates to protective layers and encapsulants. Pore-free conventional protective layers over magnetic films are too thick to be compatible with the magnetic properties of thin film disk materials. In addition, polymer films can change the adhesion properties of the surface and interfere with the operation of the magnetic head. Highly resistive but electroactive overlayers could lead to galvanic attack of the substrate through holes in the thin film. Sputtered diamond-like carbon films [51,57–60] could fall into this category (see Fig. 1).

A protective layer plated or sputtered over an active metal may have pores and defects that will permit the corrosive medium to contact the active substrate metal and thereby promote galvanic corrosion. The holes or defects may be present on a heterogeneous surface in the geometry of either regular arrays or random arrays. The mathematical

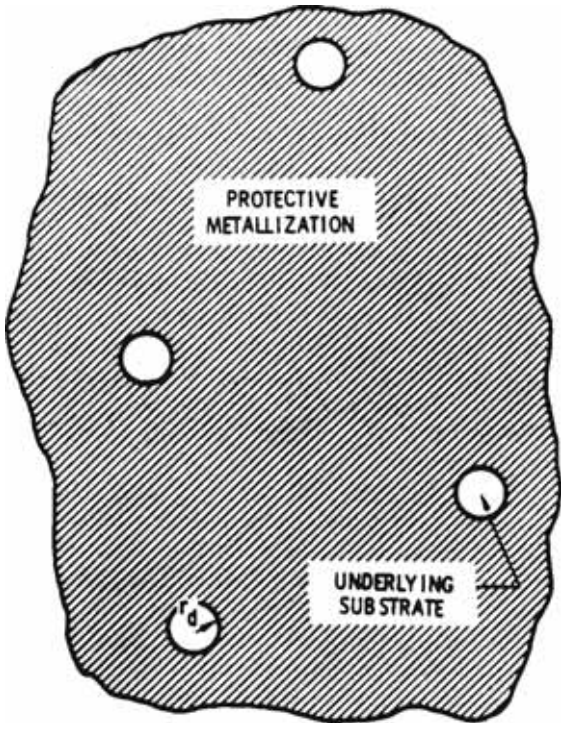

Fig. 2—Multilayer "sandwich" arrays may have underlayers exposed through holes or holidays in the overlayer, and galvanic interactions may enhance the corrosion rate in such systems.

modeling of galvanic behavior in plating corrosion systems has been discussed by Smyrl and Newman [21], where earlier work was also reviewed. They determined the current and potential distributions of galvanic corrosion system, which consisted of anodic disks in a cathodic plane as shown in Fig. 2. They solved the Laplace equation for potential with nonlinear (Butler-Volmer) boundary conditions with the use of finite difference method. The numerical modeling of galvanic corrosion in which the geometry consists of various array forms has been performed by Morris and Smyrl [61–63] in this laboratory. Either regular or random arrays of disks in the cathodic plane were used for the simulation of a heterogeneous surface. Most treatments of the regular array use the symmetry element derived from symmetrical geometry of the system. For mathematical simplicity, a particular hexagonal symmetry element can be approximated by a circular geometry, thus eliminating any angular dependence. For random arrays, the arrays simulated using a Voroni tessellation of the plane into random polygons as shown in Fig. 3 were used for the disk-cathodic plane geometry. The Voroni tessellation has proven to be useful for modelling the transport and mechanical properties of disordered or composite media. The geometrical properties of the Voroni tessellation and algorithms for generating the tessellation have been described by Winterfeld [64]. The model established by Morris and Smyrl included the Laplace equation for potential distribution with nonlinear boundary conditions, and it was solved by a finite element method. The potential distribution of the system was obtained from numerical simulation of a regular array of disks over a cathodic plane. The disks were of alternating sizes (disks with two different diameters) distributed on

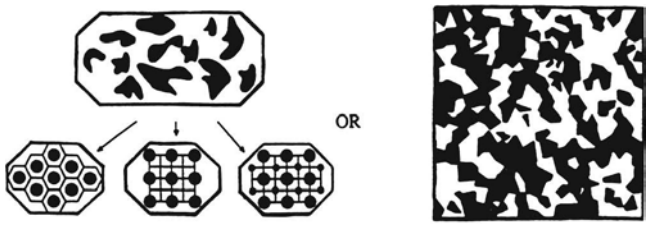

Fig. 3—Simulations of galvanic interactions in multilayer arrays have been carried out with regular patterns or with (more realistic) Voronoi tessellation representations.

the surrounding plane. The models for the tertiary current distribution, which includes both potential distribution and mass conservation with use of a geometry of the random array, are in progress in our laboratory.

Since the total anodic current must be equal to the total cathodic current, the area ratio between anodic and cathodic components of the total area is an important parameter in galvanic corrosion. If the currents to each area were uniform, the area ratio is the *only* parameter that would affect the galvanic interaction for a particular combination of metals. On the other hand, Smyrl and Newman [21] found that ohmic effects in the electrolyte may cause a nonuniform galvanic current distribution on the component areas, and this leads to the conclusion that under such conditions some parts of the cathodic area are not important in determining the total galvanic current. The effect is even more pronounced under circumstances where the electrolyte phase is very thin, that is, galvanic current from cathode to anode flows only near where they join, and more remote areas of each are relatively unaffected by the galvanic coupling. It has recently been found that the *active perimeter* measure of the interactions is more relevant than the area ratio, and the former may be used to correlate the behavior of several geometries [61–63]. The nonuniform current distribution is also obtained if the cathodic surrounding plane is highly resistive but electroactive. For example, resistive sputtered carbon films would cause the cathodic galvanic current to flow only to areas at the periphery of holes and defects [65], and the total area would not be important in determining the galvanic current. However, smaller holes would increase the galvanic current at a constant area ratio because the active perimeter would increase.

In summary, investigations in bulk solution provide a basis on which to begin to analyze atmospheric corrosion behavior. As the electrolyte phase decreases in thickness, ohmic and diffusion effects become more dominant and galvanic coupling is strongly affected. The more remote areas will show the behavior expected for uniform exposure to an aggressive environment. Effects of local composition and local physical geometry then will become more dominant. Behavior in the local areas would be expected to be very similar to the behavior in bulk electrolyte at the same composition conditions. Further general comparisons must be developed as further research is conducted.

COATINGS AND OVERLAYERS FOR CORROSION CONTROL

In the past 15 to 20 years, an explosion of interest in surface modification techniques has mostly involved the deposition

of thin films, the application of coatings, and the formation of surface alloys. The development of many of the techniques has been driven by the need for the semiconductor electronics industry to create improved processing procedures. As a spin off of the advancing technology, other fields, such as corrosion protection, have benefited from the new processes. A recent panel report [66] has summarized the general surface modification techniques that are used. The techniques are divided into three broad categories:

- Low-energy inorganic coating techniques. For the most part these are mature technologies that have been used for many years.
- Polymer coatings include traditional paints, thermoplastics, poly(vinyl chlorides), epoxies, urethanes, and poly (methylmethacrylate).
- Techniques involving the use of energetic ions. The techniques have developed rapidly in the last 10 to 15 years; several have neither reached maturity nor found use for corrosion protection. Only those designated as low cost and scalable for widespread use are viable for corrosion protection, except in critical applications. In addition, most techniques that require vacuum processing are too costly for most applications.

Inorganic sol-gel films are formed from a sol through continuous stages of increasing concentration of a solid precursor. Typically, the sol is a solution of polymeric species or a suspension of "oligomers" including particles in the colloidal size range. During deposition through states of increasing solids concentration, the sol might gel, but the gel state is often a fleeting transient that quickly empties of liquid. Nevertheless, the structures formed during this stage have varying amounts of porosity and influence the structure of the final film. This processing offers good control of composition and homogeneity at low temperatures. It is not directional nor equipment intensive. Complex shapes of arbitrary size can be coated with good uniformity. The cost of high-purity liquid precursors may be high, but for thin-film applications the materials cost would be acceptable.

Films deposited using energetic deposition techniques are dense, highly adherent, have few pinholes, and can be laid down at low temperatures. They are attractive for corrosion protection. Ion-beam-assisted deposition and ion implantation have the best adhesion properties, while RF sputtering has the best throwing power. Three important factors affecting the performance of films are porosity, adhesion, and stress. Although there are compressive stresses, in ion-implanted surfaces, for example, delamination by buckling is practically unknown. Effective porosity in the treated layer could exist due to shadowing of the surface from the beam by contaminating particles. The problem has not been observed, but the exact reason is not known. With the exception of ion implantation [67], only a few studies on corrosion have been done on films deposited using energetic deposition methods. Ion-beam-assisted deposition coatings are adherent and more ductile than bulk materials due to the microcrystalline or amorphous structures. The adhesion is better for the films deposited by energetic beam techniques as compared to films derived from physical vapor deposition. More details may be found in the cited report [66] or in the original literature.

Polymeric materials are widely used as protective coatings because they are transport barriers which limit access of reactive species (i.e., water, oxygen, ions) to the substrate surface. Leidheiser and Granata [68] have discussed the roles that each of these species may play in degradation processes on metal surfaces, and, in particular, the role of ion transport through bulk films and "ion channels" in films. Several techniques are discussed in this paper for characterizing ion transport: d-c measurements, electrochemical impedance analysis, under-the-coating sensing, and radio tracer measurements. Characteristic d-c resistances of 10^{11} ohm-cm^2 are observed for films without continuous aqueous pathways through the coating, as first described by Asbeck and Van Loo [69]. The resistance drops to the order of 10^8 ohm-cm^2 if continuous aqueous pathways exist where such pathways have high rates of transport. It is also clear that films and coatings are heterogeneous and the aqueous pathways are surrounded by regions of lower transport rates. The resistance of films may also decrease with time as the ion channels or pathways equilibrate with an external aqueous environment.

For films with high resistance and no ion channels, the impedance of the film is dominated by its geometric capacitance. For films of lower resistance, the low-frequency impedance is dominated by the sum of the resistance of the film and the resistance of the electrolyte. If corrosion proceeds under the coating because of ingress of the aqueous environment, the low-frequency impedance decreases in value. It has been argued that there is a strong correlation between the sites for corrosion under the film and the intersection of the ion channels with the underlying surface, but it has been difficult to confirm the correlation with direct observations.

The nature of the easy pathways for transport appears to be related to several factors. One of the factors is the presence of pigment and filler particles, which could facilitate the formation of aqueous pathways adjacent to the pigment or filler and would be influenced by the interaction of the particles with the polymer matrix [68]. The channels could also form by coalescence of voids or pores in the polymer matrix, and this would be influenced by the formation processes of the films. Aggregation of solvent in the film could be influenced by the prior history of the film, by the presence of impurities, and by retained solvent.

The presence of channels has been demonstrated to be a function of the glass transition temperature (T_g) of films as well. That is, below T_g, the polymer will be brittle unless a secondary, low-temperature relaxation exists, and this will favor the formation of microcracks and defects. Above T_g, the film will be more flexible and less susceptible to formation of fracture channels. Armstrong et al. [70] have investigated the influence of T_g on ion transport and permeability in chlorinated rubber films.

Pigment and filler particles can have a beneficial influence because of the reduced transport of water, oxygen, and ions. The effect will depend on the pigment volume fraction, the chemical composition, the geometry, and the dispersion as noted by Burns and Bradley [71]. Equilibrium water uptake may cause plasticization and subsequent depression of T_g, as well as swelling, which counteracts the effects of reduced transport rate caused by the solid particles [72]. Pigments that have oxidizing character can induce passivation of the underlying metal, as observed for chromate or vana-date additives [73]. Other pigments may inhibit the cathodic reaction and thus suppress corrosion as well [74].

De-adhesion of organic coatings is responsible for enhanced corrosion rates on one hand and is the result of corrosion on the other hand. Leidheiser [75] has discussed de-adhesion processes which include: loss of adhesion when wet, cathodic delamination, cathodic blistering, swelling of the polymer, gas blistering by corrosion, osmotic blistering, thermal cycling, and anodic undermining. With few exceptions, the loss of adhesion processes requires that reactive species such as water, oxygen, and ions penetrate through the coating. Bonds of the coating with the surface of a steel substrate may be attacked by high pH conditions, which are the result of corrosion reactions or imposed cathodic protection conditions. In either case, OH" ions are particularly aggressive and cause disbonding on steel. In a recent investigation by Stratman [76], disbonding was followed by monitoring the surface potential of a polymer-coated steel surface with a scanning Kelvin probe technique.

A recent international meeting [1] reviewed the unsolved problems of corrosion protection By organic coatings, described the current understanding of the technology, and outlined some focus for further progress. In addition to the principles of barrier layer transport that have been described above, there was discussion on the effects of (1) pre-treatment of surfaces, (2) the contribution made by surface inhomogeneities of the substrate, (3) the critical size of a water phase which may be responsible for corrosive attack, (4) stress in the film and stress in the substrate, and (5) incorporation of corrosion inhibitors in protective films. Funke [77] later summarized the continuing uncertainties that exist in studying corrosion protection properties of organic coatings. Some scatter of behavior is caused by the age and history of the coating—fresh coatings are more susceptible to swelling and changes in composition. Disbonding may initiate at defects, but it may also occur in the absence of holidays or defects. The water that is associated with disbonding could be transported along the surface and not by permeation through the film. Ions may also move along the interface. All these considerations have considerable implications for electrochemical characterization techniques. A review of various types of organic coatings and their applications in various service conditions is provided by Tator [78].

SUMMARY

The atmospheric corrosion of metals is one of the most important single problems facing corrosion science and technology. From small nanostructures to large buildings and bridges, coating techniques are being developed to moderate the rate of degradation with some success. The use of low-cost coatings continues to increase as the coatings are made more impermeable and more adherent to the protected substrate. Higher-cost films applied by high-energy methods are finding wider use in critical applications where conventional coatings are inadequate. In all systems where protection is necessary, the early detection of corrosion is desirable in order to plan replacement and maintenance measures and to avoid catastrophic failures. Detection of the presence of corrosion can be accomplished in two ways: detection of the agent that causes corrosion or detection of the results of the corrosion process either on the material of interest or on a specimen of the material. Sensors and monitors are receiving greater attention in accelerated life testing of materials, and eventually they will be developed more widely for operating systems or in portable monitoring systems. The savings to industry and the public at large would be in the billions of dollars if the onset of failure processes could be detected prior to their culmination in a catastrophic event [79].

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Types of Metal Corrosion and Means of Corrosion Protective by Overlayers

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INTRODUCTION

THIS CHAPTER WILL PROVIDE A GENERAL OVERview of the cause of metal corrosion, and its prevention by the use of protective coatings, or overlayers.

It must be understood, however, that a thorough discussion of corrosion and corrosion mechanisms can extend far beyond the summaries provided in this chapter. In fact, there are numerous books written solely on corrosion, manifestation of the different types of corrosions, and the reasons why such corrosion occurs.

Similarly, the use of protective overlayers over a metal to prevent corrosion is likewise a quite varied and extensive topic. The literal interpretation of the word "overlayers," as used herein, means anything applied, or overlaid on a metal to prevent, retard, or reduce corrosion. This would include monomolecular layers of gasses, oxides, or other materials that may slow or stop the corrosion process under very specific conditions. Moreover, it includes all of the possible metals and organics that can be applied to a surface. Some of the more common overlayers will be discussed herein.

Accordingly then, the discussion regarding metal corrosion consists of the following sections:

- Definitions
- Extractive metallurgy in reverse
- Electrochemical corrosion
- Forms of corrosion
- Uniform corrosion
- Galvanic corrosion
  - Sacrificial anode cathodic protection
  - Impressed current cathodic protection
- Crevice corrosion
- Pitting corrosion
  - Microbiologically influenced corrosion
- Intergranular corrosion
- Selective leaching
- Erosion corrosion
  - Cavitation
  - Fretting
- Stress corrosion
- Hydrogen damage

The sections on corrosion protective overlayers consist of:

- Conversion coatings
  - Phosphate
  - Chromate
  - Chromate free
- Hot dip galvanizing
  - Batch
  - Continuous
- Cementitious linings
- Glass and porcelain enamels
- Electroplating
- Thermal spray
- Rubber linings
- Paints, coatings, and linings

DEFINITION OF CORROSION

Corrosion, as defined by NACE, the Corrosion Society, is "the destruction of a substance 'usually a metal' or its properties because of a reaction with its environment." This definition does not make use of the terms chemical or electrochemical because such terms would define corrosion only as it relates to metals and would not allow its application to many other materials which disintegrate due to environmental exposure [1]. The American Society of Materials (ASM) defines corrosion as a "chemical or electrochemical reaction between a material and its environment that provides a deterioration (change) of the material and its properties" [2]. ASTM defines corrosion with the same definition. Skorchelletti (translated from Russian) [3] states "the spontaneous oxidation of metals, which is detrimental in industrial practice (reducing the service life of articles) is termed "corrosion" (from the Latin "corrodere," which means to eat away.

If we consider corrosion as a deterioration of a material under the influence of an environment, the discussion of corrosion mechanisms and the effects of such deterioration are many and varied. If, however, the definition is restricted to corrosion of metals, the subject becomes more manageable and limited in scope. The mechanisms of metallic corrosion are relatively well understood.

The fundamentals of corrosion, as they relate to metallic corrosion, can be summarized in the following sections.

EXTRACTIVE METALLURGY IN REVERSE

Extractive metallurgy consist of mining metallic bearing ores from the earth, such as "iron" ore, "bauxite" (aluminum ore), and the ores of other metals, such as nickel, tin, copper, etc. These ores consist of the metal in combination with oxygen and other elements. They are relatively stable

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TABLE 1—Metals in order of energy required for conversion from their ores. (Courtesy of NACE Publication.)

Common Metals	Energy Required for Conversion
Potassium	Most
Magnesium	
Beryllium	
Aluminum	
Zinc	
Chromium	
Iron	
Nickel	
Tin	
Copper	
Silver	
Platinum	
Gold	Least

[SOURCE: Corrosion Basics—An Introduction, LaQue, F. L, Chapter 2, Basics of Corrosion, NACE, Houston, TX, p. 23, 1984.]

and nonreactive in the ground, as the metal in the ore has already oxidized and reacted during the passage of time until no further reactions occur. After mining, and during refining purification, large amounts of energy, usually in the form of chemical dissolution, electrolytic separation, and smelting heat, are used to convert the ore into its pure, or alloyed metal. The energy used during the conversion process is indicative of the reactivity of the metal in the environment. The more energy used to extract the metal from its ore, the greater the propensity of the purified metal to react with the environment and return to its former oxidized ore-like state.

Some metals exist in nature in a relatively pure metallic form and need little if any energy to extract them from nature. Gold, for example, in nature is found in pure nugget form, and after shaping (into jewelry, a tooth filling, or other product), it can be placed into a variety of aggressive environments and show little, if any, corrosion or oxidation. Similarly, platinum, silver, and copper are relatively pure metals that require little refining energy compared to other metals such as iron or steel. Table 1 entitled "Metals in Order of Energy Required for Conversion from Their Ores" [4], illustrates the amount of energy required for conversion of the ore to the pure metal.

If the refining of metal from a metallic ore requires the input of energy, metallic corrosion can be described as the reverse of that process—the metal's release of energy as it naturally oxidizes and reverts to its ore-like status. Using iron as an example, the process can be illustrated, as in Fig. 1.

However, the corrosion of some metals is not necessarily bad. In fact some oxidation reactions are beneficial to a metal. For example, aluminum will quickly oxidize (corrode) forming a layer of aluminum oxide (Al_2O_3) on the aluminum surface. The aluminum oxide that is formed is a thin, impervious, tightly adherent layer that seals and protects the underlying aluminum from further oxidation and environmental reaction. Only if the oxide layer is broken down in aggressive environments will further reaction of the aluminum occur. Anodizing (the imposition of an electrical current on aluminum or other light metals in a bath to form an oxide layer) is used to provide a thicker, more

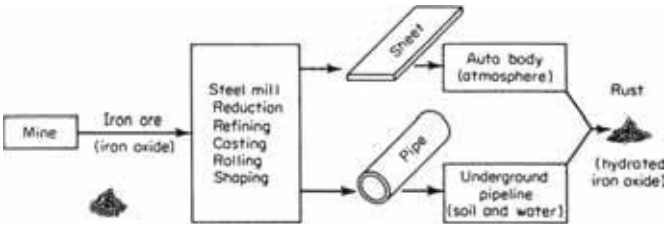


Fig. 1—Metallurgy in reverse. (Courtesy of McGraw-Hill.)

protective oxide layer coating on the metal surface than that which results from atmospheric oxidation.

Copper is another example of a metal that forms a protective oxide layer—in this case, the oxide is a characteristic color that forms as the copper oxidizes by weathering to form a patina. The main constituent of patina is a mixture of basic copper carbonates, sulfates, and chlorides. In rural areas, or areas where there are no chemical contaminates, the patina is predominately basic copper carbonate (green). In industrial areas basic copper sulfate (blue) predominates. In coastal areas where chlorides are present, copper chlorides (brownish-yellow) prevail. Patina color variations from greenish to blue-gray occur, depending on differences in chemical composition. Regardless of color, the patina-oxide surface layer slows or prevents further reaction of the copper metal.

Alloying constituents of stainless steel also enable the formation of a tightly adherent oxide layer that protects the underlying steel from further corrosion. The numerous varieties of stainless steel that exist are due to the variations of metal alloy constituents (carbon, manganese, copper, chromium, nickel, and others) that comprise the oxide layer, and composition of the alloy steel. Conversely, the oxidation of carbon steel, the common low-alloy steel most common for use in structural steel, automobiles, pipelines, and for most industrial and commercial applications, forms a brown or black oxide (rust) that is porous and nonadherent. The rust layer from carbon steel is not protective, and does not prevent further corrosion of the underlying ferrous metal as a result of atmospheric exposure. Progressive oxidative deterioration occurs in a weathering or chemical environment resulting in pitting, general corrosion, and deterioration of the steel substrate.

ELECTROCHEMICAL CORROSION

Electrochemistry involves an electric current in conjunction with a chemical reaction. Electrochemical corrosion will occur when four required elements are present: (1) anode, (2) cathode, (3) metallic pathway connecting the anode and cathode, and (4) electrolyte. Most metals already have three of the four required elements: anode, cathode, and metallic pathway. The anode and cathode form from the metal and this process is discussed subsequently. The metallic pathway is present in all metals as they are ready conductors of electrons. Only the electrolyte is missing. Once an electrolyte is present, corrosion will proceed. An electrolyte is a liquid that contains ions or "charged particles." Most electrolytes consist of water containing dissolved inorganic salts. Inorganic salts, in water solution dissociate into their respective ions (for example sodium chloride dissociates into sodium cations and chloride anions). These electrically charged species provide an excellent pathway for

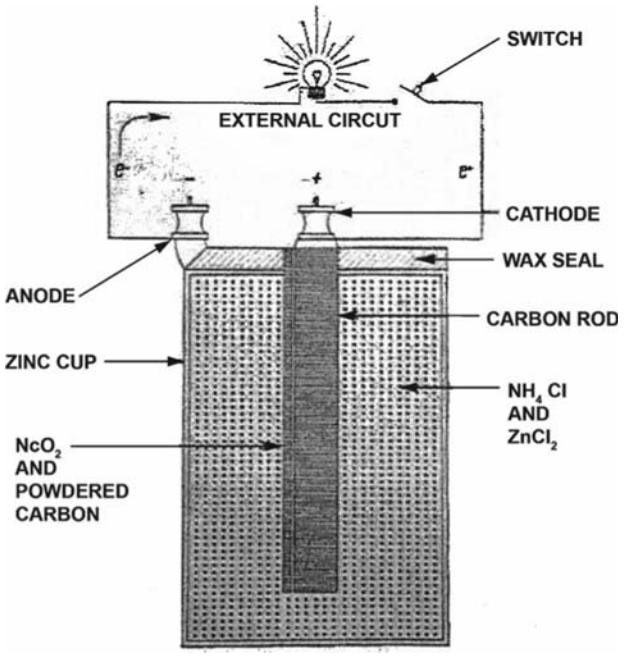
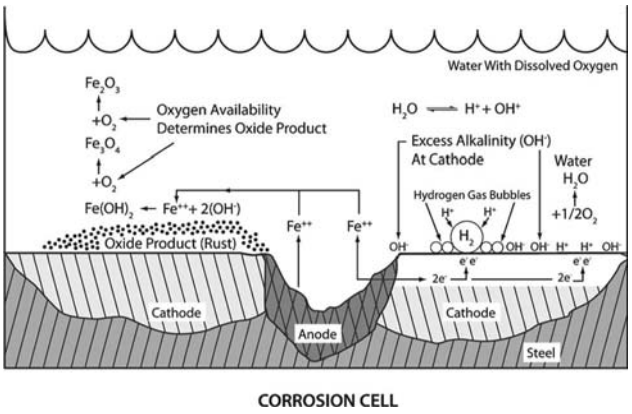


Fig. 2—Dry cell battery. (Courtesy of KTA-Tator, Inc.)

the transmission of electric currents generated during the corrosion process. Almost all water, including that in the oceans, rivers, and lakes contains dissolved mineral salts which dissociate. Rainwater, while relatively pure, forms around a small dust mote, or other particulate matter, and leaches ionic material from that particle. Furthermore, freshly condensed rainwater, which initially is "pure" water, will react with carbon dioxide from the air to form weak carbonic acid [5]. This weak acid dissociates into the hydrogen ion (H^+) and carbonate (CO_3^{-2}) ions. Pollutants in the air such as nitrogen and sulfur oxides will absorb in water, and will result in further electrolytic dissociation. Thus, when a metal is wet with water, or most chemicals, it is virtually always wetted with an electrolyte.

A common dry cell battery shown in Fig. 2 provides a good illustration of how the four elements of a corrosion cell work together to produce a beneficial form of corrosion to generate an electric current and provide power [6]. The battery is essentially a corrosion cell. The anode, and its counterpart, the cathode, are the positive and negative terminals of the battery, respectively. During the electrochemical reaction process, electrical current (or electrons) flows from the anode to the cathode via the metallic pathway or connection (see external circuit). The electrolyte carries ions from the cathode to the anode to complete the electrical circuit. The anode (negative terminal) decays during this process and generates the electron flow, while the cathode (positive terminal) remains intact and is not deteriorated. The only difference between a corrosion cell and a manufactured dry cell battery is that the battery reaction process is designed to produce an electrical current for a productive use. When the anode is depleted in a manufactured battery, the reaction will stop and the battery will "die" since it cannot produce more energy. The battery is replaced with a new one, and electric current is again generated.

In a corrosion cell, the anode is often a material that cannot be replaced readily. Corrosion of an automobile



CORROSION CELL

Fig. 3—Corrosion cell. (Courtesy of KTA-Tator, Inc.)

means deterioration of the metal body of the vehicle; structural steel rusting is deterioration of the structural member; tanks, pipelines, ships, offshore platforms, building steel and other structures that corrode cannot be as easily replaced as a dry cell battery!

An illustration of a corrosion cell is shown above in Fig. 3 [7].

The corrosion cell also consists of anode and cathode coupled by a metallic pathway in an electrolyte. During the corrosion process, the anode deteriorates by going into ionic solution.

The anodic reaction, in every case consists of the metal going into ionic solution as follows: $M \rightarrow M^+ + e^-$ where M is a metal, M^+ is the metal in ionic form, and e is the number of electrons liberated by the metal going into ionic solution. For example, the ionic reaction for steel is $Fe \rightarrow Fe^{+2} + 2e^-$ and that for aluminum is $Al \rightarrow Al^{+3} + 3e^-$.

The cathodic reaction, however, consists essentially of the neutralization of the electrons that are created as the metal goes into ionic solution. These electrons can be neutralized through one of three reactions, depending upon the cathodic environment:

Alkaline, neutral, and near-neutral chemical environments: $2H_2O + O_2 + 4e^- \rightarrow 4OH^-$

Acidic, with oxygen: $H^+ + e^- \rightarrow H$, then $2H + \frac{1}{2}O_2 \rightarrow H_2O$

Highly acidic: $2H^+ + 2e^- \rightarrow H_2$

The electron movement in a corrosion cell (the chemical concept) is defined as moving from the anode through the metallic pathway to the cathode. At the cathode, electrons are neutralized by chemicals in the electrolyte. Conversely, current flow, used in the electrical industry and for cathodic protection (the electrical concept) is opposite, and by definition, electrons comprising the electric current flow from the anode through the electrolyte to the cathode.

Fig. 4 "Chemical Concept of Electron Flow" and Fig. 5 "Electrical Concept of Current Flow" [8] illustrate the differences between the electron and current flow in the chemical and electrical concepts.

While the illustrations of the dry cell battery (electrical concept) and corrosion cell (chemical concept), as shown above, depict the anode and cathode as separate entities, in practice, anodes and cathodes are not isolated entities. For example, all metals consist of crystals, or "grains" that precipitate when molten metal is cooled from a hot melt. Grain boundaries form between grains, and are anodic

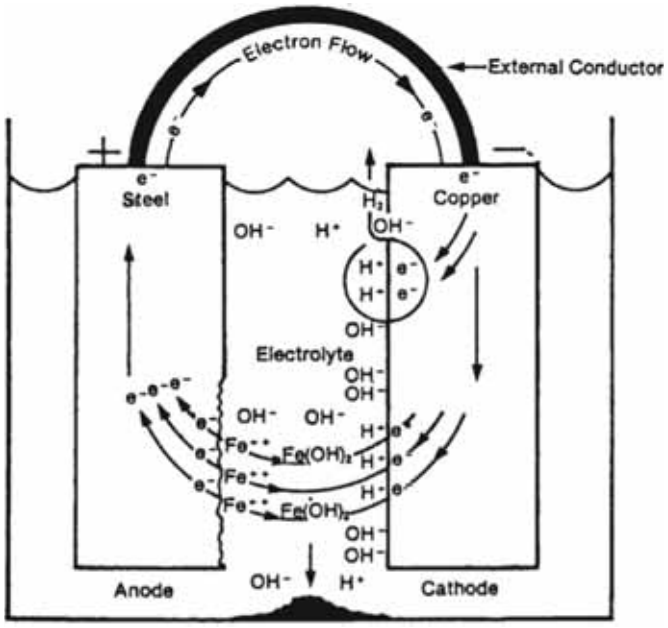


Fig. 4—Chemical concept of electron flow. (Courtesy of NACE International.)

relative to the cathodic grain. Areas of stress concentration, in a formed metal, are anodic to unstressed areas. Where temperature differentials exist, hot areas are anodic relative to cool areas. A scratch, nick, or abraded area on a metal, or mechanically worked area is anodic to adjacent unscratched or unworked areas. Oxygen concentration differences can also result in the formation of anodes and cathodes (the lesser oxygen concentration generally becomes anodic, relative to an adjacent area of greater oxygen concentration). An example of this is corrosion at the waterline of a steel piling or on the wall of a dam gate. Corrosion within a crevice occurs as an anode develops within the sheltered area within the crevice relative to the more exposed areas, which become cathodic.

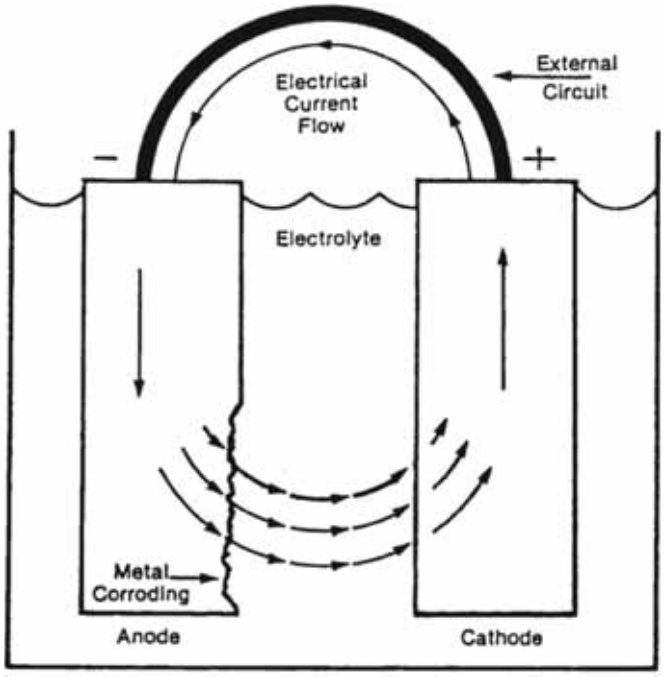


Fig. 5—Chemical concept of electron flow. (Courtesy of NACE International.)

Accordingly, to a greater or lesser extent, all metals will develop anodic and cathodic areas, and will have a comparative potential to corrode. Moreover, as corrosion proceeds and pits and crevices develop in a metal substrate, the anodic and cathodic areas may switch, and the anodes will become cathodes, and vice versa.

A metal in contact with another metal may also become an anode with the other metal becoming the cathode. The tendency of a metal to become an anode or cathode in combination with other metals in a given immersion environment is its corrosion potential. The comparative corrosion potential of a series of metals can be tabulated as the electromotive force (EMF) series. EMF corrosion potentials will vary from environment to environment, and the standard EMF series is that for sea water. Hydrogen is used as an arbitrary reference element, with elements above hydrogen more reactive, while those listed below hydrogen are increasing, inert with a lesser tendency to ionize or go into ionic solution. The EMF series for metals and solutions of their own salts is presented in Table 2 [9], while the EMF series in sea water is shown in Table 3 [10]. If two metals in the galvanic series are coupled, the greater the potential difference between the two metals, the greater the driving force for the more negative metal (anode) to corrode. Note the similarities between the EMF and galvanic series tables with that of the order of metals in order of energy required for conversion from their ores (see Table 1).

Thus, all metals, when wetted, either by immersion, precipitation, condensation, or even high relative humidity (generally 50 % RH or more) have an inherent ability to corrode, as the anode, cathode, metallic pathway, and electrolyte are all present.

Although, not a prerequisite for the initiation and early commencement of corrosion, oxygen is critical, as without it, the corrosion reaction will slow or stop. Oxygen is a depolarizer in that it removes hydrogen from the cathode and allows additional electrons to be neutralized, enabling the process to proceed. If oxygen is not present, the hydrogen accumulation at the cathode may result in a hydrogen surface film, essentially isolating the electrons migrating to the cathode from the electrolyte and slowing or stopping their electron neutralization process.

FORMS OF CORROSION

The appearance or a manifestation of corrosion has been categorized in various schemes by a number of authors. Categorization by environmental condition (immersion, atmospheric, hot, wet, dry, etc.) is one means of grouping corrosion. Covino and Cramer [11] sub-categorize "forms of corrosion" into six subsections. Four of those forms, "uniform corrosion," "localized corrosion," "metallurgically influenced corrosion," and "microbiologically influenced corrosion" fit under the classification of corrosion that is not influenced by any outside process. The remaining two, "mechanically assisted degradation" and "environmentally induced cracking" address corrosion as influenced by another process (Table 4).

Fontana [12] describes eight forms of corrosion that can be identified by visual observation, in most cases with

TABLE 2—Electromotive force series

Electrode Reaction	Standard Electrode Potential E (Vs), 25°C
$K = K^{+} + e^{-}$	–2.922
$Ca = Ca^{++} + 2e^{-}$	–2.87
$Na = Na^{+} + e^{-}$	–2.712
$Mg = Mg^{++} + 2e^{-}$	–2.34
$Be = Be^{++} + 2e^{-}$	–1.70
$Al = Al^{+++} + 3e^{-}$	–1.67
$Mn = Mn^{++} + 2e^{-}$	–1.05
$Zn = Zn^{++} + 2e^{-}$	–0.762
$Cr = Cr^{+++} + 3e^{-}$	–0.71
$Ga = Ga^{+++} + 3e^{-}$	–0.52
$Fe = Fe^{++} + 2e^{-}$	–0.440
$Cd = Cd^{++} + 2e^{-}$	–0.402
$In = In^{+++} + 3e^{-}$	–0.340
$Tl = Tl^{+} + e^{-}$	–0.336
$Co = Co^{++} + 2e^{-}$	–0.277
$Ni = Ni^{++} + 2e^{-}$	–0.250
$Sn = Sn^{++} + 2e^{-}$	–0.136
$Pb = Pb^{++} + 2e^{-}$	–0.126
$H = 2H^{+} + 2e^{-}$	0.000
$Cu = Cu^{++} + 2e^{-}$	0.345
$Cu = Cu^{+} + e–$	0.522
$2Hg = Hg2^{+} + 2e^{-}$	0.799
$Ag = Ag^{+} + e^{-}$	0.800
$Pd = Pd^{++} + 2e^{-}$	0.83
$Hg = Hg^{++} + 2e^{-}$	0.854
$Pt = Pt^{++} + 2e–$	ca1.2
$Au = Au^{+++} + 3e^{-}$	1.42
$Au = Au^{+} + e^{-}$	1.68

[SOURCE: Encyclopedia of Chemistry, Clark and Hawley, Electrochemistry, Reinhold Publishing Co., p. 338, 1957.]

TABLE 3—Galvanic series in seawater flowing at 13 FTPS (temperature, approx. 25°C)

Material	Steady-StateElectrode Potential, V (Saturated Calomel Half-Cell)
Zinc	–1.03
Aluminum 3003-(H)	–0.79
Aluminum 6061-(T)	–0.76
Cast Iron	–0.61
Carbon Steel	–0.61
Stainless Steel, Type 430, active	–0.57
Stainless Steel, Type 304, active	–0.53
Stainless Steel, Type 410, active	–0.52
Naval Rolled Brass	–0.40
Red Brass	–0.33
Bronze, Composition G	–0.31
Admiralty Brass	–0.29
90Cu 10Ni, 0.82Fe	–0.28
70Cu30Ni, 0.47Fe	–0.25
Stainless Steel, Type 430, passive	–0.22
Bronze, Composition M	–0.23
Nickel	–0.20
Stainless Steel, Type 410, passive	–0.15
Titanium[a]	–0.15
Silver	–0.13
Titanium[b]	–0.10
Hastelloy C	–0.08
Monel-400	–0.08
Stainless Steel, Type 304, passive	–0.08
Stainless Steel, Type 316, passive	–0.05
Zirconium[c]	–0.04
Platinum[c]	+0.15

[a]Prepared by power-metallurgy techniques, i.e., sheath compacted powder, hot rolled, sheath removed, cold rolled in air.
[b]Prepared by iodide process.
[c]From other sources.
[SOURCE: Fink, F. W., et al., the Corrosion of Metals in Marine Environment, Battelle Memorial Institute, DMIC Report 254, Distributed by N.T.I.S. AD-712 585-S, pp. 7, 13 (1970), with permission from NACE.]

the naked eye, but sometimes magnification is necessary. The listing is arbitrary, and the eight forms are more or less interrelated, but they cover practically all corrosion failures and problems. The eight forms of corrosion are described in summary below, with some modifications by the writers.

The eight forms are:

1. Uniform corrosion;
2. Galvanic corrosion;
3. Crevice corrosion;
4. Pitting;
5. Intergranular corrosion;
6. Selective leaching;
7. Erosion corrosion;
8. Stress corrosion.

Hydrogen damage—Fontana discusses this last form but does not consider it a corrosion phenomena. Fig. 6 depicts each of the corrosion forms itemized above.

UNIFORM CORROSION

Uniform corrosion is the most common form of corrosion and it is characterized by a chemical or electrochemical reaction that proceeds relatively uniformly over a large area. The metal is relatively uniformly attacked, and the rateofdeterioration of relatively uniform over all areas where corrosion occurs.

TABLE 4—Forms of corrosion—adapted from Covino and Cramer
1. Uniform Corrosion
a. Aqueous corrosion
b. Atmospheric corrosion
c. Galvanic corrosion
2. Localized Corrosion
a. Pitting corrosion
b. Crevice corrosion
c. Filiform corrosion
3. Metallurgically Influenced Corrosion
a. Stainless steels
i. Austenitic
ii. Ferritic
iii. Duplex
iv. High Performance
b. Nickel Alloys
c. Aluminum (1xxx through 7xxx series alloys)
d. Weldment Corrosion
i. Steel
ii. Stainless steel
iii. Non-ferrous alloys
4. Mechanically Assisted Degradation
a. Erosion
b. Fretting corrosion
c. Fretting fatigue
d. Cavitation erosion
e. Corrosion fatigue
5. Environmentally Induced Cracking
a. Stress corrosion cracking
b. Hydrogen damage
c. Liquid metal embrittlement
d. Solid metal embrittlement
6. Microbiologically Influenced Corrosion

GALVANIC CORROSION

This type of corrosion occurs when two metals are in contact, and there is a potential difference between the metals when they are immersed or in a wet environment. The less resistant metal becomes anodic and the more resistant metal becomes cathodic (see Table 3). The anodic metal goes into ionic solution as previously described.

In a service environment where two metals are in contact in a corrosive environment, galvanic corrosion can be readily detected, as one of the metals (the anode) will be aggressively attacked, with the most extensive deterioration closest to the other metal (the cathode). If possible, it is best to avoid dissimilar metal contact in immersion or wet environments unless the consequences of galvanic corrosion are known and anticipated. However, there are many instances of inadvertent contact between dissimilar metals in tanks, pipelines, heat exchangers, and other fabricated items. To prevent unwanted corrosion, sometimes the dissimilar metals are both painted in an attempt to stop galvanic attack. However, this usually makes the situation even worse, because if any defect develops in the coating, the galvanic attack will be concentrated at the small defect in the coating on the anodic metal. This may lead to rapid

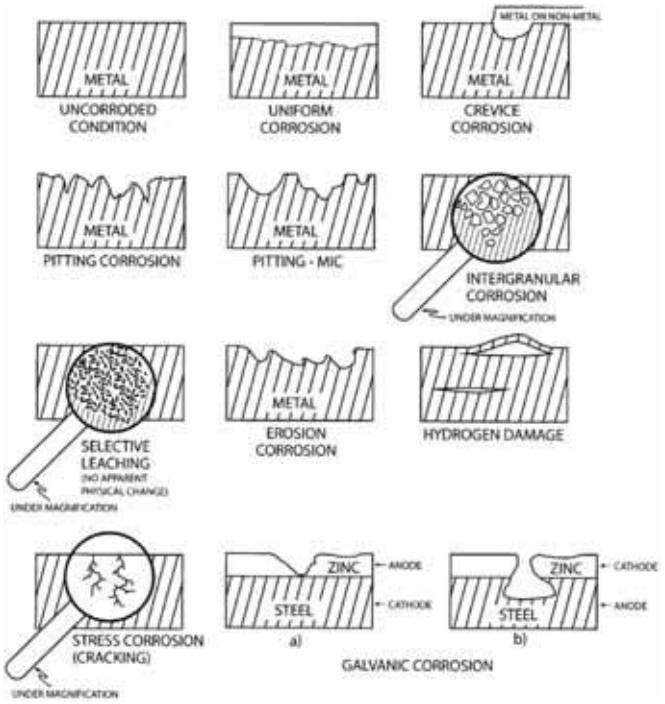


Fig. 6—Depiction of forms of corrosion.

pitting and perforation. Painting, however, may work if only the cathode, or more resistant metal, is painted. This reduces the cathodic area and with a small defect in the coating on the cathode the corrosion current will be distributed over the much larger unpainted anode. Accordingly, pitting does not occur due to the small cathode/large anode relationship.

Cathodic protection is the beneficial use of galvanic corrosion. There are two types of cathodic protection: (1) use of the sacrificial anode and (2) use of impressed current.

Both types of cathodic protection utilize an anode that is designed to deteriorate and protect the cathode, which is, by design, the metal that is to be protected.

Cathodic Protection by Sacrificial Anode

Zinc, in the form of a zinc-rich coating, or as a galvanize layer on steel, corrodes preferentially as the anode, and protects the steel, which becomes the cathode in the galvanic couple. The steel is usually a pipeline, tank, ship hull, or another steel item in immersion or in the soil. For pipelines, tank interiors, and ship hull exteriors, zinc, magnesium, or aluminum alloy anodes in the form of blocks or ribbons of metal, are attached or connected to the steel to be protected.

Irrespective of whether the anode is a piece of metal or a coating, when it becomes exhausted due to sacrificial galvanic protection, it is replaced by either a new metal anode or a new sacrificial coating system. The costs of replacement of the sacrificial anode are designed to be substantially less than the cost of replacement of the structure being protected. Fig. 7 [13] illustrates a pipeline being protected by a sacrificial anode system.

Impressed Current Cathodic Protection

In this means of corrosion protection, the normal corrosion current is reversed beneficially to make the structure being protected the cathode and the anode an inert material.

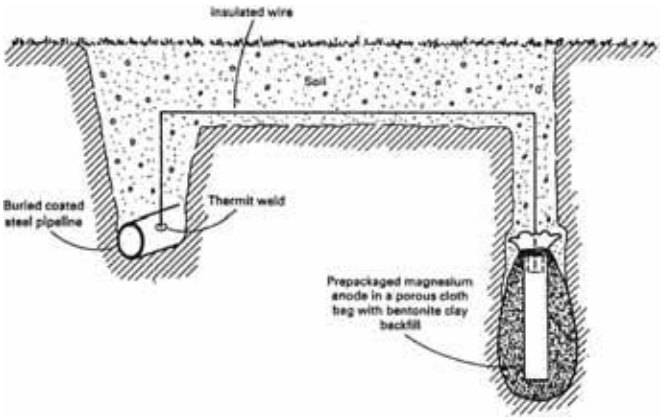


Fig. 7—Cathodic protection of a buried pipeline using anodes. (Courtesy of ASM International.)

Usually, an ordinary AC current is rectified to direct current (DC) with the negative terminal of the DC supply connected to the structure being protected, and positive terminal to the inert anode. The choice of the inert anode depends upon the service environment and the associated current demand for protection. Commonly used inert anodes consist of high silicon cast iron, graphite, conductive polymers, lead alloys, precious metals (platinized titanium or tantalum), and mixed metal oxides, or ceramic oxides. Fig. 8 [14] depicts a pipeline being protected by an impressed current cathodic protection system.

Cathodic protection, using either a sacrificial anode or impressed current, is almost always done in conjunction with coating the object being protected. If the object being protected is uncoated, the current demand required to protect the entire surface would be quite high, and accordingly, the rate of consumption of the sacrificial anode, or the power demand for the impressed current protection system, would be quite high also. However, if the structure being protected is coated with an appropriate coating system, cathodic protection would be needed only at defects in the coating system, such as pinholes, scratches, impact, and other mechanical damage, and, as such defects usually make up only a very small percentage (generally much less than 1 %) of a coated structure's surface, the current demand and the anode consumption is proportionally reduced.

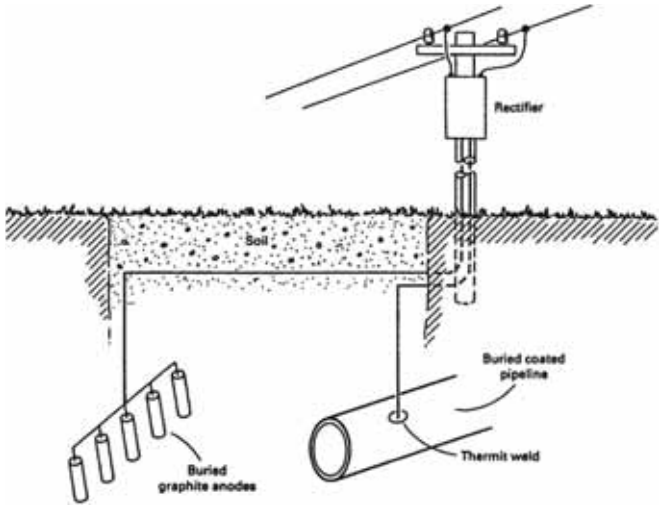


Fig. 8—Cathodic protection of a pipeline using impressed current. (Courtesy of ASM International.)

CREVICE CORROSION

Intensive, localized pitting can occur within crevices or other areas shielded by corrosion products, dirt, or other materials that enable the creation of a stagnant condition beneath the shield. This often occurs between metals and nonmetallic surfaces in contact. As with most forms of corrosion, the environment must be wet or highly humid, resulting in wetness. In general, the tighter the crevice, the more severe the crevice attack. Crevice attack exists principally on passive metals (stainless steel, nickel, titanium, and aluminum-based alloys). This is because there is a need for a large cathode (the passive surface of the metal) to support the high rate of anodic pitting activity within the shielded area.

Initially, crevice corrosion initiates as general corrosion over all surfaces of the metal. The corrosion reaction consists of oxidative dissolution of the metal, and reduction of oxygen to hydroxide ions as shown below:

$$\text{Oxidation:} \quad M \rightarrow M^{+} + e^{-}$$

$$\text{Reduction:} \quad O_2 + 2H_2O + 4e^{-} \rightarrow 4OH^{-}$$

After a short time, the oxygen within the crevice is depleted, and oxygen reduction ceases. However, the metallic oxidation process continues, building up an excess of positively charged metal cations. As these cations cannot be neutralized by oxygen reduction, they draw anions, often chlorides, a ubiquitous highly mobile anion, into the crevice. Chlorides are particularly aggressive compared to most other anions in breaking down protective oxide passivation and accelerating corrosion. This results in increased concentrations of metal chloride within the crevice. The metal chlorides hydrolyze in water, precipitating a metal hydroxide and forming hydrochloric acid, as shown below:

$$M^{+} + Cl + H_2O \rightarrow MOH + HCl$$

The metal hydroxide precipitation drives the metallic oxidation reaction, resulting in a rapidly accelerating, or autocatalytic corrosion process.

Filiform corrosion (a special type of crevice corrosion occurring beneath protective coatings or films) and pitting corrosion of metals are related phenomena.

PITTING CORROSION

Pitting is an aggressive, insidious, destructive form of corrosion that results in holes, or pits in a metal that is otherwise unattacked, or has only general corrosion. Pits are generally small in diameter, with a depth generally exceeding the pit diameter, but in some cases (notably microbiologically induced corrosion) the pits may be broad and bowl shaped in appearance. Pits generally grow downward in the direction of gravity. Pitting on vertical surfaces is less common, and on overhead surfaces (where the growth would be upward), is rare.

Pitting may occur within weeks, or may take years to form. Pits are hard to detect and measure because they are often hidden by general corrosion, and are filled with

corrosion product. The most common form of pitting failure is perforation. Structural strength of the member (plate, tube, pipe, etc.) is otherwise unaffected, except that the pitted item has a small hole in its cross-section.

The mechanism of pit growth is essentially identical to that for crevice corrosion—the pit bottom is anodic, and rapid metal dissolution into ions occurs there, while the sides of the pit are cathodic where oxygen reduction takes place. As metal ions build up in the bottom of the pit, the excess of positively charged ions attract chloride ions and form metal chlorides. The metal chlorides hydrolyze and precipitate, as illustrated previously under for crevice corrosion, driving more metallic dissolution, and accelerating pit growth. Most pitting is associated with chlorides, bromides and hypochlorites. The best means of preventing pitting are to use a metal alloy resistant to pitting in the environment of service, or to isolate the metal from the environment by a resistant overlayer.

Microbiologically Influenced Corrosion

Bacterial induced corrosion can cause pitting in immersion conditions. Sulfate reducing and oxidizing bacteria are responsible for corrosion in sewage piping, and many petrochemical environments (in tanks, and downhole) where sulfur compounds are present. Sulfates are ubiquitous in the environment, as sulfur comprises 0.06 % of the earth's crust. Sulfur is important in the building of plant and animal tissues. It is found in combination with many other elements, and is a constituent of coal and petroleum, and the cause of acid rain. Sulfates are found in most soils and waters.

Anaerobic (oxygen deficient) sulfur reducing bacteria *Desulfovibrio desulfuricans* reduce sulfate to sulfide as follows:

$$SO_4^{-2} + 4H^2 \rightarrow S^{-2} + 4H_2O$$

For steel, the corrosion product is iron sulfide, which precipitates when ferrous (steel) ions and sulfide ions react. The FeS precipitate film forms on exposed steel, and where continuous, is protective. However, FeS is cathodic to steel, and where the film is broken, aggressive galvanic corrosion may occur, resulting in pitting.

Conversely, aerobic (oxygen present) bacteria *Thiobacillus thioxidans* can oxidize elemental sulfur or sulfur containing compounds to sulfuric acid, as follows:

$$2S + 3O_2 + 2H_2O \rightarrow 2H_2SO_4$$

The sulfuric acid so formed will aggressively attack metals and concrete. The cycle of anaerobic sulfate reduction to sulfides, and sulfide oxidation to sulfuric acid is a major problem in the corrosive deterioration of concrete sewage piping, and buried steel piping. Metallic attack by this process will result in somewhat distinctive bowl shaped pits. There are other oxidizing and reducing families of bacteria, but those cited above are perhaps the best known and most prolific. Other metals pitted by bacterial action can include aluminum, stainless steels, and copper.

INTERGRANULAR CORROSION

As previously mentioned, grain boundaries are anodic with respect to the grain. As a rule, this is not a problem, as the grain boundary is only slightly more anodic than the grain matrix. However, under certain conditions, such as in highly acidic environments, the interface between the grains becomes very reactive, and aggressive intergranular corrosion results. With most forms of intergranular corrosion, only the grain boundary deteriorates, and there is little, if any, corrosion to the grain matrix.

Intergranular corrosion can be caused by impurities at a grain boundary, enrichment of one of the alloy elements, or depletion of one of these elements in the grain-boundary area. Depletion of chromium in the grain-boundary regions of stainless steels results in intergranular corrosion. Austenitic (18-8) stainless steels are particularly susceptible, particularly when heated within a temperature range of 950 to 1,450°F. Chromium carbide precipitates from the solid solution, depleting a zone near the grain boundary. This leads to corrosion because the chromium-depleted zone does not have sufficient resistance in a given corrosive environment. The appearance of intergranular corrosion results in a "sugary," granular appearance due to attack of the grain boundaries, leaving small, protruding "grains" (appearing like sugar granules) of metal. Intergranular corrosion sometimes occurs when austenitic stainless steels are welded and not annealed by water quenching after heating. Annealing, a rapid cooling by quenching, does not give sufficient time for chromium carbide precipitation.

SELECTIVE LEACHING

Selective leaching is the removal of one element from a metal alloy. The removal of zinc from brass alloys, or the removal of iron or steel from a cast iron alloy, are perhaps the two most common examples of selective leaching. The mechanism of dezincification of brass alloys is that initially, the brass dissolves in the corrosive environment; the zinc ions stay in solution; and the copper from the brass (approximately 30 % zinc and 70 % copper) plates back onto the brass, resulting in a copper-rich, zinc-deficient plug or layer.

Dezincification of brass is usually prevented by using a less susceptible brass alloy (for example, 15 % zinc, 85 % copper) or adding small amounts of arsenic, antimony, or phosphorus as dezincification inhibitors.

Graphitization of gray cast iron occurs because the iron is anodic to graphite and dissolves, leaving a porous mass consisting of graphite (a form of carbon) with little or no iron. There is no dimensional change to the cast iron, and graphitization is visually hard to detect, even though the metal has lost its ductile strength and becomes very brittle because the structure (often a pipe) looks the same as it did before graphitization occurred.

Many old, buried sewer and water pipes are made from gray cast iron, which after graphitization, crack due to soil settlement, movement of heavy equipment over them, excavation, or impact.

Graphitization may be prevented by using ductile (nodular) cast iron, because the graphite agglomerates in nodes and a graphite network is not present in the malleable cast iron to hold the residue together in the original form after loss of iron from the alloy.

EROSION-CORROSION

Erosion-corrosion is the acceleration or increase in the rate of deterioration by the relative movement between a corrosive fluid and a metal surface.

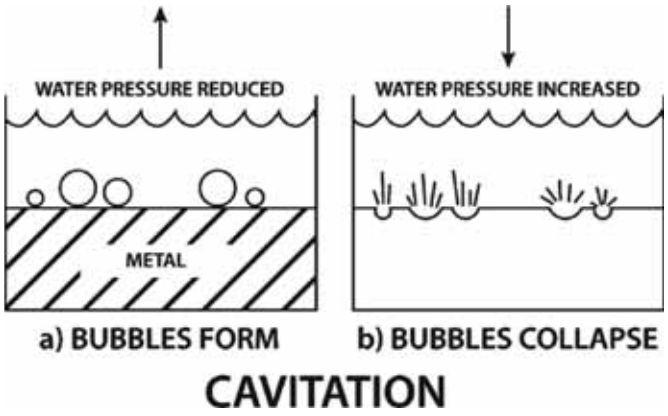


Fig. 9—Depiction of cavitation. (Courtesy of KTA.)

The appearance of erosion-corrosion is distinctive as grooves, gulleys, waves, and rounded holes and valleys appear on the surface in a directional pattern. An Illustration is shown above.

Velocity, either of the metal through the corrosive fluid or the corrosive fluid over the metal, increases the rate of attack, as a general rule. However, in some cases, increased velocity will reduce corrosion if it prevents deposition of materials that may cause crevice corrosion, or exposes the metal to inhibitors (chromates and sodium nitrite) in the fluid. Many stainless steels have a tendency to pit and suffer crevice corrosion in relatively stagnant water, but with movement or increased fluid velocity, that same metal can be used successfully because the motion prevents formation of deposits on the surface that could cause the initiation of pits and crevice corrosion. Metals that form a passive layer on their surfaces, such as stainless steels, aluminum, lead, copper, and brass, are susceptible to erosion-corrosion, because the eroding fluid may wear away the passive layer, exposing the metal to the corrosive immersion environment.

Erosion-corrosion can be prevented or minimized by the choice of more resistant materials; design to slow flow or turbulence; removal of entrained solids; the addition of inhibitors; and the use of coatings, including hard, abrasion resistant metallic coatings or soft, energy absorbing rubberlike coatings to isolate the metal from the environment.

Cavitation is a special form of erosion-corrosion caused by the formation and collapse of vapor bubbles in the liquid adjacent to the metal surface. If pressure on water is reduced sufficiently, it will boil at room temperature. Similarly, any dissolved air or other gases, will form bubbles at reduced pressure. When these bubbles are formed on or adjacent to a metal surface, and then subjected to rapidly increasing pressure, the bubble will collapse and cause an explosive shock to the surface. The surface shock causes a localized deformation and pitting, resulting in removal of the surface metal and a general roughening of the surface. Cavitation produces rounded microcraters on the metal surface. Sharp pressure pulses caused by collapsing bubbles are highly localized and can remove weak or soft portions of microstructural phases of an alloy. Fig. 9, depicts cavitation corrosion.

Examples of cavitation can occur when pumping water with a piston. When a cylinder is full of water and the piston is raised away from the water, pressure is reduced and the water vaporizes, forming bubbles. If the piston is again pushed toward the water, pressure is increased and the bubbles condense or collapse. In a similar fashion, the turning of a pump impeller through a liquid draws the liquid into the flowstream, reducing its pressure. As the impellor pushes the liquid downstream, pressure on the liquid is increased at the impellor surface, collapsing any bubbles that may have formed. A ship's propeller, pushing the ship through the ocean, is subject to cavitation for the same reason. Calculations have shown that rapidly collapsing vapor bubbles produce shock waves with pressures as high as 60,000 pounds per square inch [15].

Fretting corrosion is related to erosion-corrosion and occurs at contact areas between materials under load subject to vibration and slip. Fretting corrosion appears as pits or grooves in the metal surrounded by corrosion products. Fretting occurs in the atmosphere rather than under aqueous conditions.

STRESS CORROSION

Stress corrosion results in cracking caused by the simultaneous presence of tensile stress and a specific corrosive medium. Stress corrosion cracking (SCC) is particularly insidious, as it is not predictable in many cases, and may result in a catastrophic loss of metal strength. The metal surface is generally unattacked, but fine cracks progress through it as a result of the SCC. For SCC to occur, the metal must be stressed and be in a corrosive environment. Metallic stress alone may result in creep, metal fatigue, and ultimately tensile failure; and a corrosive environment alone will cause deterioration of a metal, the simultaneous presence of both stress and a corrosive environment will sometimes produce disastrous SCC.

Both intergranular (between grains) and transgranular (through grains) occur with SCC. Cracking generally proceeds perpendicular to the applied stress. Increasing the stress decreases the time before cracking occurs. As is the case with most chemical reactions, SCC is accelerated by increasing temperature.

Most metal alloys are subject to SSC in specific environments. Carbon steel, high-strength steels, austenitic stainless steels, high nickel alloys, aluminum, titanium, magnesium, and zirconium will all crack under stress in certain specific environments.

Environments that cause SCC are usually aqueous, and an environment that causes SCC in one alloy may not cause SCC in other alloys. Changing the temperature, degree of aeration, and/or the concentration of ionic species within the corrosion solution may change an innocuous environment into one that causes aggressive SCC failure. Also, an alloy that is immune in one heat treatment may be susceptible in another. As a consequence, the listing of all possible alloy environment combinations that may cause SCC is virtually infinite.

SCC can initiate and propagate with little evidence of corrosion until catastrophic failure occurs. Cracks frequently initiate at surface flaws or defects in the metal as a result of rolling processes, corrosion, or wear. The cracks, under stress, grow with little evidence, even in metals that are normally quite ductile. Often, microscopic examination is necessary to verify the presence of SCC.

Corrosion fatigue is a related form of SCC and is the tendency of a metal to fracture under repeated cyclic stressing.

Because SCC is hard to predict, it is also difficult to anticipate means for prevention. However, some generalized methods for reducing SCC are reducing the stress of the metal (perhaps by stress-relief annealing); changing the metal alloy to one more resistant in a given environment; the use of coatings (to isolate the metal from the corrosive environment); work hardening by shot-peening to produce residual compressive stresses on the metal surface; the use of inhibitors such as phosphates in water solution; application of cathodic protection, where it is positively known that SCC is the cause of failure.

HYDROGEN DAMAGE

The penetration of nascent hydrogen (atomic hydrogen) into a metal structure may cause blistering and embrittlement of that metal. Hydrogen penetration may be accelerated by cathodic protection using either impressed cathodic currents or sacrificial anodes. Acid pickling or corrosion in environments containing hydrogen and sulfide, typically that in vessels handling sour [hydrogen-sulfide containing hydrocarbons], may also increase the incidence of hydrogen damage to steel.

Atomic hydrogen (H), because of its extremely small atomic size, is capable of diffusing through steel and other metals. The reduction of hydrogen ions involves the production of hydrogen atoms that can be in contact with a metal surface prior to their combination into a hydrogen molecule. The application of cathodic protection, electroplating, and other processes are sources for introduction of nascent or atomic hydrogen into a metal. Certain substances such as phosphorus, arsenic compounds, and sulfide ions reduce the rate of hydrogen ion reduction by decreasing the rate at which hydrogen combines to form molecules. Accordingly, in the presence of these materials, there is a greater concentration of atomic hydrogen on a metal surface.

Because of its small size, the hydrogen atom can penetrate into a metal. Hydrogen pick-up can result from welding, heat treating, corrosion, or during melting of the alloy. Once in a metal, the hydrogen atoms may accumulate at voids or other internal surfaces within the alloy to form molecular hydrogen. As the concentration of molecular hydrogen increases at these micro-structural discontinuities, high internal pressure is created that can initiate cracking or blistering.

The presence of atomic hydrogen in a metal matrix has been theorized to lower the cohesive force between metal atoms such that local tensile stress perpendicular to the plane of a crack becomes equivalent to or greater than the lattice cohesive force, causing fracture and cracking.

At high temperatures (400 to 1,110°F; 200 to 595°C), hydrogen can react with carbon in the metal alloy to form a hydrocarbon—typically methane. This can result in a surface or internal decarburization, whereby carbon is removed from the alloy, leading to embrittlement of the metal.

With all hydrogen permeation, higher strength alloys are more susceptible to hydrogen cracking, and higher stresses caused by nascent hydrogen penetration cause cracking to occur more rapidly.

Hydrogen embrittlement (penetration of atomic hydrogen at low temperatures) is a reversible process, as opposed to hydrogen attack (penetration of high temperature, high-pressure hydrogen). Baking at 190°C (375°F) for four hours will usually suffice in removing hydrogen from most steels. Cadmium coatings on steel require a longer baking time because atomic hydrogen diffuses more slowly through that metal. Baking times up to 24 hours at 190°C (375°F) are common for cadmium-plated parts.

USE OF PROTECTIVE OVERLAYS TO PREVENT CORROSION

Corrosion Prevention with Protective Overlayers

A number of overlays on a metal surface (in the form of coatings) can be used to isolate the metal from a corrosive environment (barrier coating), provide galvanic sacrificial protection, or inhibit corrosion by the use of passivating pigments. The common type, of coatings used as overlays on a metal surface are discussed herein: conversion coatings (phosphate, chromate, and chromate–free); cementitious linings; glass and porcelain enamels; electroplating; thermal spray coatings; rubber linings; and paints, coatings, and linings.

CONVERSION COATINGS

Conversion coatings can be defined as a material applied to a metal surface that chemically reacts and converts the surface of the metal into a compound that becomes part of the coating. There originally were two principal kinds of conversion coatings: those based on phosphate chemistries and those on chromate chemistries. Because of chromate toxicity, a third type of conversion coating is emerging—those based upon chromate-free chemistries.

Phosphate Conversion Coatings

A phosphate layer $M_3(PO_4)_2 \cdot (nH_2O)$ is formed on a metal substrate by exposure to a phosphating bath. M stands for a metal and represents divalent metallic cations of one or more metallic alloying elements in the phosphating bath that deposit onto the metal being phosphated. n is the number of waters of hydration attached to the metal phosphate molecule comprising the phosphate layer. Steel, aluminum, copper, and magnesium, and their alloys are most commonly phosphated. Zinc phosphate is by far the most commonly used phosphate solution and it is applied usually by immersing the work piece in a bath or by spraying in a cabinet or tunnel.

For painting purposes, crystalline zinc phosphate layers are formed on steel, zinc galvanized steel, and aluminum. The weight of the phosphate coating ranges from 1 to 7 g/m² (0.0033 to 0.023 ounces per square foot).

The phosphate solution consists of a primary phosphate dissolved in a dilute solution of phosphoric acid. When a metal component is immersed in the solution or sprayed with the solution, the acid attacks the metal surface. The attack to the metal reduces the concentration of the acid in the localized area of the attack at the metal interface. With a less acidic environment, the primary phosphate decomposes into a sparingly soluble secondary phosphate and an insoluble tertiary phosphate, both of which precipitate onto the surface at the areas of lower acid concentration. In the process, they are molecularly bonded to the metal. The resulting phosphate layer consists principally of phosphate crystals, but may have amorphous phases between crystals.

The decomposition of the primary phosphate to the secondary tertiary phosphates release hydrogen ions that restore the acid level in the acid-depleted region. The process continues until the desired thickness of the phosphate layer is attained. This mechanism of coating formation is the same for both zinc and iron phosphatizing processes. Manganese phosphate baths are used for heavier coatings. Most conversion coatings used for painting pretreatments consist of zinc in combination with various amounts of Fe^{++}, Ni^{++}, or Mn^{++} ions.

The major advantage of phosphating pretreatments are an increase in surface area for paint bonding provided by the crystalline phosphate layer and a significant reduction of underfilm corrosion at scribes, discontinuities, and mechanical damage when the phosphate-treated steel is exposed to a corrosive, aqueous environment compared to an unphosphated metal.

Most automobile bodies are zinc phosphated prior to painting to increase corrosion resistance and paint adhesion.

Chromate Conversion Coatings

Chromate conversion coatings are formed by chemical or electrochemical treatment of metals or metallic coatings in solutions containing hexavalent chromium (Cr^{6+}). The process results in the formation of an amorphous protective coating comprised of the substrate, complex chromium compounds, and other components in the chromating bath. The most common chromating solution is zinc chromate, and the film formation is similar to that for phosphatizing. The metal being passivated is attacked by the acid (chromic acid and some sulfuric acid), bringing about a decrease in acidity at the metal surface as the acid is consumed during the attack. The hexavalent chromate is reduced to trivalent chromium, which precipitates as a complex chromate gel, bonding itself to the metal. The reduction of the hexavalent chromium results in the formation of hydrogen ions, raising the acidity level at the metal/liquid interface after precipitation of the chromate gel. It is believed that the gel film is formed with chromic hydroxide, providing an insoluble matrix with basic chromic chromate absorbed in it as a soluble component. The gel is soft for the first 24 h or so, after which it hardens and becomes relatively abrasion resistant. Chromate films can be produced on steel, cadmium, copper, and magnesium substrates. Aluminum and aluminum alloys are passivated principally by an acid process consisting of chromate-fluoride and chromate-fluoride-phosphate treatments. Chromate conversion coatings are most frequently applied by immersion or spraying, but can be brushed, roll coated, dipped, squeegeed, or applied in other ways. Chromate conversion coatings are applied primarily to enhance bare or painted corrosion resistance to undercutting and underfilm corrosion, and to improve the adhesion of paint or other organic coatings.

Galvanized steel is passivated by immersing or spraying the freshly prepared galvanized strip in a chromating solution for one to three seconds immediately before removing excess chromate by squeegee rolls. The conversion coating is applied to a weight range from 0.01 to 0.02 g of chromium per square meter (1 to 2 mg of chromium per square foot). Chromium passivation of galvanized steel can be classified as clear, iridescent, and colored (yellowish), depending upon its thickness. Corrosion protection provided by these coatings increases with color (thickness).

Chromate-Free Conversion Coatings

Because hexavalent chromium (Cr^{6+}) is a carcinogen and toxin, there has been an attempt to replace chromate-containing products with safer and more environmentally acceptable alternatives.

However, chromate conversion coatings have been successfully used for a long time and the chromating process consists of both cleaning and deoxidizing/desmutting prior to application of the conversion coating. These preparation procedures, prior to application of the chromate conversion coating, have been developed and refined over the years to optimize the performance of the chromate conversion coating. For chromate-free substitutions, the development and optimization of surface preparation and cleaning methods is not as nearly perfected. However, there are technologies under development that may be promising for chromate-free conversion coatings used in various industries. Some of the chromate-free conversion coatings currently under development or evaluation are based on the following technologies:

Titanium and zirconium fluorocomplexes—These systems consist of an acidic hexafluoro metal complex (H_2ZrF^6 or H_2TiF^6) compound, and commonly a polymer. The added polymers improve corrosion resistance and adhesion of subsequent coats. Titanium and zirconium fluorocomplex conversion coatings are in use on sheet stock for the canning industry and are being evaluated by the automotive industry.

Cerium-based conversion coatings—These coatings are being developed for use on aluminum, both for architectural and aerospace applications. The coating generally consists of cerium chloride ($CeCl_3$) or cerium nitrate [$Ce(NO_3)_3$] and a silicate (SiO_2) seal coat.

Cobalt-based conversion coatings—A cobalt nitrate [$Co(NO_3)_2$] bath produces layers of cobalt oxides over an aluminum substrate. Cobalt-based conversion coatings are being developed for the marine, automotive, and aerospace industries.

Molybdenum-based conversion coatings—These coatings are being developed for use on tin plate and zinc for galvanized surfaces. They have met with little success on aluminum.

Hydrotalcite coatings—These consist of clay-like mineral compounds such as hydromagnesite compounds in conjunction with an alkaline lithium salt solution. A system of polycrystalline compounds is formed on aluminum and aluminum alloy substrates that has good corrosion resistance. Subsequently applied organic coatings adhere well to the hydrotalcite coating surface.

Siliane coatings—Silanes form a silicate layer on a metal surface; they tend to have good corrosion resistance due to a lack of organic groups, and the ability of surface silanol groups to form siloxane bonds as they age. These are being developed for the automotive industry.

Conductive polymer coatings—Conductive polymers, including polyaniline, polypyrroles, and polythiophene-based coatings dispersed in a polymer matrix react with iron on a steel surface and form an iron oxide coating from 0.04 mils to 0.8 mils (1–20 μm thick). These coatings are being developed for ferrous metals.

HOT-DIP GALVANIZING

Hot-dip galvanizing consists of immersing an object to be protected in a bath of molten zinc. The protective coating so developed consists of zinc-iron alloy of variable composition on the surface of the steel. Closest to the surface, the iron content is high relative to the zinc, and proceeding through the protective layer cross section, the zinc content increases in the alloy until the surface layer is all zinc with no iron. Fig. 10 [16] shows a photomicrograph of the cross section of a hot-dip galvanize coating. At the zinc/steel interface, there is an alloying and diffusion of the zinc into the steel and a gradual transition of iron-zinc intermetallics until a relatively pure zinc layer is reached at the outer layer. The outer zinc layer is relatively soft, but the iron-zinc alloy layers are quite hard and from four to six times more resistant to abrasion than the pure zinc layer. The compositions of the various alloy layers are shown adjacent to the photomicrograph.

Galvanizing is applied by either of two methods: batch galvanizing or continuous galvanizing. Batch galvanizing involves cleaning of the steel to be protected, applying a flux to the surface of the zinc bath, and immersing the steel item through the flux into the molten bath of zinc for various periods of time. Thickness of the coating is controlled by the composition of the steel substrate, immersion time, and bath withdrawal rate. (Fast withdrawal rates result in thicker galvanized films.) Batch galvanize thickness is usually between 2 and 4 oz/ft², or 1.7 to 3.4 mils per side (610 and 220 g/m² and 43–86 μm in thickness).

Continuous galvanizing consists of moving a steel sheet, strip, or wire through a tank of molten zinc in a continuous flow. Continuous galvanize coatings are applied at speeds of over 90 m/min (300 ft/min). Coating weights vary from 90 to 1100 g/m² (0.29 to 3.6 oz/ft²). Coating thickness equivalents are from 6 to 78 μm; 0.24 to 3.1 mils.

The zinc coating may be on only one side of the sheet, of equal weight on both sides of the sheet, or of different weights on each side of the sheet. Most sheet coating lines use a gas-wiping technique in which a stream of air or nitrogen gas is directed against the emerging sheet, blowing off excessive zinc and cooling it. A coated galvanized sheet is often oiled or coated with a chromate conversion coating to inhibit white rusting and superficial corrosion during storage in transit. Application of a wax on galvanized wire serves as a white rust preventative and facilitates handling during subsequent processing.

All galvanized coatings on steel protect by acting both as a barrier and providing cathodic protection to the underlying steel. A fresh galvanized surface reacts with oxygen to form zinc oxide (ZnO). In the presence of moisture, zinc oxide converts to zinc hydroxide ($ZnOH_2$) and further reaction with carbon dioxide in the air results in the formation of zinc carbonate ($ZnCO_3$), which is relatively insoluble and provides a gray patina on the surface of weathered galvanize. Cathodic protection is provided to the steel at discontinuities, scratches, and mechanical damage due to the fact that zinc is anodic to steel in most environments.

Layer	Alloy	Iron, %
Eta (η)	Zinc	0.03
Zeta (ζ)	$FeZn_{13}$	5.7-6.3
Delta (δ)	$FeZn_7$	7.0-11.0
Gamma (Γ)	Fe_3Zn_{10}	20.0-27.0
Steel Base Metal	Iron	99+

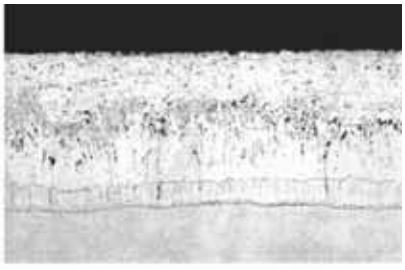


Fig. 10—Photomicrograph of galvanized steel cross-section, and alloy layer compositions. (Courtesy of GalvInfo Center.)

CEMENTITIOUS LININGS

Linings based upon cement are used as sprayable linings, as centrifugally-cast linings for water pipe interiors, and to add weight to submersed pipelines. For corrosion protection purposes, the high alkalinity (pH of 12) of the cement, due principally to calcium silicates and some aluminum silicates, prevents corrosion of steel. Additionally the great thickness (1/2 to 2 in. or more) and inorganic nature of the lining renders it highly abrasion resistant, and resistant to mechanical damage. Ductile and steel water pipes sometimes have a Portland cement lining centrifugally cast to their interior as part of the manufacturing process. Centrifugal casting provides a more dense cement lining making it more resistant to leeching of alkalinity and more abrasion resistant than sprayed linings.

Sprayed cement linings, are more porous, but still provide good corrosion resistance, abrasion resistance, and heat resistance. Spray application is necessary on in situ structures. Often polymers, such acrylic, styrene-butadiene, and polyvinyl acetate latexes, and epoxy emulsions are added to the cement mixture in percentages up to about 20 % to provide better moisture impermeability, acid resistance, tensile strength, and adhesion.

Cement is also added to pipeline exteriors as a coating or as a casting to provide weight to keep the pipe from rising when buried or submersed in water.

GLASS AND PORCELAIN ENAMELS

These coatings are based on complex borosilicate glasses that are produced by quenching a molten glassy mixture. Frits are formed by shattering the glass into small granules by mechanical means. The composition of the frits will vary widely depending upon the intended use for the enamel coating. Porcelain enamels are used widely for chemical processing vessels, agricultural storage tanks, piping and pipe components, and as well for water heater tanks, cookware, and as appliance coatings. They can be formulated to have excellent chemical resistance, particularly to alkalis (at room temperature) and many acids. Water resistance is excellent at room temperature and decreases somewhat at elevated temperatures. Weather resistance, even in highly corrosive, polluted, industrial environments, is excellent. Solvent resistance to common organic solvents, greases, and oils is also excellent. High temperature resistance, depending upon formulation, is excellent up to 2,000°F (1,095°C). However, as might be imagined, glass and porcelain enamels do not have good flexibility and will crack when subjected to bending or twisting. Additionally, when impacted, the thicker coatings may fracture and chip.

ELECTROPLATING

Electroplating involves the electrodeposition of a metallic coating onto a base metal to improve the corrosion resistance, appearance, or properties of that base metal.

Electroplating is commonly done to improve corrosion resistance, and examples are: chrome-plated steel automobile bumpers; electrogalvanizing or zinc plating of steel strip and sheet metal; zinc and cadmium plating of screws, nut, bolts, and other small hardware items; tin plating of steel strip for food packaging and other container uses.

Electroplating consists of the deposition of a layer, usually a thin metal, on an object by passing an electric current, usually DC, through a bath within which the object being plated is immersed. The object being plated is one of the electrodes, usually the cathode. The anode is the metal being deposited, and it dissolves as the plating process proceeds. The plating bath contains dissolved salts of the metals that are being deposited. The bath also contains appropriate acids, bases, and buffering salts to hold the pH to the desired level. Addition agents, such as boric acid, glycine, urea, and gelatin may be added to the bath to regulate plating texture to give, for example, a smooth mirror-like finish. To plate out metals above hydrogen from an aqueous solution, the concentration of hydrogen in the cathodic film must be low. Hence, a basic solution such as that provided by a cyanide bath may be used.

To plate out monovalent ions such as silver (Ag^{+1}) will require one electron per ion. Multivalent ions such as gold (Au^{+1} and Au^{+3}) will require one and three electrons per ion, respectively. In theory, one Faraday of electricity will deposit one equivalent weight of any metal; 107.868 grams of silver, 196.967 grams of Au^{+1}, and 196.967/3 = 65.66 grams of trivalent gold. However, this ideal is almost never realized and the current efficiency is defined as the actual mass of metal deposited/the theoretical mass of metal that would have been deposited using the same amount of electrical current.

Metals commonly plated are copper, chromium, nickel, iron, cadmium, zinc, indium, tin, lead, silver, and gold. Brass, bronze, zinc-iron and zinc-nickel alloys are also plated. Each of these metals require a different bath, and different bath operating parameters (temperature, cathode current density, voltage, pH, addition agents, etc.).

THERMAL SPRAY COATINGS

Thermal spray utilizes heat to melt a material (usually a metal, ceramic, organic polymer, or combinations thereof) for corrosion protection. Steel surfaces are by far the most widely used substrate for thermal spray coatings, although any metal or non-metal compatible with the coating may be coated. The heating methods used are flame (combustion), electric arc, and electric plasma spray processes. In all cases, a feed stock, usually consisting of a powder or wire, is heated, atomized, and propelled onto a suitably prepared substrate where, upon impact, it consolidates for form a protective, adherent coating. For purposes of corrosion protection, often metallic and ceramic coatings are sealed with one or more layers of a polymeric topcoat. Sealers are typically thinned coatings including epoxies, polyurethanes, phenolics, and silicones. Thermally sprayed coatings can be readily built to thicknesses from 0.004 to 0.08 in. (0.1 to 2 mm). Thermally sprayed metals for protection of steel substrates are most commonly metallic zinc, aluminum, and zinc-aluminum alloys (85/15 zinc-aluminum). Other metals can be thermally sprayed such as stainless steel, bronze, nickel, tin, and other exotic metals.

Ceramics are usually applied over a thin, metallic bond coating. Glass frits, ground to a powder for easier melting, based on borosilicate glasses and other ceramics, can be applied.

Polymer coatings, including polyethylene, polypropylene, nylon, polyethylene-tetrafluoroethylene copolymers, as well as thermoplastic acrylics and thermoset epoxies, can be thermally spray applied. These polymers are ground into a powder and fed into the combustion zone by a carrier gas where, upon heating, they melt and as droplets, are transported to a preheated substrate. The molten particles impinge on the substrate, flattening and solidifying into an interlaced network of "splats." The thickness of the coating is governed by the number of spray passes.

RUBBER LININGS

Rubber, in the form of prefabricated sheets, have been used successfully as a lining material in a variety of immersion environments such as storage tanks, flue gas desulfurization units, chemical scrubbers, pipelines, valves, and pumps. Because of superior impact, abrasion, and chemical resistance, rubber linings in the range of 3–6 mm (1/8–1/4 in.) can often outperform conventional liquid-applied linings.

A steel or other metal surface is thoroughly cleaned, usually by solvent cleaning and abrasive blast cleaning. An adhesive system, designed to adhere the rubber to the metal, is then applied. The adhesive may be a single or multicoat system. The rubber sheet is then cut to fit and applied to the surface using rollers and stitchers to press out air pockets and to press the sheet into the adhesive. The applied rubber must then be cured or vulcanized by steam in an autoclave, by heating with exhaust steam, or by a chemical curing agent applied to the rubber surface.

The seams where adjacent rubber sheets join are of particular concern, as most rubber lining failures occur at the seams.

Rubber sheets used for corrosion protection usually comprise two or more different types of rubbers laminated together to form the finalized sheet. Natural rubbers derived from latex-producing plants (principally in Malaysia, Indonesia, and Thailand) account for nearly 90 % of the global production of raw, natural rubber.

Synthetic rubber is made principally from petroleum feedstock. Principal synthetic rubber compounds used for linings are neoprene or chloroprene rubber (CR); butyl rubber (IIR—a blend of isoprene and isobutylene copolymers); chlorobutyl rubber (CIIR—manufactured by the chlorination of IIR); ethylene-propylene rubber (EPDM—a copolymer of ethylene and propylene with the addition of a diene monomer); nitrile rubber (NBR—a copolymerization of acronitrile and butadiene); styrene-butadiene (SBR—formed by copolymerization of styrene and butadiene); and chlorosulfonated polyethylene (CSM—marketed as Hypalon by DuPont).

Each of the rubbers, including the various types of natural rubbers, has advantages and disadvantages, along with specific chemical and temperature resistances, and hardness and flexibility.

Rubber lining systems are chosen for their resistance to the intended service, and are applied, cured, and inspected for defects prior to placing the rubber-lined structure in service.

TABLE 5—Advantages and limitations of principal coating resins. (Courtesy of ASM International.)

Resin type	Advantages	Limitations	Comments
Autooxidative cross-linked resins			
Alkyds	Good resistance to atmospheric weathering and moderate chemical fumes; not resistant to chemical splash and spillage. Long oil alkyds have good penetration but are slow drying: short oil alkyds are fast drying. Temperature resistant to 105°C (225°F)	Not chemically resistant; not suitable for application over alkaline surfaces, such as fresh concrete, or for water immersion	Long oil alkyds make excellent primers for rusted and pitted steel and wooden surfaces. Corrosion resistance is adequate for mild chemical fumes that predominate in many industrial areas. Used as interior and exterior industrial and marine finishes
Epoxy esters	Good weather resistance; chemical resistance better than alkyds and usually sufficient to resist normal atmospheric corrosive attack	Generally the least resistant epoxy resin. Not resistant to strong chemical fumes, splash, or spillage. Temperature resistance: 105°C (225°F) in dry atmospheres. Not suitable for immersion service	A high-quality oil-based coating with good compatibility with most other coating types. Easy to apply. Used widely for atmospheric resistance in chemical environments on structural steel, tank exteriors, etc.
Thermoplastic resins			
Acrylics	Excellent light and ultraviolet stability, gloss, and color retention. Good chemical resistance and excellent atmospheric weathering resistance. Resistant to chemical fumes and occasional mild chemical splash and spillage. Minimal chalking, little if any darkening on prolonged light exposure.	Thermoplastic and water emulsion acrylics not suitable for any immersion service or any substantial acid or alkaline chemical exposure. Most acrylic coatings are used as topcoats in atmospheric service. Acrylic emulsions have limitations described under "Water emulsion latex."	Used predominantly where light stability, gloss, and color retention are of primary importance. With cross-linking, greater chemical resistance can be achieved. Cross-linked acrylics are the most common automotive finish. Emulsion acrylics are often used as primers on concrete block and masonry surfaces.
Water emulsion latex	Resistant of water, mild chemical fumes, and weathering. Good alkali resistance. Latexes are compatible with most generic coating types, either as an undercoat or topcoat.	Must be stored above freezing. Does not penetrate chalky surfaces. Exterior weather and chemical resistance not as good as solvent or oil-based coatings. Not suitable for immersion service	Ease of application and cleanup. No toxic solvents. Good concrete and masonry sealers, because breathing film allows passage of water vapor. Used as interior and exterior coatings
Asphalt pitch	Good water resistance and ultraviolet stability. Will not crack or degrade in sunlight. Nontoxic and suitable for exposure to food products. Resistant to mineral salts and alkalies to 30 % concentration	Black color only. Poor resistance to hydrocarbon solvents, oils, fats, and some organic solvents. Does not have the moisture resistance of coal tars. Can embrittle after prolonged exposure to dry environments or temperatures above 150°C (300°F), and can soften and flow at temperatures as low as 40°C (100°F)	Often used as relatively inexpensive coating in atmospheric service, where coal tars cannot be used. Relatively inexpensive. Most common use is as a pavement sealer or roof coating.
Coal tar pitch	Excellent water resistance (greater than all other types of coatings); good resistance to acids, alkalies, and mineral, animal, and vegetable oils	Unless cross-linked with another resin, is thermoplastic and will flow at temperatures of 40°C (100°F) or less. Hardens and embrittles in cold weather. Black color only; will alligator and crack on prolonged sunlight exposure, although still protective	Used as moisture-resistant coatings in immersion and underground service. Widely used as pipeline exterior and interior coatings below grade. Pitch emulsions used as pavement sealers. Relatively inexpensive
Cross-linked thermosetting resins			
Bisphenol-F epoxies	Lower volatile organic compound (VOC) content than Bis-A epoxies. Better temperature and chemical resistance than Bis-A types. Intermediate temperature and chemical resistance between Bis-A and novolacs	Less flexible; requires thorough blast cleaning surface preparation	Increasing use due to high reactivity and low VOC content

TABLE 5—Advantages and limitations of principal coating resins. (Courtesy of ASM International.) (Continued)

Resin type	Advantages	Limitations	Comments
Epoxy novolacs	Greatest chemical resistance and highest temperature resistance of all epoxy resins used for most severe immersion service	Least flexible of epoxy resins. Costly	Used for high-temperature chemical immersion service
Polyamide, cured epoxies	Superior to amine-cured epoxies for water resistance. Excellent adhesion, gloss, hardness impact, and abrasion resistance. More flexible and tougher than amine-curved epoxies. Some formulations can cure on wet surfaces and underwater. Temperature resistance: 105°C (225°F) dry; 65°C (150°F) wet	Cross-linking does not occur below 5°C (40°F). Maximum resistances generally require 7 day cure at 20°C (70°F). Slightly lower chemical resistance than amine-cured epoxies	Easier to apply and topcoat, more flexible, and better moisture resistance than amine-cured epoxies. Excellent adhesion over steel and concrete. A widely used industrial and marine maintenance coating. Some formulations can be applied to wet or underwater surfaces.
Polyurethanes (aromatic or aliphatic)	Aliphatic urethanes are noted for their chemically excellent gloss, color, and ultraviolet light resistance. Properties vary widely, depending on the polyol coreactant. Generally, chemical and moisture resistance are similar to those of polyamide-cured epoxies, and abrasion resistance is usually excellent.	Because of the versatility of the isocyanate reaction, wide diversity exists in specific coating properties. Exposure to the isocyanate should be minimized to avoid sensitivity that may result in an asthmatic, like breathing condition on continued exposure. Carbon dioxide is released on exposure to humidity, which may result in gassing or bubbling of the coating in humid conditions. Aromatic urethanes may darken or yellow on exposure to ultraviolet radiation.	Aliphatic urethanes are widely used as glossy light-fast topcoats on many exterior structures in corrosive environments. They are relatively expensive but extremely durable. The isocyanate can be combined with other generic materials to enhance chemical, moisture, low-temperature, and abrasion resistance.
Amine-cured epoxies	Excellent resistance to alkalies, most organic and inorganic acids, water, and aqueous salt solutions. Solvent resistance and resistance to oxidizing agents are good as long as not continually wetted. Amine adducts have slightly less chemical and moisture resistance.	Harder and less flexible than other epoxies and intolerant of moisture during application. Coating chalks on exposure to ultraviolet light. Strong solvents may lift coatings. Temperature resistance: 105°C (225°F) wet; 90°C (190°F) dry. Will not cure below 5°C (40°F); should be topcoated within 72 h to avoid intercoat determination. Maximum properties require curing time of approximately 7 days.	Good chemical and weather resistance. Best chemical resistance of epoxy family. Excellent adhesion to steel and concrete. Widely used in maintenance coatings and tank linings
Epoxy powder coatings	Good adhesion, chemical and moisture resistance. Allows cathodic protection in shielded areas on pipelines	Color change is difficult due to extensive cleanup of old powder. Like all epoxy resins, chalks on ultraviolet exposure. Must be applied in shop. Hard to field repair	Applied by electrostatic spray/ fluidized bed. Increasing use because of VOC used as pipeline, original equipment manufacturer coatings
Coal tar epoxies	Excellent resistance to saltwater and freshwater immersion. Very good acid and alkali resistance. Solvent resistance is good, although immersion in strong solvents may leach the coal tar.	Embrittles on exposure to cold or ultraviolet light. Cold weather abrasion resistance is poor. Should be topcoated within 48 h to avoid intercoat adhesion problems. Will not cure below 10°C (50°F). Black or dark colors only. Temperature resistance: 105°C (225°F) dry; 65°C (150°F) wet	Good water resistance. Thicknesses to 0.25 mm (10 mils) per coat. Can be applied to bare steel or concrete without a primer. Low cost per unit coverage
Epoxy phenolics	Excellent hot water resistance and acid resistance. More flexible than phenolic. Better alkali resistance than phenolics	Not as alkali resistant as other apoxy resins. Applies in thin films: somewhat brittle	Linings for food and beverage processing and storage tanks

(*Continued*)

TABLE 5—Advantages and limitations of principal coating resins. (Courtesy of ASM International.) (Continued)

Resin type	Advantages	Limitations	Comments
Phenolics	Greatest solvent resistance of all organic coatings described. Excellent resistance to aliphatic and aromatic hydrocarbons, alcohols, esters, ethers, ketones, and chlorinated solvents. Wet temperature resistance to 95°C (200°F). Odorless, tasteless, and nontoxic; suitable for food use	Must be baked at a metal temperature ranging from 175 to 230°C (350 to 450°F). Coating must be applied in a thin film (approximately 0.025 inch, or 1 mil) and partially baked between coats. Multiple thin coats are necessary to allow water from the condensation reaction to be remove. Cured coating is difficult to patch due to extreme solvent resistance. Poor resistance to alkalies and strong oxidants	A brown color results on baking, which can be used to indicate the degree of cross-linking. Widely used as tank lining for alcohol storage and fermentation and other food products. Used for hot water immersion service. Can be modified with epoxies and other resins to enhance water, chemical, and heat resistance
Polyureas	Extremely fast curing, highly elastic thick film coatings with good strength. Abrasion resistance, chemical resistance	Requires specialized spray equipment due to fast curing Not resistant to strong acids.	Concrete coatings for use in secondary containment of chemical tanks. Elastomeric roof coatings

PAINTS, COATINGS, AND LININGS

The application of a pigmented coating to a metal surface to provide corrosion protection, and as well to provide color and appearance is by far the most common means of corrosion protection of steel and most other metals. The reason for this is that coating materials are relatively inexpensive and can be inexpensively and quickly applied as a liquid by brush, roller, or spray to an irregular, complex surface. The applied liquid coating wets and conforms to the shape of a complex surface and, upon drying or curing, form a protective layer, sealing the object from a corrosive environment.

Sometimes the words "paint," "coating," and "linings" are used to describe a liquid blend of resins and pigment that will dry or cure into a protective layer on a metal. In general usage, however, "paints" are usually materials that are used primarily for decorative purposes, "coatings" are used for corrosion protection purposes in atmospheric environments, and "linings" are used for corrosion protection purposes in immersion or subsoil environments. As can be seen by these general categories, there is much overlap and, under many circumstances, the terms can be used interchangeably.

Coating materials generally consist of a resin (or resin blend), pigments, and solvents or water. Most resins are

TABLE 6—Advantages and limitations of zinc-rich coatings. (Courtesy of ASM International.)

Resin type	Advantages	Limitations	Comments
Organic zinc-rich	Galvanic protection afforded by the zinc content, with chemical and moisture resistance similar to that of the organic binder. Should be topcoated in chemical environments with a pH outside the range 5–10. More tolerant of surface preparation and topcoating than inorganic zinc-rich coatings	Generally have lower service performance than inorganic zinc-rich coatings, but case of application and surface preparation tolerance make them increasingly popular.	Widely used in Europe and the Far East, while inorganic zinc-rich coatings are most common in North America. Organic binder can be closely tailored to topcoats (for example, epoxy topcoats over epoxy-zinc-rich coatings) for a more compatible system. Organic zinc-rich coatings are often used to repair galvanized or inorganic zinc-rich coatings.
Inorganic zinc-rich	Provides excellent long-term protection against pitting in neutral and near-neutral atmospheric, and some immersion, services. Abrasion resistance is excellent, and dry heat resistance exceeds 370°C (700°F). Water-based inorganic silicates are available for confined spaces and compliance with regulations regarding volatile organic compounds.	Inorganic nature necessitates thorough blast-cleaning surface preparation and results in difficulty when topcoating with organic topcoats. Zinc dust is reactive outside the pH range of 5-10, and topcoating is necessary in chemical fume environments. Somewhat difficult to apply; may mudcrack at thicknesses in excess of 0.13 mm (5 mils)	Ethyl silicate zinc-rich coatings require atmospheric moisture to cure and are the most common type. Widely used as a primer on bridges, offshore structures, and steel in the building and chemical-processing industries. Used as a weldable preconstruction primer in the automotive and shipbuilding industries. Use eliminates pitting corrosion.

organic polymers, although some, notably the silicones, silanes, and silicates (used principally for inorganic zinc-rich coatings) are inorganic.

Pigments provide color, moisture impermeability, strengthening, and reinforcement of the dried film, and in some cases, inhibition (chromates, molybdates, borates), and sacrificial protection (zinc). Pigments are ground or mixed into the resin blend and either dissolved in the solvent mixture or emulsified in water (sometimes with a solvent coalescing aid).

The principal characteristics of a coating are derived from the resin or resin blend. Proper choice of pigments must be made for the intended service, as the pigment must have the appropriate acid, alkali, moisture, temperature, and weatherability resistances for the environment of intended use.

In order for any coating system to perform properly in a given environment, the metal must be cleaned of oils, grease, salts, and contaminants that may compromise its performance. Common surface preparation methods include hand and tool scraping, brushing and grinding; abrasive blast cleaning; solvent cleaning; water washing; and high pressure water jetting. Often, more than one layer of coating is used, with primers formulated for adhesion, corrosion inhibition, and sacrificial protection. Topcoats are formulated for environmental resistance, and intermediate coats (when used) provide a means for the topcoat to adhere to the primer and provide additional thickness and resistance to the coating system.

Coating systems are usually chosen for their environmental resistance, and the surface preparation and specific coating design are dependent upon the desired environmental service and anticipated service life.

Table 5 [17,18] describes the advantages and limitations of principal coating resins used to formulate coatings and linings.

Zinc-rich primers, and when untopcoated, zinc-rich coatings, consist of an organic (commonly epoxy, or polyurethane) or inorganic (silicate) binder highly loaded (75 % solids by volume or higher) with zinc dust. The zinc in the zinc-rich is anodic to the underlying steel, and corrodes preferentially to the steel which is the cathode in the galvanic couple. Accordingly, in time, when the zinc dissipates, it can be replaced by reapplication. This is usually much safer and less expensive than steel replacement. Zinc-rich primers are widely used in aggressive neutral and near-neutral marine industrial and atmospheric environments as they virtually eliminate pitting corrosion.

Table 6 lists the advantages and disadvantages of organic and inorganic zinc-rich coatings.

CONCLUSIONS

Metallic corrosion, its mechanisms, and forms have been summarized in the preceding paragraphs, along with some of the more common means to prevent corrosion by use of protective overlayers. A more exhaustive treatment of either subject is beyond the scope of this chapter.

As knowledge of corrosion increases as a result of research into corrosion mechanisms and the means to detect and study corrosion, new methods to combat corrosion will be discovered, along with new corrosion protection materials and methods. When one considers the state of the art of corrosion knowledge, and the methods used to deter corrosion 50 years ago, it is evident we have come a long way baby! It is almost unimaginable to think where the science will be in another 50 years. What an exciting future for workers, technicians, scientists, and technologists in the field of corrosion, and corrosion protection!

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Accelerated Weathering

Valerie S. Sherbondy[1]

PREFACE

IN PREPARATION OF THIS CHAPTER, THE CON-tents of the fifteenth edition were drawn upon. The current edition will review, clarify and update the topics as addressed in the previous edition. New technology and reference materials are acknowledged and included to update the reader with the advances in this industry.

Paints and coatings are used both to protect substrates and to provide an aesthetically pleasing appearance. In an outdoor environment, both of these functions can be affected by weathering. The four major factors involved in weathering are solar radiation (sunlight), moisture, oxygen, and heat. Sunlight, especially in the short wavelength/high energy ultraviolet (UV) region, has been proven to lead to discoloration, loss of gloss, scaling, embrittlement, and chalking. Moisture, in the form of rain, dew and humidity can cause blistering, flaking, loss of adhesion and promote the growth of mildew and algae. Heat exposure may cause embrittlement, cracking, peeling, and checking. Oxygen in the atmosphere participates in the oxidation of the surface of the coating, which may eventually lead to oxidation of internal layers, causing embrittlement, softening, cracking, or crazing. The oxygen is often left out of the discussion since it is more constant than the other factors, but this degradation process is a contributing factor to the other three factors of weathering. These elements contribute individually as well as in combination to cause coating failures.

Naturally occurring and man-made chemicals in the environment also contribute to coating degradation and could be considered a fifth element of weathering. However, the type and levels of chemicals can vary dramatically, even over short distances. Therefore, they cannot be considered as universal in influencing the degradation process as the four factors mentioned previously. Perhaps as a consequence of this, and also partly due to tradition, chemical resistance testing is usually considered to be separate from artificial weathering. Although the effects of chemicals cannot be ignored, they are discussed elsewhere in the manual. One of the most common chemical exposure tests that is often grouped with accelerated weathering continues to be salt fog or salt spray testing, which is discussed in the corrosion section of this manual. In summary, this chapter will consider only devices that incorporate an UV light source, temperature control or monitoring, and moisture exposure monitoring.

Accelerated or artificial weathering involves the use of laboratory equipment (either indoors or outdoors) to simulate the degradation that occurs during actual outdoor exposure [1–3]. Accelerated weathering is the term most often applied to artificial weathering because at least one of the elements of light, heat, and moisture are either longer in duration or more intense than the actual time and conditions encountered in outdoor exposure. This increased exposure causes the coating to weather or degrade more rapidly than when placed in an environment without the intensified weathering factor. However, in an attempt to accelerate the effects of natural weathering, the laboratory conditions may be overly aggressive and thus cause results that are not attained during natural weathering. In some cases, the modes of failure identified by accelerated weathering do not occur in natural conditions, which is at least partially due to the unpredictability of the exposure environment. To evaluate the applicability of the results from any accelerated test, background information about the material being exposed and actual field results of similar materials may be referenced. Internal controls, consisting of materials with known performance characteristics, provide helpful information and can be used to predict expected service life expectations.

Artificial weathering devices should be designed to produce test conditions that are controllable and reproducible, so that data are reproducible on a day-to-day basis and comparable on a laboratory-to-laboratory basis. This differs from outdoor or natural weathering where there is natural variation and no control over environmental factors. Due to this variability of conditions, the results of short-term natural weathering often are not reproducible. For example, weathering factors are different for various parts of the world and for different countries and can be broken down to represent various known climates, which are further addressed in the "Natural Weathering" chapter of this book. Some locations receive more sunlight and heat, while others are cloudy and cool. There are also seasonal variations. Even for long-term testing, the data for a specimen placed outside during January would not necessarily concur with data for a duplicate specimen placed outside in July because of initial exposure effects. When considering short term exposure, even if the same location and time of year are used, the natural weathering factors change from year to year. It should be noted that the longer term outdoor weathering does settle into a pattern and exposures of greater than 3 years have shown correlation to other samples exposed over a similar time. The long term outdoor exposure monitoring has indicated that the variations within particular climates vary within a characterized range. In contrast to natural weathering, data produced

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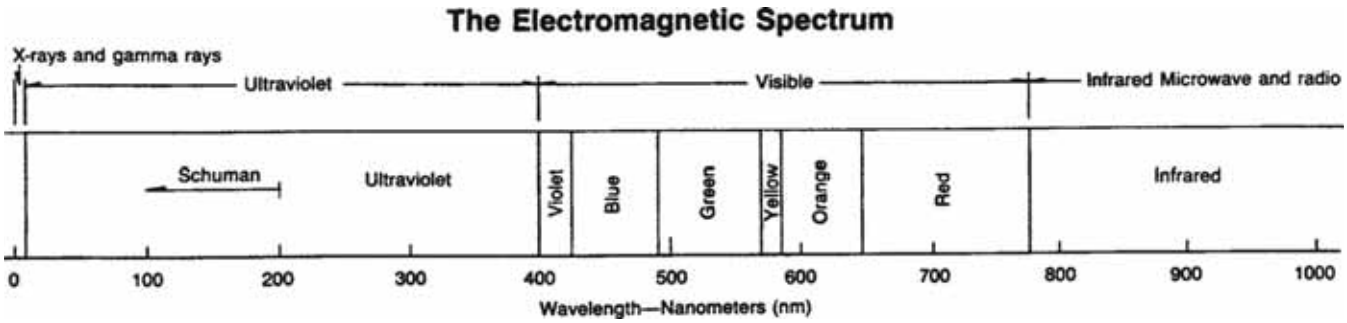

Fig. 1—The electromagnetic spectrum.

under controlled laboratory conditions can be used as comparative data (assuming the same equipment, equally aged lamps, etc.) even if testing was conducted during different times of the year or over several years.

In addition to reproducibility, a great advantage of accelerated weathering is that the results are available more quickly than with natural weathering, which is a phenomenon that may take years. The time saved on testing can translate into cost savings when developing new products or when choosing a new coating system for buildings, tanks, or equipment where historic data about coating performance is not available. This acceptance of data should be used cautiously since not all accelerated data is representative of natural weathering degradation processes.

Even though there are many advantages to accelerated weathering, it is important to recognize that the data is most often used for comparative purposes only. Although there are correlation tables available for many devices for a variety of materials, the correlation between artificial and natural outdoor results should be validated before using the results as a basis for business decisions. One reason an accepted overall correlation has not been developed is that the data obtained through artificial weathering has been produced by subjecting the sample to unnatural conditions, and the results may or may not duplicate those that occurred during natural weathering. If similar failure modes are experienced in an accelerated weathering device and at an outdoor test site, a direct correlation may be developed for that product. The calculated correlation would be valid only for the tested material under the stated, specific conditions. Note that the correlation is often extended to a variety of similar environments, making further estimates of service life possible, but this correlation is not a universal correlation and should not be represented as such.

Although the previous information makes it sound like the only way to get reproducible data is accelerated weathering devices, it should be noted that not all results obtained by accelerated weathering devices are as reproducible as those using and producing the data would like [3]. Studies have concluded that even though the settings may be the same, the maintenance of the device—including light source, filters, and gages—affect the exposure levels and thus the results of the testing. The cleaning and disposal of light filters is often subjective and a major source of variation that changes the amount of light at critical wavelengths. The intensity of the light is also dependent on the changing of, rotation of, and power supplied to the light source. These factors may speed up or slow down the degradation process due to changes in both temperature and UV light exposure. Since this is known to occur, testing specifications are sometimes written to include a standard material be exposed with the test specimens or to include an actual measurement of the light during the testing. This measurement is discussed later in this chapter. Updates to methods and equipment are decreasing the variability by increasing the requirements for monitoring, ease of monitoring, and required documentation. [See ASTM G151 "Standard Practice for Exposing Non-metallic Materials in Accelerated Test Devices that Use Laboratory Light Sources" for an example of care. The manufacturer of the device should provide exact information.]

Even if the light source was not changing with time, each device has regions of more intense exposure. For this reason, most devices have recommended manual rotation procedures for the exposed specimens. These procedures should be performed at regularly spaced intervals to decrease the effects of increased or decreased light intensity on the specimens during the duration of the exposure. These effects would be greater on short-term tests, where the specimens would not be moved through the different exposure zones.

Aside from the conditions of the device, the conditions surrounding the device also affect performance. Most devices require a surrounding area that is ventilated and able to maintain ambient conditions, so that temperature changes within the device can be maintained or obtained. For example, a relatively high ambient temperature may reduce the amount of condensation on some devices, while high amounts of ventilation may slow the temperature recovery after water spray in other devices. It should be noted that ambient conditions are not specified by all of the accelerated weathering ASTM standards, although the manufacturers of the testing equipment often recommend general guidelines. Ambient conditions could vary between laboratories, adding an unknown variable that may affect the results.

ELEMENTS OF WEATHERING

There are many component factors that contribute to the weathering of a coating. The general components are light, moisture, heat, and oxygen, which are always present in various amounts. This section concentrates on these general components and on how they are simulated and intensified.

Light

Sunlight is composed of radiation from the visible, UV, and infrared regions of the electromagnetic spectrum

(Fig. 1) [4]. The most damaging region of sunlight for polymeric materials has been determined to be the UV light region, especially the shorter wavelengths ranging from 400 to 295 nm. The portion of sunlight in the UV region is relatively small, only 5 to 7 %, due to the filtering effects of the atmosphere. The UV region has been divided into three domains: UV-A, UV-B, and UV-C. The UV-A region is 315 to 400 nm, the UV-B region is 280 to 315 nm, and the UV-C region is 100 to 280 nm. Although the high energy/short wavelength UV-C is the most damaging region, these wavelengths are essentially filtered out by ozone in the upper levels of the atmosphere. Therefore, if light sources produced output only in this region, they would cause abnormal degradation unless the coating was to be used for aerospace applications.

Radiation in both the UV-A and the UV-B regions cause degradation of coatings. The energy of the shorter wavelengths present in the UV-B region, ~91 to 102 kcal/mol (3.8 to 4.3 J/mol), cause more severe and rapid degradation of coatings than the wavelengths in the UV-A region. In the UV-B region, the energy levels are high enough to break carbon-nitrogen, carbon-carbon, nitrogen-hydrogen, carbon-oxygen, and carbon-hydrogen bonds in the polymeric portion of the coating. In the UV-A region, the longer wavelengths do not have sufficient energy, (~71 to 91 kcal/mol) (3.0 to 3.8 J/mol), to break certain bonds, namely carbon-hydrogen. Thus, it is important to characterize the output of the light source used in the weathering device and determine if the spectral power distribution adequately correlates to the electromagnetic spectrum of sunlight and the actual exposure of the product being evaluated.

One type of degradation caused by exposure to solar radiation is classified as erosion. The breaking of chemical bonds first leads to a degradation of the coating surface layers and is manifested by chalking, fading, and loss of gloss. Once the protective outer layer of polymer is lost, pigments are exposed. Without the protective polymeric binder, the pigments can fade and erode, causing a change in color and/or appearance. Although pigments can and do fade even in intact polymer films, this example is provided to show one of the possible effects of solar radiation on the polymer which can lead to a visual performance defect. This is by no means the only mode of degradation, or even the most common. The modes of degradation are variable and are determined by the UV light resistance of the individual components of the coating formulation.

Sunlight has been simulated in accelerated weathering devices by filtered and unfiltered mercury arcs, open and enclosed carbon arcs, xenon arcs, and fluorescent lamps, as well as concentrated onto the paint surfaces by reflection of collected sunlight. However, as the results produced by early accelerated testing devices were compared to the results obtained from natural weathering, the light sources were modified to attempt to achieve results more similar to the natural weathering defects. Depending on the exact coating type and the service environment, several different specifications have been developed that indicate which light source should be used. Most of these test specifications require the use of open or "sunshine" carbon arcs, xenon arcs, or fluorescent lamps. These light sources were chosen based on their ability to more closely simulate the degrading UV light range of sunlight or to rapidly produce dramatic changes in the coating. Each of the light sources provides benefits as will as pitfalls to the testing process. The source chosen will depend on the current research at the time, the light sources currently available, the material being tested, the expected environmental conditions, and historical testing of competitive compounds. Since these factors will vary with each exposure and the advances in the exposure devices, a recommendation of source cannot be made in this chapter and the manufacturers of the devices and current literature should be referenced.

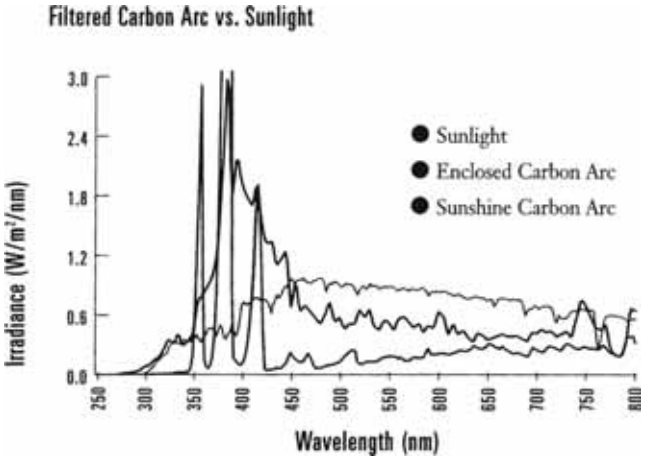

Fig. 2—Spectra of light produced by an enclosed carbon arc and a sunshine carbon arc. Used with permission of the Atlas Electric Devices Co.

ENCLOSED CARBON ARC

Originally, these lamps were used to test the light fastness of textiles. They were then combined with a water spray to be an industry-wide artificial testing device. Although mercury and carbon arc sources have been in use for over 75 years, when they were used to test paint products, it was discovered that they produce light that accelerates chalking and fading more than cracking and further testing of light sources was initiated. The carbon arc source consists of neutral solid and cored carbon electrodes. The flame portion of the lamp is enclosed in a borosilicate globe. The globe creates a semisealed atmosphere that sustains the arc and filters out UV light below 275 nm. The lamps produce two large spectral peaks that center near 350 and 380 nm, but they deliver essentially no emission below 340 nm, where the light is more severe in its degradation capabilities and more damaging to polymeric materials (Fig. 2). In addition, even the light in the visible region, 400 to 800 nm, was also low compared to sunlight, meaning that any visible color change due to the change of the pigment would require a lengthy exposure. As a result, there was incentive to produce a light source that provided a better simulation of natural sunlight, especially since more durable materials were being developed. In addition, a rigorous maintenance routine was essential for consistent operation. The rods and globe need to be cleaned daily, and the globe checked for deterioration and replacement.

OPEN-FLAME CARBON ARC

Innovation of the open flame carbon arc, or sunshine carbon arc, from the basic carbon arc was a welcomed change

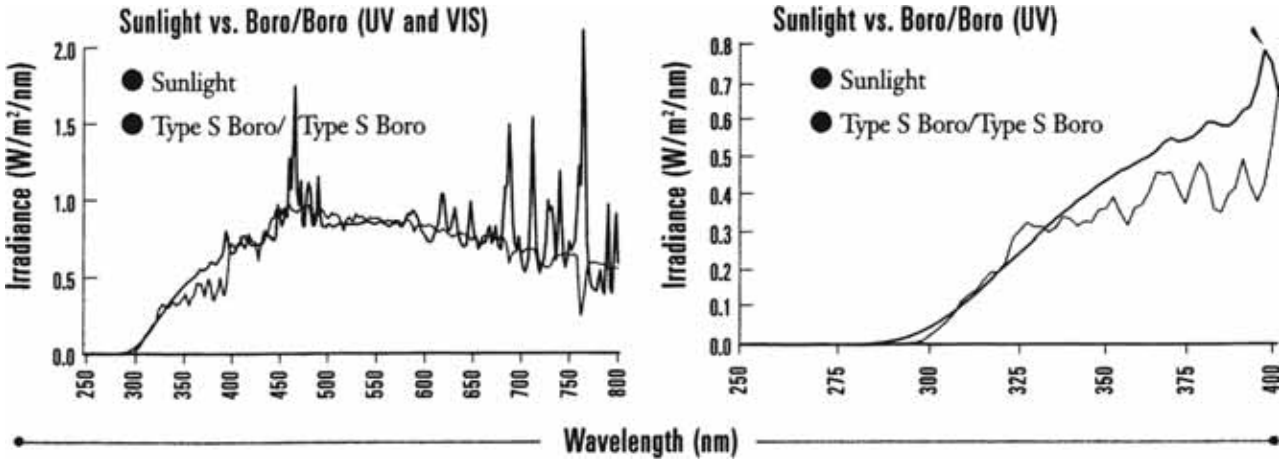

Fig. 3—Spectrum of light produced by a xenon arc with Boro/Boro filters. Used with permission of the Atlas Electric Devices Co.

since the industry saw the need for a special distribution spectrum closer to that of sunlight. The lamp operates in a free flow of air instead of in a globe. The lamp is composed of copper-coated electrodes and a central core of rare earth. The lamp is surrounded by a stainless-steel filter frame that also acts as an air duct. The frame holds flat, optical, heat-resistant, borosilicate glass panels that filter portions of the lower wavelength light from the spectrum. The spectrum produced by this light source is more similar to that of sunlight in the region between 310 and 370 nm (Fig. 3). However, there was still a spectral imbalance due to large bands between 370 and 450 nm, but the region between 450 and 800 nm was closer to natural sunlight than the enclosed carbon arc lamp shown in Fig. 3. The disadvantage of this light source is the emission between 260 and 310 nm, which includes a portion of the undesirable UV-C region. Although this light source was an improvement, the industry requested the spectral distribution of the light be even closer to that of sunlight. Maintenance issues could lead to variability since the carbon rods need to be replaced daily and the filters need to be cleaned daily and replaced periodically. A good laboratory will perform these functions as a matter of the daily routine; however, fewer laboratories are offering this service. The current use of the filtered carbon arc sources to simulate the effects of outdoor weathering has been widely deprecated by the weathering science community due to the poor simulation of the spectral distribution of the terrestrial solar radiation.

XENON ARC

The adoption of the filtered xenon arc solar radiation sources for accelerated weathering devices was the next improvement in artificial weathering equipment. The xenon lamp consists of a burner tube and a light filter system. There are two types of xenon arc lamps. One type of xenon arc lamp is cooled by water circulated through the lamp housing. The cooling water also filters out a portion of the long-wavelength infrared light. The other type of xenon lamp is air-cooled. Both lamp types produce a spectrum closer to sunlight when filtered and set at the correct irradiance setting. There are several filters and combinations of filters that can be used. The three common filter combinations used for artificial weathering of paint are quartz/borosilicate, borosilicate/borosilicate, and quartz/quartz. The first combination allows the UV region to extend down to 270 nm (Fig. 4). The borosilicate/borosilicate combination is the most common combination and has a cutoff at 280 nm, which makes the spectrum closer to that of natural sunlight, which cuts off at 295 nm. The quartz/quartz combination produces a spectrum that extends to below 250 nm, i.e., into the undesirable UV-C region, and although used to test coatings, it is the least popular of the three filter combinations. If a more precise match for the solar cutoff and full UV spectrum match is needed, an option of lower temperatures is available with a coated infrared absorbing (CIRA) quartz/soda lime filter combination. With all of these combinations there is an increased spectral output in the 450–500 nm region when compared to the spectral output of natural sunlight.

Recently, an additional filter has been introduced to the market [5]. The spectra distribution of this filter used as an inner filter with a quartz or CIRA filter provides a spectral distribution of xenon light that matches the spectral distribution of sunlight more closely than any testing light source to date (Fig. 5).

Since the xenon arc source decays as the lamp ages, the irradiance of the light source should be monitored and can be controlled by adjusting the lamp wattage. All modern devices have a monitoring system that adjusts the lamp power to compensate for the decay. The settings for the lamps are referenced in many of the standards and should be referenced depending on the exposure required. Common settings produce a spectrum with approximately the same cutoff wavelength (determined by the filter) as natural sunlight. The settings are chosen to be within the range of natural sunlight. Note that a variance in the wattage settings results in changes of the degradation rate of the coatings.

FLUORESCENT UV LAMPS

Another development in light sources is the fluorescent UV lamp [6,7]. These lamps were not developed to simulate the entire spectral range of natural sunlight. Rather, they simulate only the damaging UV region found in sunlight. Currently there are three types of fluorescent UV bulbs. The QFS-40 and UVB-313 produce light with a maximum output at 313 nm (Fig. 6). The UVB-313 has a higher

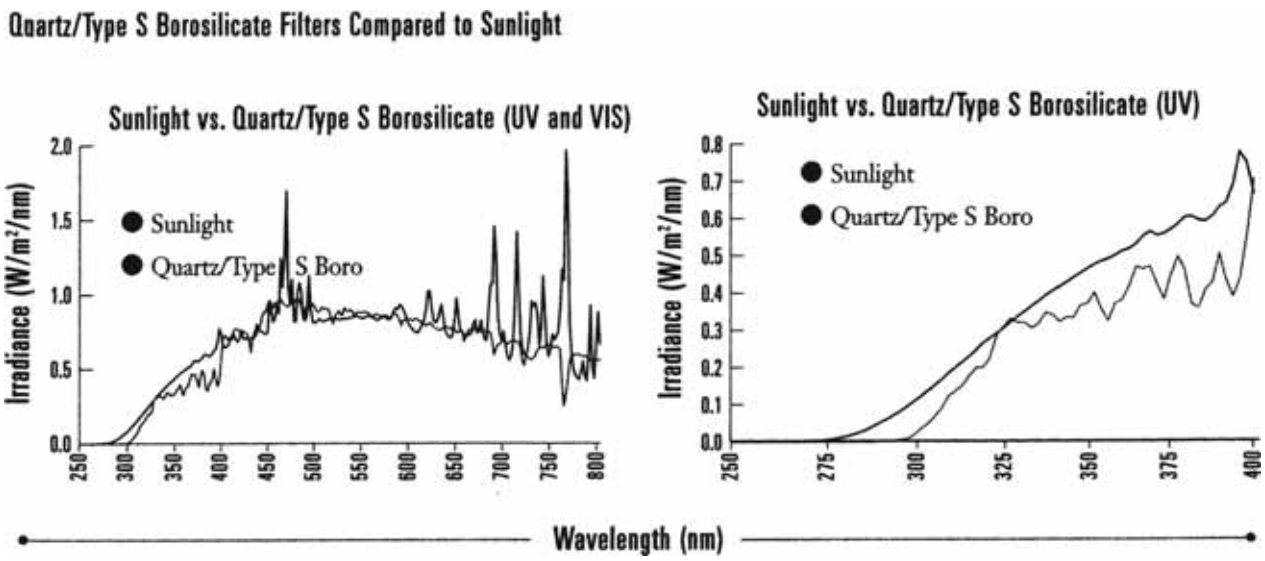

Fig. 4—Spectrum of light produced by a xenon arc with Quartz/Boro filters. Used with permission of the Atlas Electric Devices Co.

intensity and thus a greater weathering acceleration rate than the QFS-40. Since the UVB-313 has a higher, more stable output than the QFS-40 and the devices can now be adjusted to lower the irradiance, the QFS-40 bulb is being phased out of production. Both of these lamps have outputs down to 275 nm, which is below the cutoff of natural sunlight, and can lead to anomalous results [8]. The third type of fluorescent lamp is the UVA-340 lamp that produces a spectrum very similar to that of natural sunlight (Fig. 7). The spectrum is made up of wavelengths in the UV-A region with a small amount of the UV-B region wavelengths. The cutoff matches that of natural sunlight, but provides little exposure to light above 390 nm. Although the results produced by the UVA-340 lamp are closer to that of sunlight, the UVB lamp had been a widely used fluorescent light source because of the rate at which degradation occurred. In some cases the degradation produced by the higher output UVB-313 bulbs was not found to match the actual degradation that occurred in actual application. The bulbs continued to be used

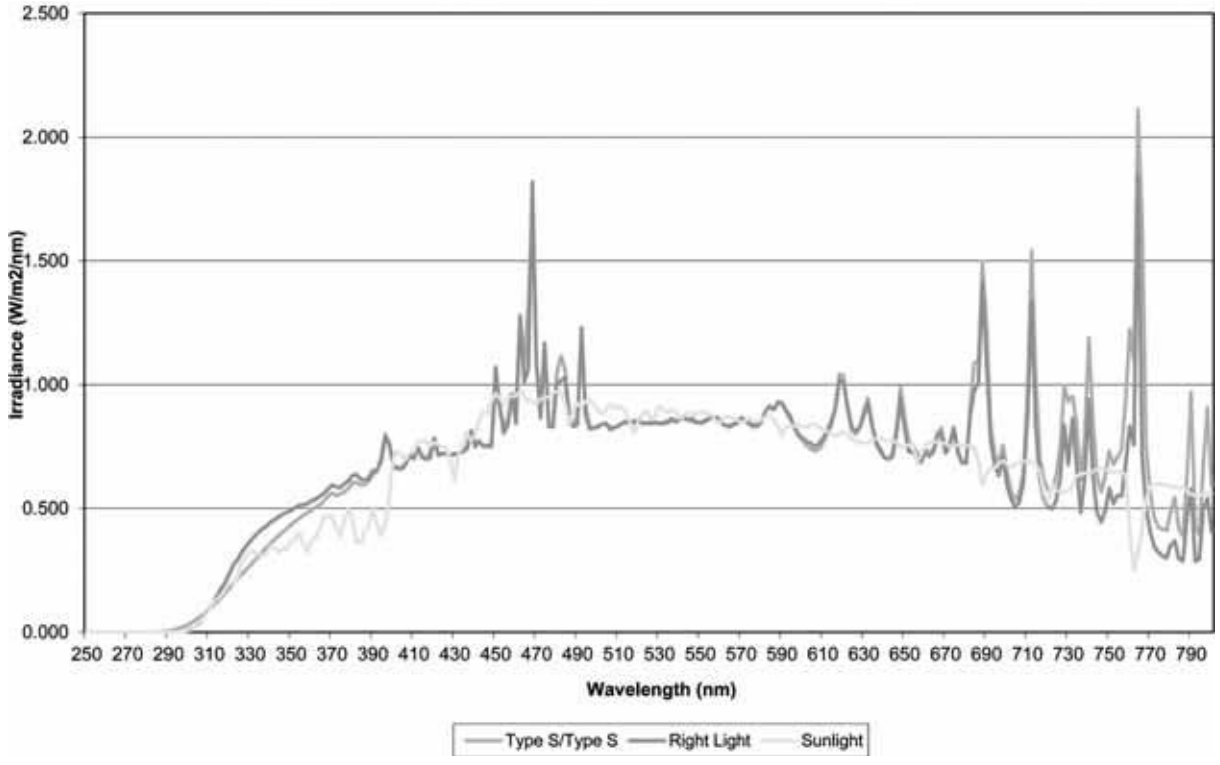

Fig. 5—Right light filter system versus sunlight. Used with permission of the Atlas Electric Devices Co.

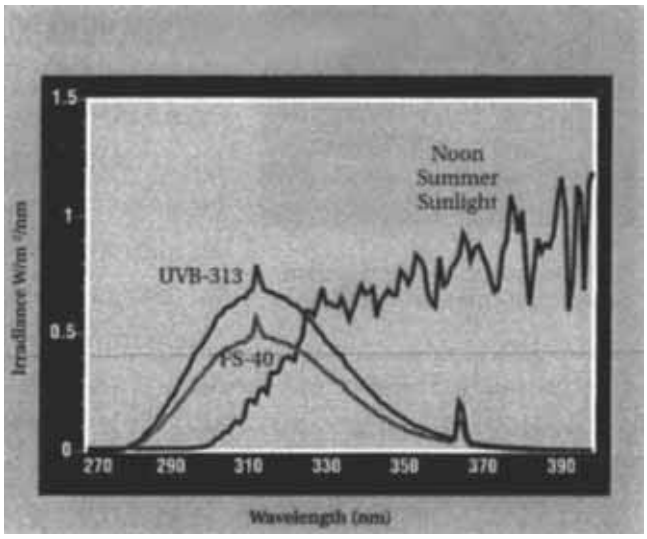

Fig. 6—UVB-lamps versus summer sunlight. Used with permission of the Q-panel Co.

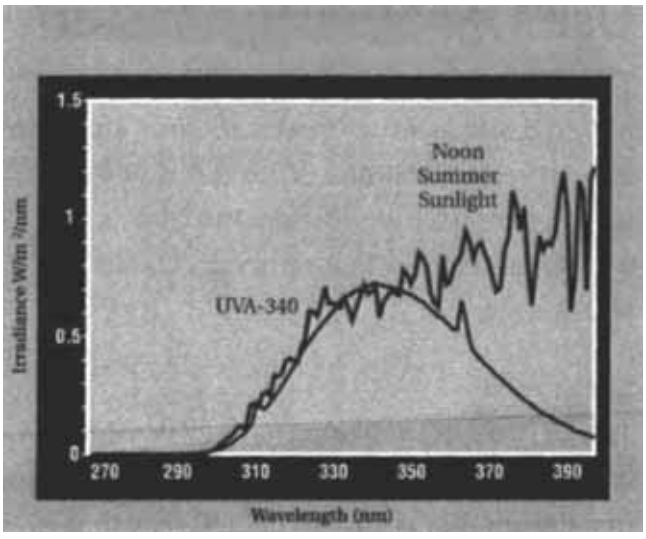

Fig. 7—UVA-340 lamps versus summer sunlight. Used with permission of the Q-panel Co.

since so much of the historical comparative data had been obtained using the UVB-313 bulbs. The change to the UVA-340A bulb has taken time, but these bulbs are currently the most used fluorescent bulb. Since the UV cutoff of the UVA-340 lamp is higher, the degradation process takes a longer period of time than with the UVB lamps, but often more closely matches the degradation seen in the field and is still accelerated when compared to outdoor exposure tests. The degradation of the coatings produced by the fluorescent bulbs may be significantly different from those of natural weathering due to the lack of long wavelength radiation. Beyond the peak output for these lamps, the spectrum is much weaker than the visible light spectrum. Due to the lack of output in the visible light region, coatings of different colors do not vary much in surface temperature, unlike variations produced by natural sunlight.

Changes in instrument technology and uses of monitoring devices have been used to increase the irradiance of the fluorescent bulbs. The bulbs can be operated at up to 1.75× the normal level to increase the intensity of the light, without changing the spectral distribution. In this way, the UVA-340 bulbs, set at a higher irradiance, can be used to produce quicker results without introducing an unnatural wavelength as produced by the UVB-313 bulbs. The bulbs used at the higher irradiance level should be monitored to evaluate bulb aging and decay in irradiance output [8].[2]

METAL HALIDE

New technology and testing requirements are pushing manufacturers to perform additional exposure tests on all of the products offered to the consumer. One of the other advances in artificial weathering is the use of metal halide lamps. These do not have a continuous spectrum, but a large number of individual spectrum lines over a wide spectral range. Several rare earth metals are present and when used together produce a spectrum similar to sunlight. These lamps have to be used with filters, measuring devices to stabilize the irradiance, and electronic power supplies to provide a spectral power distribution that matches solar radiation. These lamps are high efficiency and thus suited for use in large-scale chambers. Several different radiation units are used for the large-scale exposure and can be moved around the testing area to simulate different light exposure conditions, such as sunrise, sunset, and other incident angles of interest. While it has been determined that the metal halide devices can reproduce the relative energy with a defined range, these are not known to be good overall simulators of sunlight. Additionally, the current lamps vary in output from one to another, which means that each lamp must be measured to determine the suitability to the exposure project. The temperature of the environment surrounding the lamps must also be monitored since the spectral distribution will vary with temperature changes.

LAMP STABILITY

Once a light source has been selected, it is assumed that several tests run over a period of months or years can be used to evaluate the relative performance of the paints. However, this assumption is not always true. Essentially all new accelerated weathering devices are now sold with irradiance control. Even with this control, the output of the light source may vary depending on the care and maintenance of the device. All of the devices should be cleaned and the light sources changed as recommended to ensure the most reproducible and even spectral distribution and irradiance. The newer devices have the option of monitoring and adjusting the light output, or irradiance, for all of the different light sources. Many of the methods used for testing now recommend monitoring the irradiance. In the future, these settings may become a required part of the report for the testing results. The monitoring devices take the guesswork out of determining exactly when to clean or change a light source. The monitoring can lead to

[2] ASTM has found suitable devices available and used by DSET Laboratories, Inc., Box 1850 Black Canyon Stage 1, Phoenix, AZ 85029 and at Sub-Tropical Testing Service, 8290 S. W. 120th St., P.O. Box 560876, Miami, FL 33156.

extended service of the light source, increased reproducibility of results and better overall maintenance of the testing devices. In summary, the maintenance of the device according to sound practices and manufacturers recommendations is required for reliable operation and consistent data for comparison purposes.

There are several monitoring instruments available to measure the light output including pyranometers, radiometers, spectroradiometers, and light-sensitive materials. However, each of these devices may be used to measure different characteristics of light. Two different-colored light sources could produce the same response if a pyranometer is used to measure the light. These devices measure the amount of radiant power regardless of the spectral distribution. Even when filtered to restrict the wavelength of light being measured, it was found that the response was not sufficiently sensitive for the UV range.

Radiometers have been modified with filters to select areas of the spectral distribution. These are classified as wide band, broad band, or narrow band. The wide-band instruments measure the light output over a range of several hundred nanometers. Broad-band instruments function over a range of 20 to 100 nm, while narrow-band instruments measure less than 20 nm. The most commercially successful radiometer measured the total UV light using a wide-band UV filter. However, when these devices were used to measure natural sunlight in comparison to the light sources, it was found that sensitivity to shorter wavelength UV was less than its peak sensitivity to visible light, which could be affected by temperature changes.

The currently used radiometer, developed for exterior monitoring, has a narrow band filter and a thermoelectrically cooled detector. This is suited for long-term use and is easily operated in the field or laboratory by relatively inexperienced personnel.

For internal use and for the most accurate measurements, spectroradiometers are available. These would not withstand external use and normally require operation by skilled personnel.

In contrast to actual light measurements, there are industries, other than the paint industry, that rely on the use of light-sensitive reference materials. The reference material is placed in the cabinet at the same time as the test samples and monitored, usually for color changes, to evaluate the effectiveness of the light source. These materials must be inherently unstable to achieve the desired result. This instability should be considered when choosing a reference material. The reaction of some materials may vary widely, and the sensitivity is often a result of the total environment, so all of the other factors of exposure must remain constant. One of the major problems with using this technique in the paint industry is the short life of these materials relative to the more durable paint systems.

Even with all of the variability of light sources, proper care of the instrument can yield consistent results between laboratories. Most of these instruments have been run for many years with less monitoring and fewer quality-control procedures than are in use today, and the data have been acceptable over many years. This is due to the fact that most companies understand that the test results can vary, and to that end often include several competitive materials in the test protocol.

Moisture

Another important characteristic of weathering is moisture. Moisture is commonly overlooked as a significant factor of paint degradation because it is a common belief that structures are only wet when it rains, when they are splashed, or when they are immersed in fluids. Actual time-of-wetness studies have shown that samples placed outside in several different locations in the United States and Canada were wet approximately 30 % of the time [9]. This averages to approximately 8 h per day. The water in a natural environment is caused by dew (high relative humidity), rain, or melting snow or ice. During contact, the water may be absorbed or pass through the coating and several types of degradation may be initiated. One example is the liquid passing through the coating and interacting or reacting with a water-soluble material resulting in the formation of an osmotic cell. Another process could be initiated if moisture passes through the coating and reacts with the substrate, for example wood; the interfacial bond between coating and substrate may be destroyed or weakened. The process that affects most coatings is the cyclic absorption and desorption of water.

The theory behind cyclic moisture exposure is based on the permeation, or absorption, of the liquid into the coating, which may cause certain coatings to swell. During the drying, cycle desorption, evaporation will occur, causing the coating to shrink, resulting in cyclic stressing of the system. Inner layers of the coating material may be at different points in the cycle, relative to the top surface, adding additional stress within the coating system. The cyclic changes can lead to flaking and surface stress cracking, as well as cracking and peeling of the entire coating system.

The process by which degradation takes place and how fast it will occur is influenced by the permeability of the coating and the contact time required to initiate water penetration. Additionally, the rate of water and chemical degradation is increased by increased temperature and UV light exposure.

The temperature of the coating when the exposure to moisture occurs can change the way the moisture affects the coating. Rain in particular can cause thermal shock and lead to erosion of the paint surface. If the surface of the paint is warm, the rain striking the surface initiates an evaporation process, which quickly cools the surface and may lead to surface degradation. Freeze-thaw cycles and frozen rain or hail can also cause surface degradation to occur more rapidly, but are not addressed in this chapter.

For testing purposes, moisture can be simulated by water spray, condensation, fog, or immersion. Depending on the device used, degradation acceleration is possible by increasing the number of wet/dry cycles or increasing the time of exposure. Since accelerated weathering devices run around the clock (and day after day for that matter), it is possible to cycle the specimen through several wet and dry periods and still meet or exceed the 8 h of average wetness found in natural weathering. Another way to accelerate the damage caused by moisture is to increase the time period of exposure to moisture. Prolonged exposure may degrade coating just as much as the stresses caused by wet/dry cycling.

Although the time of wetness is a big factor in the initiation and perpetuation of the degradation process, it is important to consider the purity of the water itself. The

water used for testing should be clean and meet the specifications outlined in the device manufacturer's instructions. Introduction of chemical contamination through the water source could greatly change the degradation of the exposed coating and lead to corrosion within the exposure device, thus altering the exposure even more. The contaminant may initiate the degradation prematurely, or enhance color changes. Even small amounts of a contaminant can be of great influence since heat is applied and evaporation is induced. The heat and evaporation may concentrate the contaminant before it can be diluted or washed away by another cycle of moisture exposure. Recommendations for purification and consistency in the water supply include distillation or a combination of deionization and reverse osmosis. The cleanliness of the water supply can also determine the life of the testing equipment, which often contains items susceptible to corrosion.

Temperature

The third factor of weathering is heat or temperature. Testing performed over the years has indicated that degradation of coatings occurs more rapidly at elevated temperatures and temperature variation can lead to expansion and contraction stresses in the coating. These stresses may be magnified by the expansion and contraction of the substrate itself, which can lead to cracking, peeling, checking, or loss of adhesion. Temperature can also accelerate the effects of other weathering factors such as light and moisture. In accelerated weathering, cyclic testing at only slightly elevated temperatures can produce accelerated results. The temperature chosen for testing should be within the expected temperature range of the service environment. Drastic increases in temperature are not necessary to produce noticeable effects and in fact should be avoided. Testing at excessive temperatures can either cause premature or unreasonable failures or even enhanced performance that would not be realized under actual use condition. High temperatures may cause the coating to bake or cure excessively and cause it to become brittle with decreased impact resistance, or it may become more resistant to the environment than would occur if it were only air dried under ambient conditions. To prevent these occurrences, temperatures near those of actual or expected exposure should be used. The temperature should be monitored so the data have meaning relative to other test results.

Oxygen

Changing the degree of oxygen exposure of specimens by introduction of ozone or pure oxygen is possible with a few testing devices, but this modification in technique is not commonly practiced. Oxygen exposure is usually inadvertently changed in artificial weathering devices. The condensation, fog, immersion, or water spray used to create moisture can introduce oxygen to the test environment and the surface of the panels. Even in natural weathering, oxidation of a coating surface usually occurs in the presence of moisture.

Oxidation involves breaking bonds within a cured coating. Either primary or secondary bonds may be affected by oxidation. Since the oxidation process is different for different chemical types (acrylic, epoxide, vinyl, etc.) of coatings, the results of oxidation can range from embrittlement to softening, along with crazing, cracking, or discoloration. Oxidation usually begins as a surface phenomenon that breaks down the outer polymeric binder layers. Water can then pass through the film to the inner layers and cause further breakdown (often at an accelerated pace) of binder and additives.

Other Factors

Although light, heat, moisture, and oxygen play important roles in the deterioration process, it should be recognized that there are other factors that affect coating stability. Weather resistance is dependent on the curing or drying process, the substrate being painted, and application methods. These conditions cannot be fully simulated under controlled laboratory conditions since, as with natural weathering, these conditions are seldom consistent.

In actual service, most coatings experience environmental factors that often continually change, are not reproducible, or are unforeseeable at the time of application. Examples include acid rain or other transient environmental pollutants. Chemical exposure, particularly in the vicinity of chemical plants or other heavy industrial environments, can also contribute to degradation. Testing for chemical resistance would be relevant when such factors can be identified and is discussed elsewhere in the manual.

ACCELERATED WEATHERING DEVICES

Carbon Arc and Xenon Arc

Carbon arc and xenon arc lamp devices are used to expose specimens to UV radiation, elevated temperature, and water spray. The test conditions for paint and coatings are outlined in ASTM Standard Practice for Filtered Open Frame Carbon Arc Exposures of Paint and Related Materials (D822). The basic principles and operating procedures for xenon arc devices are found in ASTM Standard Practice for Operating Xenon-Arc Light Apparatus for Exposure of Nonmetallic Materials (G155). Additional information for these devices can be found in Standard Practice for Operating Open Flame Carbon Arc Light Apparatus for Exposure of Nonmetallic Materials (G152) and ASTM Standard Practice for Operating Enclosed Carbon Arc Light Apparatus for Exposure of Non-metallic Materials (G153).

There are several devices manufactured by several companies that use either carbon arc or xenon arc light sources. The light source for these devices should be chosen by the chemical nature of the material to be tested since the spectra of the various light sources are different and produce different weathering results. For both the carbon arc- and the xenon arc-based devices, it is very important to monitor the levels of irradiance at a selected wavelength if the data are to be used for comparison purposes. This is required because there is a progressive decrease in radiation intensity as the lamp ages. This can be overcome by progressively increasing the lamp wattage, thereby minimizing the changes in intensity, and by monitoring the radiation output as described in the corresponding ASTM procedure. The newer devices include the monitor and automatically adjust the wattage to keep the intensity constant.

Both carbon arc and xenon arc procedures include four test methods:

1. Continuous exposure to light and intermittent exposure to water spray.

2. Alternate exposure to light and darkness and intermittent exposure to water spray.
3. Continuous exposure to light without water spray.
4. Alternate exposure to light and darkness without water spray.

A typical cycle used for evaluating coatings with these devices is 102 min of light at 145 ± 5°F (63 ± 3°C) and 18 min of light and water spray at 60 to 63±2.5°F (15.5 to 17±1.5°C).

Fluorescent UV/Condensation

With fluorescent UV bulb devices as described in ASTM Standard Practice for Operating Fluorescent Light Apparatus for UV Exposure of Nonmetallic Materials (G154), specimens are cycled between exposure to UV light and condensation in a heated environment.

The light source for the QUV[3] and UV2000[4] is composed of eight fluorescent lamps that produce light in the UV range. The light source may be any of the UV fluorescent bulbs produced for accelerated weathering. The particular bulb used will determine the nature of and speed at which the results are acquired. The exterior of the specimen rack is exposed to room temperature, and the inside is exposed to heat and humidity produced by the lights and a heated water bath. The condensation is caused by the temperature differential that exists between the front and back of the mounted specimens. The exposure can be varied by changing the temperature, the length of the light, and/or the condensation segments of the cycle. A few models are also available with a spray option. The spray option can be used to simulate thermal shock or erosion by water.

The samples are mounted in brackets, which form the cabinet wall. The panels are stationary and set at an angle so condensate can run off the test surface and be replaced by fresh condensate in a continuous manner. Vents along the bottom of the chamber permit an exchange of ambient air and water vapor to prevent oxygen depletion of the condensate. The specimens are placed approximately 50 mm from the lamps. In instruments with irradiance control, the lamps and samples do not need to be rotated and the lamps are changed only when irradiance drops below the set point. In instruments without the irradiance control, both the lamps and the panels have to be manually rotated at specified intervals to ensure even UV exposure.

Various tests can be selected. If no conditions are specified, ASTM G154 suggests 4 h of UV light at 60°C and 4 h of dark condensation at 50°C. Test temperatures of 50, 60, and 70°C are widely used.

Fluorescent UV-Salt Fog

The Mebon Prohesion Cabinet [10], a cyclic corrosion chamber, was originally developed as an alternative to the standard salt fog cabinet, ASTM Standard Practice for Operating Salt Spray (Fog) Apparatus (Bl17) for conducting corrosion resistance studies. Further studies revealed that when used in conjunction with a device providing a light source, there was use as an accelerated weathering device. The procedure is outlined in ASTM Standard Practice for Cyclic Salt Fog/UV Exposure of Painted Metal, (Alternating Exposures in a Fog/Dry Cabinet and a UV/Condensation Cabinet) (D5894).

The cyclic corrosion chamber introduces a spray or fog by means of an external reservoir and a peristaltic pump operating at a flow rate of from 0.5 to 1.5 ml/h. Although a variety of solutions can be used, one consisting of 0.35 % ammonium sulfate and 0.05 % sodium chloride (Harrison's solution) is recommended for corrosion studies. A series of experiments with this device indicated that, at least for corrosion rate studies, this solution provided more realistic results than the warm, 5 % sodium chloride solution used in salt fog cabinets[2] [11,12]. The conclusion that these test results were more realistic was based on an analysis of the corrosion products. This analysis revealed that the amount of sulfur and chloride salts on panels exposed to the particular salt solution was similar to the amount and type found on the panels that had been corroded at an outdoor location. Due to the nature of the instrument, almost any exposure solution can be used to customize the testing for the location.

The fog, introduced at ambient temperature, is eliminated by forcing air through the device at 23 to 55°C. Not only does this assist in drying the panels, it also replenishes the oxygen. The wet-dry cycles can be varied from 1 to 10 h. Since the cabinet is not outfitted with a light source, it is necessary to manually move the panels from the cyclic corrosion chamber to a fluorescent UV/condensation device to incorporate the element of light into the test. The standard practice outlined in ASTM D5894 involves weekly rotation between the two instruments.

Fresnel Reflector

There are three methods for accelerating natural weather exposure: black box, heated black box, and Fresnel reflector. These are described in ASTM Practice for Conducting Black Box and Solar Concentrating Exposures of Coatings (D4141). The first two methods accelerate the weathering by increasing the temperature of the exposed surface and are discussed in the natural weathering section. The Fresnel reflector is the only method that collects and intensifies natural sunlight to accelerate weathering. The basic principles for this method are found in ASTM Practice for Performing Accelerated Outdoor Weathering of Nonmetallic Materials Using Concentrated Natural Sunlight (G90). It is performed in the desert region of Arizona using Sun-10, FRECKLE, EMMA, EMMAQUA, or other similar devices that involve the use of a mirror array [7, 13]. A more detailed description of this device is presented in the chapter that deals with natural weathering.

The concentration of sunlight is achieved by collecting sunlight on ten mirrors and focusing the reflected light onto the specimen. The assembly is designed to actually follow the track of the sun as it moves through the sky. The device is equipped with a blower to regulate the surface temperature of the specimen. The maximum surface temperature that can be reached is limited to no more than 10°C above the maximum temperature normally achieved by natural

[3] ASTM has found suitable devices available from Atlas Electric Devices Co., 4114 Ravenswood Ave., Chicago, IL 60613 and from Quartzlampen GmbH, 6450 Hanau/Main, Germany (domestic distributor is Batson Machinery, Inc., P.O. Box 3978, Greenville, SC 28608).

[4] ASTM has found suitable devices available from Q-Panel Co., 26200 First St., Cleveland, OH 44145 and from Atlas Electric Devices Co.

weathering. The test may be performed with or without water spray. The water spray is provided by an oscillating nozzle assembly, which supplies deionized water as a fine, dense mist. The water spray provides a thermal shock effect and is sprayed on the samples for set cycle times. A common cycle is 8 min of water spray per hour. Exact cycles are given in ASTMG90.

Since this method uses natural sunlight, the spectrum produced follows that of natural sunlight but at a higher intensity level. The testing can be performed for specific levels of solar exposure or for specific time periods. The quantity of light is measured by a radiometer, and it is expressed as total solar radiant exposure. The preferred method is based on solar exposure since this quantification accounts for the natural seasonal variations of sunlight. This allows, for example, results obtained in January to be directly compared to those obtained in July.

Newer technology has permitted better temperature control during cloud cover and night time exposures. Additionally, changing the number of mirrors used at different times of the year can control the irradiance levels throughout the exposure time and lead to results that may be correlated to results obtained in the future [13].

Ultrafast Weathering

In contrast to all of the above methods, this technique of ultrafast weathering does not wait for visual changes to occur on the surface. At the present time, this method is still being evaluated to determine if there is any correlation between the information gathered using electron spin resonance (ESR) spectroscopy to monitor radical formation and natural weathering results [2]. The theory behind ultrafast weathering is based on the assumption that the radicals, which form within the first several hours of the test, will reveal the relative stability of the coating. For this testing, the process of radical formation is induced by UV radiation greater than that of sunlight. The light is filtered to remove unwanted shorter wavelengths and also focused on the sample using a cooled mirror. The sample is placed between the poles of a magnet in the microwave resonator of the spectrometer. The radical formation is plotted as a function of light-exposure time. Each paint will produce a characteristic curve. If a correlation is found to exist, the curves of different paints are then to be compared to determine which exhibits the best UV light stability. This testing could be completed over several hours instead of days, months, or years.

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Chemical Resistance

Latoska N. Price[1]

THE ABILITY OF A COATING TO RESIST CHEMICAL deterioration or staining is an essential element in its evaluation [1]. Aesthetics play a key role in the decoration of a coated object. Certainly more purchasers of coated products are moved initially by appearance than by price. It has been said that a coating is a complex material that is often a component of a coatings system, which in turn provides added value to a final product.[2] What follows is a review of established test procedures with various levels of complexity and equipment sophistication that provide standardized tools for evaluation of potential flaws such as discoloration, softening, swelling, adhesion loss, gloss reduction, and pitting of the paint finish. Some methods include visual standards such as those for blister size and density or for corrosion which offer a common ground for communication or performance properties between the manufacturer and the end user of a coating. Other tests are less definitive, and while they can give insight as to how the paint may function during service, they do not necessarily correlate precisely with real life conditions. Yet, since these tests are to function in lieu of actual field exposure to predict ultimate performance, it is crucial that accelerated or simplified test parameters reproduce both the chemical as well as the physical effects of field exposure.

STAINING

Staining tests provide a thorough method of determining the ability of a coating to resist discoloration from household chemicals, chemical reagents, and other materials common in today's environment. The tests generally expose the coating surface to a spot of the reagent on the coating surface or by immersion of a coated test panel in the reagent for a specified period with timed checkpoints.

Staining from Household Chemicals

ASTM D1308, Test Method for Effect of Household Chemicals on Clear and Pigmented Organic Finishes, encompasses the evaluation of discoloration, change in gloss, blistering, softening, swelling, loss of adhesion, or other phenomena resulting from a variety of household chemicals such as distilled water, ethyl alcohol, or vinegar. Materials or chemicals suggested as reagents are outlined in Table 1.

Other materials can also be used as specified by the customer or seller. The procedure utilizes open and watch glass covered spot tests with the reagent at ambient temperature as well as immersion tests in the reagent.

Staining in the Transportation Industry

ASTM D1308, as previously mentioned, was the supplement to ASTM D1540, Test Method for Effect of Staining Agents on Organic Finishes Used in the Transportation Industry. The latter document has been withdrawn, but is available from Internet sources. Some materials or chemicals suggested as reagents are listed in Table 2.

As with ASTM D1308, discoloration, change in gloss, blistering, softening, swelling, loss of adhesion, or other phenomena are examined after testing. With some reagents, exposure to sunlight or UV radiation for a specified time is required. Elevated temperature is also used to more closely simulate surface conditions in hot, sunny climates. Gasoline resistance tests combine dripping of fuel at ten drops per minute at a 20° angle with a UV lamp trained on the surface at a 90° angle. Adequate ventilation and safe handling of the dispensing and collecting vessels are essential to safety when working with gasoline. The staining potential of solid materials requires close contact of the reagent with the surface and heat exposure before evaluation.

Staining Resistance of Furniture Finishes

Decorative finishes for wood and metal furniture can include substrates such as wood, multi-density fiber board, steel or aluminum which require more from coatings to withstand normal use. Coatings for these substrates can be waterborne or solvent borne and used for such painting techniques as marble and stone replication, the creation of visual and physical textures, painted distressed finishes, glaze effects, one of the various crackle techniques or simply to provide color. One detail these finishes all have in common is that they require a high degree of stain resistance in order to preserve the decorative surface.

Staining resistance of furniture finishes is covered as part of ASTM D3023, Standard Practice for Determination of Resistance of Factory-Applied Coatings on Wood Products to Stains and Reagents. This procedure is concerned with materials such as cosmetics, alcohol (ethanol), boiling water, and coffee. Cosmetics contain a number of waxes (e.g., candelilla, carnauba, microcrystalline) and/or oils (e.g., olive, castor) that are particularly staining. Ethanol, the alcohol found in liquors, can do particular damage since ethanol can oxidize in the air to produce acetic acid while coffee, rich in phenol acids (tannins), will wreck havoc on a furniture finish if left in contact with the surface for a period of time. Think of the dreaded coffee ring

[1] *Technical Manager Decorative Coatings, BASF Corporation, 205 South James St., Newport, DE 19701. 302-996-2913, latoska.price@basf.com.*
[2] Hegedus, C. R., "A Holistic Perspective of Coatings Technology," JCT Research, Vol. 1, No. 1, January 2004.

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TABLE 1—Staining from Household Chemicals		
Item	**Contains**	**Found in**
Alkali solution	Sodium hydroxide	Oven cleaners
Acid solution	Acetic acid	Vinegars
Soap and detergent solutions	Sodium percarbonate based bleaching systems, antimicrobial agents	Laundry detergents, soap scum removers, degreasers
Lighter fluid	Petroleum distillates	Starter for charcoal briquette fires
Fruit cut	Citric acid, tartaric acid, malic acid	Oranges, apples, grapes
Oils and fats	Simple or mixed glycerol esters of organic fatty acids	Meats, salad dressings, margarines, butter, cooking oils
Condiments	Turmeric, ascorbic acid	Mustard, ketchup, grape jelly
Beverages	Phosphoric acid, food dyes	Colas, wines, Kool-Aid
Lubricating oils and greases	Petroleum distillates	Furniture polish

left by a coffee cup, sans coaster, in direct contact with the furniture surface.

Boiling water and hot coffee, prepared by various methods, are poured on a horizontal panel surface and allowed to dry, and the surface is examined for graying, spotting, softening, staining, or other film deterioration. Cosmetics are applied to the coating surface and placed in a 50°C oven overnight and examined for discoloration or film failure. Fifty percent alcohol or 100 proof vodka is trapped on the coating surface using a 25-mm (1-in) square of double acid washed quantitative filter paper to maintain a longer wet contact with the surface of the finish.

SOLVENT/FUEL RESISTANCE

ASTM D2792, Test Method for Solvent and Fuel Resistance of Traffic Paint, relates a method of evaluating the resistance of a coating to solvent and fuel that causes blistering, wrinkling, loss of adhesion, and loss of hardness. The coating is applied to tin panels and air dried for 90 h. Half the panel is immersed in the test liquid, and the vessel is covered for a period of 4 to 18 h as may be specified by the customer. The panels are then removed and examined for defects. The panels are allowed to dry for another 24 h and re-examined for film defects and softening as compared to the unimmersed portion of the control panel.

If subtle differences between coatings are important such as comparative research and development efforts, then the panels can be examined more often without drying at intervals such as 1, 2, 4, 6, 24, and 48 h.

Battelle Chemical Resistance Cell

Several advantages over other immersion methods are claimed for this cell [2], which was developed in the course of research sponsored by Steel Shipping Container Institute, Inc. at Battelle Memorial Institute:

- Panels may be flat or indented
- Edge effects area voided
- Simultaneous testing in liquid and vapor
- Wider range of temperature

The cell consists of a Pyrex glass tube, open at both ends, held horizontally between coated test panels (Fig. 1). A convenient glass tube size is 2 in. (5.08 cm) in diameter and 3 in. (0.762 cm) in length with the ends ground flat. Gaskets are used between tube and panels to give a liquid-tight seal. The frame has screw adjustments for tightening the assembly. A sponge rubber pad behind one panel evens the pressure. A glass ring is used to surround the dimple when an indented panel is under test. The cell is filled through a hole in the middle of the tube. In use, the cell is half filled and stoppered tightly.

Bratt Conductivity Cell for Chemical Resistance

This cell [3], was designed to use conductivity of a film during chemical resistance tests as a measure of its chemical resistance. The cell proper is a 2-oz vial from which the bottom has been removed, in effect becoming a short piece of glass tubing. The cell is formed by the base plate and an additional plate with a hole that fits over the top of the vial and rests on the shoulder.

TABLE 2—Sources of stains	
Reagent	**Examples**
Glycol-based antifreeze up to 100 %	Glycol ethers
Acid, alkali, and salt solutions	Roads salts like sodium chloride or calcium chloride
Polish abrasives, creams, and waxes	Carnauba wax
Road oils and tars	Binders for asphalt, road dust control
Gasoline	Petroleum distillates
Water	Minerals
Hydraulic fluids	Glycols or silicones
Alcohol windshield washing solutions	Isopropyl alcohol
Sunscreen	Cinnamates, benzophenone, anthranilates or para-aminobenzoic acid
Insect spray	N,N-diethyl-m toluamide (DEET)

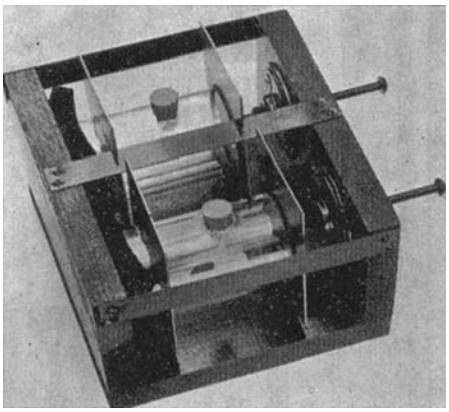

Fig. 1—Battelle chemical resistance cell. (Courtesy of Battelle Memorial Institute.)

During a test, a potential of 15 V is applied to the cell. The metal substrate serves as the positive electrode. The external resistance is selected to produce a voltage drop of about 14 V across the cell.

Resistance

Gearhart-Ball [4] solvent resistance tests utilize free coating films. The cup test employs a free film fastened over the top of a beaker or dish. Approximately 20 ml of solvent is poured over the film, and the length of time required to puncture the film is noted. This test would be considered a crude screening test. More precise data can be derived from the Distensibility test where a tensile strength strip (see ASTM D2370) is clamped with either a tensile tester jaw or an alligator clip on the upper end, and the bottom end is clamped with an alligator clip with a 12-g weight and immersed in a clear beaker containing the solvent reagent. The beaker is immediately marked with the initial length, and the time required to elongate the strip one inch is recorded.

Solvent Rub Resistance

Although solvent resistance can be evaluated using ASTM D1308, many use or adapt a solvent rubbing technique with a gauze cloth soaked in a solvent (MEK is common) and rubbing with the thumb back and forth in 2-in. (5.08-cm) strokes. This procedure, ASTM D4752, Test Method for Measuring MEK Resistance of Ethyl Silicate (Inorganic) Zinc-Rich Primers by Solvent Rub, is imprecise because the person's strength and the size of the thumb are variable. Nevertheless, it provides a quick relative test without having to wait for exposure results. The MEK resistance of some two-component ethyl silicate zinc-rich primers has been shown to correlate well with the cure of the primer as determined by diffuse reflectance infrared spectroscopy.

ACID RESISTANCE AND ACID ETCH RESISTANCE

Acid resistance is determined by exposing a coated panel to freshly prepared mortar as well as a hydrochloric acid solution and is fully described in ASTM D3260, Test Method for Acid and Mortar Resistance of Factory-Applied Clear Coatings on Extruded Aluminum Products. The acid resistance test is performed by first sealing the edges of a specially coated panel with a paraffin and beeswax mixture and then immersing the panel in a 10 vole % solution of 31.6 % solution of HCl at ambient temperature for 6 h, followed by rinsing, drying, and examination for blistering, peeling, lifting, crazing, flaking, or discoloration. Acid resistance however, should not be confused with "acid etch" resistance which is a completely different chemical resistance property. The acid etching of an exterior coating results from sulfur dioxide emissions from the atmosphere. In an automotive clearcoat, for example, etching appears as a non-removable water spot. The physical damage of etch is associated with a localized loss of material resulting in visible pitting of the surface. Evaluation of acid etch resistance is typically evaluated through the use of field testing usually in Jacksonville, Florida. While there is no definitive ASTM test for acid etch resistance, several laboratory tests have been developed.[3,4] Mortar resistance is performed by applying a fresh mortar patty, prepared to a specified formula, to both sides of the specially coated panel and then placing it in a high relative humidity cabinet for seven days. The mortar is then carefully removed and the panel wiped off with a damp cloth followed by examination as with the acid test.

ALKALI AND DETERGENT RESISTANCE

ASTM D1308, Test Method for Effect of Household Chemicals on Clear and Pigmented Organic Finishes, is also recommended for evaluating alkali and detergent resistance. It is a simple common sense technique that can be used for many materials or chemicals that can stain or discolor a coating. The choice of testing materials should be related to the coatings end use. As previously mentioned, ASTM D1308 describes techniques for either immersing the coated substrate in the reagent, putting a small amount of the material on the coated surface and covering with a small watch glass, or just leaving the material on the surface uncovered. The coating is then checked for staining after a period of time or at 1, 2, 4, 6, 24, and 48 h intervals.

For detergent resistance of appliance finishes, a solution of a specified detergent containing a high percentage of sodium phosphate is applied and the temperature maintained at 165°F (73.8°C) for the duration of exposure, usually 250 to 500 h. The test panel is submerged at least six inches into the solution. This is a more severe test than a spot test, but it is more representative of actual service conditions. Examination is done after rinsing and blotting the panel and looking for any manifestation of coating failure.

ASTM D154, Standard Guide for Testing Varnishes, and related but withdrawn ASTM D1647, Test Method for Resistance of Dried Films of Varnishes to Water and Alkali, describes an alkali resistance immersion test using coated test tubes. The use of test tubes coated by dipping into the coating prevents the reagent from creeping under the edge of a flow-on film. As many as 20 tubes are prepared for this test, allowing examination after 1 to 8, 16, and 24 h. The exposed specimens are rinsed with water and allowed to dry for 30 min before examining for whitening, blistering, or removal of the film.

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WATER AND MOISTURE RESISTANCE

Resistance to water/moisture is potentially affected by many variables such as water source (deionized, tap, pH, saltwater, fresh), exposure format (water vapor or liquid), immersion conditions (static or stirred, stagnate or refreshed), application schedule (cyclic or continuous), temperature (heat/ drying; freeze/thaw). A number of exposure chambers are commercially available including salt fog cabinets, humidity cabinets, and cyclic chambers, that test moisture resistance as well as other resistance criteria, especially weathering.

For resistance to continuously wet conditions, a simple practical test is to partially immerse a coated sample in a glass beaker containing water. The water is maintained at 100°F (37.7°C) for an extended period of time, and panels are periodically checked for discoloration, whitening, or blistering of the film. The test results are compared to a specification or standard sample run concurrently. The procedure for this test is ASTM D870, Standard Practice for Testing Water Resistance of Coatings using Water Immersion.

SALT FOG TEST

Salt fog resistance is important for marine, automobile, and aircraft coatings and any other exterior coating exposed to salt spray by being near the ocean or exposed to salted road conditions. The severe corrosion caused by salt is well known. Salt Fog testing (ASTM B117) is popular because it is simple to run and powerfully accelerates corrosion. However, reproducibility is highly dependent on strict process control of the equipment operating parameters. The use of replicate panels plus positive and negative controls is likewise critical.

Caution is required when comparing salt fog resistance among various coating/substrate combinations in order to predict service life. Certain substances are notorious for poor resistance to salt fog, yet have an excellent record of field exposure corrosion resistance. Additional factors such as sample configuration (especially the presence of moisture traps such as hem flanges or coach joints) also strongly influence corrosion.

Familiarity with ASTM G1 Practice for Preparing, Cleaning, and Evaluating Corrosion Test Specimens and G16 Guide for Applying Statistics to Analysis of Corrosion Data will also be beneficial. Communication of corrosion results will be facilitated by reference to visual standards such as those for blister size and density (ASTM D714 Standard Test Method for Evaluating Degree of Blistering of Paints) and for corrosion (ASTM D610 Standard Test Method for Evaluating Degree of Rusting on Painted Steel Surfaces).

The test requires a salt fog cabinet and coated panels. The coating is scored to the bare substrate with an X shape (Fig. 2). The edges are sealed with a weatherproof tape, and the panel is placed in the cabinet for a specified period of time. The metal panels are exposed to the settling fog of an atomized neutral (pH 6.5 to 7.2) sodium chloride solution consisting of five parts by weight sodium chloride and 95 parts distilled or deionized water. The sample is then periodically checked to see if the rusted exposed metal has propagated under the coating causing coating failure (Fig. 3). As with water resistance, the results are compared to a standard or a specification.

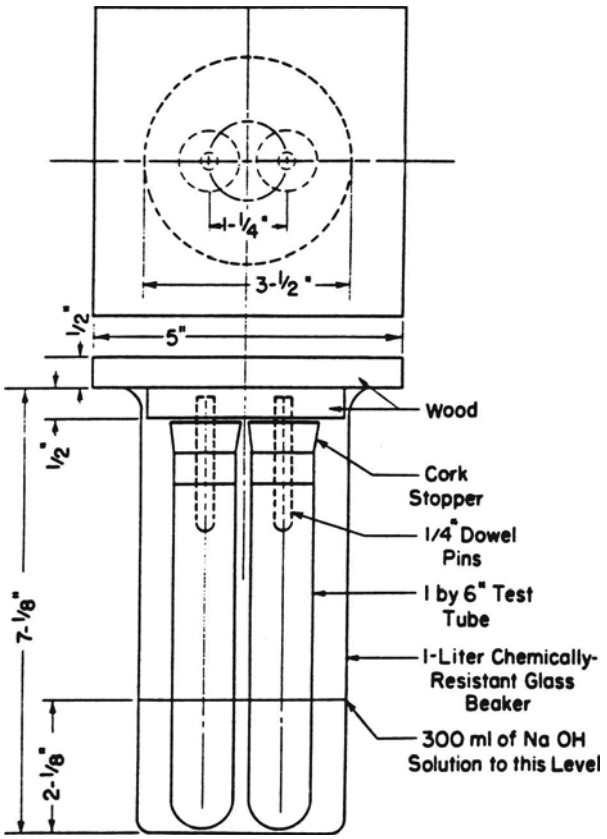


Fig. 2—Apparatus for alkali resistance test.

A typical salt spray cabinet as shown in Fig. 4 incorporates a basic chamber, an air saturator tower, a salt solution reservoir, atomizing nozzles, specimen supports, a heater, and controls for maintaining specified temperature. Such chambers are available commercially from several suppliers. The testing procedure, ASTM B117, Practice for Operating Salt Spray (Fog) Apparatus, describes this method in more detail.

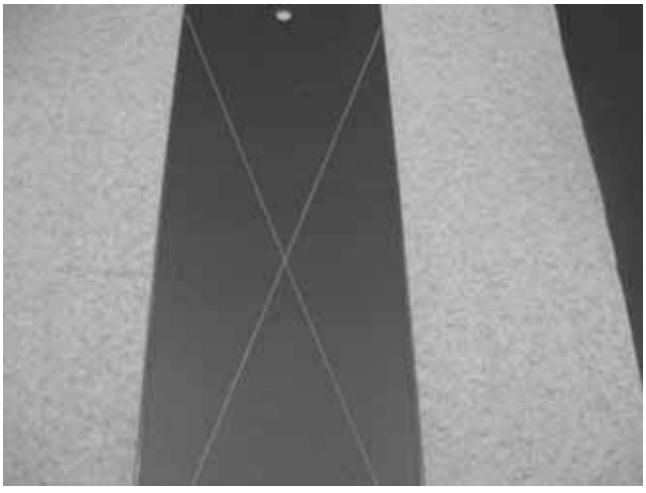
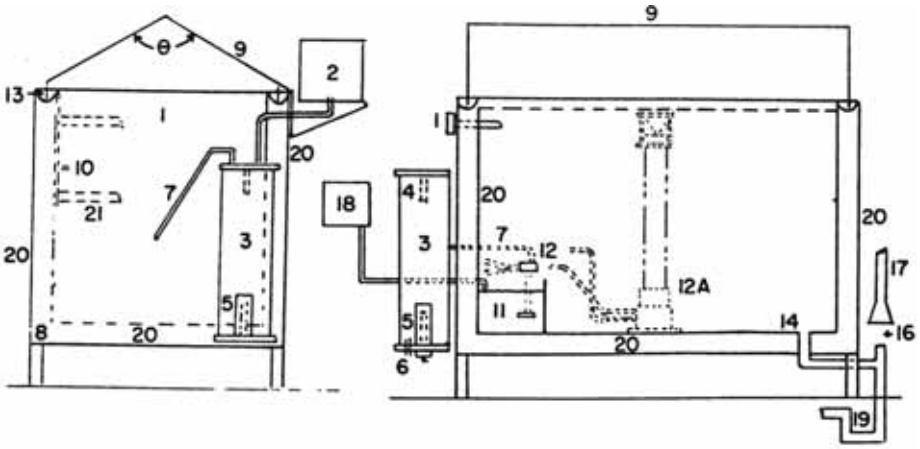


Fig. 3—Q panel is scored with an "x" to expose bare substrate.



θ—Angle of lid, 90 to 125 deg.
1—Thermometer and thermostat for controlling heater in base.
2—Automatic water levelling device.
3—Humidifying tower.
4—Automatic temperature regulator for controlling heater.
5—Immersion heater, nonrusting.
6—Air inlet, multiple openings.
7—Air tube to spray nozzle.
8—Strip heater in base.
9—Hinged top, hydraulically operated, or counterbalanced.
10—Brackets for rods supporting specimens, or test table.
11—Internal reservoir.
12—Spray nozzle above reservoir, suitably designed, located, and baffled.
12A—Spray nozzle housed in dispersion tower located preferably in center of cabinet.
13—Water seal.
14—Combination drain and exhaust. Exhaust at opposite side of test space from spray nozzle, but preferably in combination with drain, waste trap, and forced draft waste pipe.
16—Complete separation between forced draft waste pipe and combination drain and exhaust to avoid undesirable suction or back pressure.
17—Forced draft waste pipe.
18—Automatic levelling device for reservoir.
19—Waste trap.
20—Air space or water jacket.
21—Test table or rack, well below roof area.

Fig. 4—Diagram of salt-spray (fog) cabinet.

HUMIDITY EXPOSURE

Humidity exposure tests are widely used to test paint film integrity. Exposure to humidity can cause deleterious effects to a coating which can manifest as blisters, or delamination. In ASTM D2247 Practice for Testing Water Resistance of Coatings in 100 % Relative Humidity, the panel face is exposed to 100 % relative humidity at 38°C while the back of the panel is exposed to room temperature conditions. This allows for water to continually condense on the panel surface. ASTM D1735-08 Standard Practice for Testing Water Resistance of Coatings Using Water Fog Apparatus covers the basic principles and operating procedures for testing water resistance of coatings in an apparatus similar to that used for salt spray testing. Alternative practices for testing the water resistance of coatings include ASTM D870 Practice for Testing Water Resistance of Coatings Using Water Immersion and ASTM D4585 Practice for Testing Water Resistance of Coatings Using Controlled Condensation.

PHOTOCHEMICAL WEATHERING

Virtually all exterior field service on earth includes exposure to UV radiation and photochemically induced changes are a key factor in reproducing changes in chemical resistance during use. ASTM D4141, Conducting Black Box and Solar Concentrating Exposures of Coatings, describes several procedures for use in evaluating the degradation of coatings as a result of outdoor exposure. Environmental factors such as acid rain or alkaline bird droppings, as well as repeated heating and cooling, also contribute to a loss of coating film integrity which can result in loss of adhesion and a decrease in gloss. For these reasons, accelerated weather testing now frequently includes cyclic exposure to elevated temperatures and moisture as well as UV radiation. ASTM G155 Operating Xenon Arc Light Apparatus for Exposure of Non-Metallic Materials describes a frequently used artificial weathering method.

Cyclic Testing

The recognition that a warm, continuously wet environment does not accurately simulate the field exposure condition for many coatings/substrate systems, has led to implementation of cyclic test methods. The objective is to shorten test length while preserving the chemical degradation that occurs in the actual field service as well as replicating damage to coating and substrate. Research has documented the transitions from wet to dry more accurately replicated forms of corrosion such as pitting observed in the field. Similarly, cycling above and below the Tg of the coating also accelerates degradation.

ASTM D6675 Practice for Salt-Accelerated Outdoor Cosmetic Corrosion Testing of Organic Coatings on Automotive Sheet Steel, GM 9504P General Motors Accelerated Corrosion Test, JASO M610 Cosmetic Corrosion Test

Method for Automotive Parts, SAE J1563 Guideline for Laboratory Cyclic Corrosion Test Procedures for Painted Automotive Parts, and SAE J2334 Cosmetic Corrosion Lab Test describes practice and schedules for various moisture, heat and electrolyte exposure combinations for automotive products. Other cyclic methods are oriented to the specifics of other application and expected field conditions.

Apparatus for cyclic test can be fully or partially automated. Equipment may or may not include exposure to radiation. In partially automated systems, samples may manually move between different test chambers such as in D5894 Practice for Cyclic Salt Fog/UV Exposure of Painted Metal, Alternating Exposures in a Fog/Dry Cabinet and a UV/ Condensation Cabinet.

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Water-Resistance Testing of Coatings

John Fletcher[1] and Joseph Walker[2]

PREFACE

IN PREPARATION OF THIS CHAPTER, THE CONTENTS of the fourteenth edition were drawn upon. The authors acknowledge the author of the fourteenth edition, Wayne Ellis (Deceased). The current edition will review and update the topics as addressed by the previous author, introduce new technology that has been developed, and include up-to-date references.

Other chapters in this manual cover the influence of water on the formulation and durability of organic coatings. Recent ASTM publications about the moisture effects in building materials are listed in the Bibliography at the end of this chapter. These publications describe moisture problems and solutions involving coatings and their uses. Although this chapter is intended to describe only the principal testing and evaluation of water resistance, some general remarks may be helpful in understanding the test conditions.

EFFECTS ON COATINGS OF EXPOSURE TO WATER AND WATER VAPOR

The adhesion of coatings to substrates is strongly influenced by the absorption of water and by the permeability of the coating to water vapor. The mechanism of this influence proceeds as follows [1]:

1. Absorption of water molecules in the coating film.
2. Inclusion of water in the interface between film and substrate.
3. Blister formation.
4. Corrosion/erosion of the substrate.
5. Flaking or peeling of the film.

Although there is no fixed relationship between water absorption and water vapor permeability, generally the higher the water absorption the more permeable the film is to water vapor. Normally the permeability measurements are made on freshly applied films. It should be noted that with progressive aging and weathering, films become more cross-linked, and in the case of water-sensitive binders, the water-soluble additives are washed out by exposure to rain and dew. Hence such films will show decreasing permeability with time.

Water resistance is defined by ASTM as "measured ability to retard both penetration and wetting by water in liquid form" [2]. It is a required property for coatings in almost all cases. Water resistance generally is measured on specimens of coatings applied to nominally impermeable substrates such as metal, wood, or masonry. (Water vapor permeability, on the other hand, is evaluated on free films.) Water resistance may be evaluated as part of other test regimes, such as exposure testing, water repellency, corrosion, chemical resistance, salt-fog resistance, and cycling tests such as humidity-cycling and light-and-water-exposure testing.

Water repellency is defined as the property of some materials which makes water hardly stick to them (hydrophobic). Chapter 67 of the Gardner Sward Coating Handbook deals with water repellent coatings.

Water-repellent coatings appear in some ASTM test methods for coatings on concrete and wood. D6489, Standard Test Method for Determining the Water Absorption of Hardened Concrete Treated with a Water Repellent Coating, describes a procedure for the determination of the water absorption by a core of concrete taken from a surface treated with a water repellent. The specimen is dried to a constant weight and the portions of the specimen not treated with the water repellent are sealed with an impervious sealing material. The specimens are weighed and immersed in water. The specimens are removed from the water, weighed, and percent water absorption is calculated.

Water repellent coatings on wood are described in D4446 and D5401. D4446, Standard Test Method for Anti-Swelling Effectiveness of Water-Repellent Formulations and Differential Swelling of Untreated Wood When Exposed to Liquid Water Environments, describes measurement of the swelling after immersion. Wood samples in the form of elongated slats that represent the timber species or product/treatment combination to be evaluated are exposed in soak containers. The elongated slats are immersed in the water-repellent formulation, conditioned with appropriate weighing, and then subjected to immersion in distilled water for a prescribed period. The untreated slats omit the immersion in the water-repellent formulation. The swelling resulting from immersion for the selected time period is determined by reading a dial gage calibrated in increments of 0.025 mm (0.001 in.). A water repellent efficiency of 60 % is required to pass this test.

D5401, Standard Test Method for Evaluating Clear Water Repellent Coatings on Wood, evaluates the effectiveness of clear water repellent coatings on wood before or after exterior exposure. Five ponderosa pine specimens are treated with the clear water repellent under test and allowed to dry for seven days. Five untreated specimens serve as controls. The treated and untreated specimens are each weighed and then allowed to float in water for 30 min. The specimens are removed, the excess water is wiped off, and each is reweighed. The effectiveness of the water repellent coating is then calculated.

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PERMEABILITY CUPS

ASTM E96, [3] Standard Test Methods for Water Vapor Transmission of Materials and D1653 [4], Standard Test Methods for Water Vapor Transmission of Organic Coating Films, both include wet cup methods using the Payne Cup (Fig. 1). A free film of paint is created on a surface that can be peeled off the film when it is cured, for example, silicone paper is suitable for some types of paint. This film is used to cover the aluminum cup, which contains a quantity of water. The film is tightly clamped with a sealing gasket to the lip of the cup and the cup together with the film and the water are carefully weighed. The cup is left for the period of the test so that the water evaporates and the cup and its contents are weighed and the weight loss is noted. The permeability of the film can be calculated from the weight loss, the area of the cup and the duration of the test.

There is a useful paper describing problems with the wet cup method for films with moderate to high water vapor permeability and how to improve results [5].

There are instruments on the market that measure the water vapor transmission of films more easily and rapidly than the methods described in ASTM E96 and D1653. However, it appears that no side-by-side tests have been run comparing such instruments to the wet cup methods for precision and accuracy. It is probable that instrumental methods offer considerable advantages where water vapor transmission measurements must be carried out often and/or in large numbers, but where only occasional measurements are needed, Payne Cups are adequate and economic.

TRADITIONAL TEST METHODS

Spot tests and immersion tests of coatings applied to substrates traditionally have been used as "quick and dirty" techniques to compare specimens. Criteria for evaluation include softening, blistering, solvation, color change, loss of adhesion, and rusting or other deterioration of the substrate. These observations should lead to further and more comprehensive testing related to intended conditions of product use. Such testing may include immersion, exposure to controlled condensation, 100 % relative humidity, or water fog to evaluate moisture-blistering resistance. Even more intensive testing may involve washability and scrub resistance.

SPECIMEN PREPARATION

Careful preparation of coated specimens is essential to assure a proper and meaningful relationship to field exposure and to avoid false test results. The substrate composition and surface preparation, specimen preparation, and the number of specimens should be agreed upon between involved parties prior to testing. Applicable methods for the preparation of test panels are given in ASTM Methods D609 [6], D1734 [7], and Practice D1730 [8]. Test Methods D823 [9] cover application techniques for the production of uniform films.

EVALUATION

ASTM D1654, Standard Test Method for Evaluation of Painted or Coated Specimens Subjected to Corrosive Environments describes the evaluation in terms of the blistering associated with corrosion, the loss of adhesion at scribe marks on the specimen, softening of the film or other film failure.

IMMERSION TESTING

ASTM Practice for Testing Water Resistance of Coatings Using Water Immersion (D870) describes basic principles and operating procedures for testing water resistance of coatings by the partial or complete immersion of coated specimens in distilled or demineralized water at ambient or elevated temperatures. Coated specimens are partly or wholly immersed in water in a container that is resistant to corrosion (Fig. 2). The exposure conditions are varied by selecting the temperature of the water and the duration of the test.

Failure may be caused by a number of factors, including a deficiency in the coating itself, contamination of the substrate, or inadequate surface preparation. Any effects such as color change, blistering, loss of adhesion, softening, or embrittlement are observed and reported. These test results typically are a pass or fail determination, but the degree of failure also may be measured.

Fig. 1—Payne Permeability Cup. (Reprinted by permission of Elcometer Inc.)

Fig. 2—Ford Bath Immersion Test. (Reprinted by permission of Elcometer Inc.)

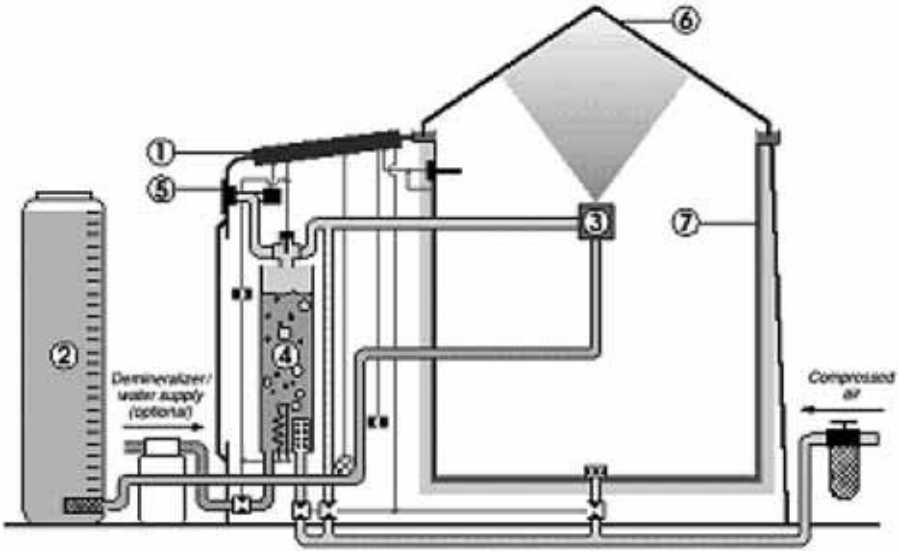

Fig. 3—Typical Salt-spray Cabinet. (Reprinted by permission of Elcometer Inc.)

WATER FOG TESTING

ASTM Practice for Testing Water Resistance of Coatings Using Water Fog Apparatus (D1735) covers the basic principles and operating procedures for testing water resistance of coatings in an apparatus similar to that used for salt spray testing [10]. The apparatus required (Fig. 3) consists of a fog chamber, a water reservoir, a supply of suitably conditioned compressed air, one or more atomizing nozzles, specimen supports, provision for heating the chamber, and necessary means of control. Coated specimens are placed in an enclosed chamber where a water fog surrounds them. The temperature of the chamber is usually maintained at 100°F (38°C). The exposure condition is varied by selecting the duration of the test.

Failure in water fog tests may be caused by a number of factors, including a deficiency in the coating itself, contamination of the substrate, or inadequate surface preparation. Any effects such as softening (measured by pencil hardness), color change, gloss change, blisters, loss of adhesion, embrittlement, and rusting or corrosion of substrate are observed and reported.

100 % RELATIVE HUMIDITY TESTING

Practice for Testing Water Resistance of Coatings in 100 % Relative Humidity (D2247) covers the basic principles and operating procedures for testing water resistance of coatings by exposing coated specimens in an atmosphere maintained at 100 % relative humidity so that condensation forms on the specimens. The apparatus (Fig. 4) consists of a test chamber, a heated water tank, and suitable controls. Heated water vapor is generated at the bottom of the chamber, causing saturation of the air immediately above the water tank. As the saturated mixture rises, it cools below the dew point temperature, causing condensation on the specimens suspended above. Condensation is uncontrolled. (For testing at 100 % RH with controlled condensation, see ASTM D4585, described below.)

Effects of exposure at 100 % relative humidity may be color change, blistering, loss of adhesion, softening, or embrittlement. Any such effects are observed and reported. They may be caused by a number of factors including a deficiency in the coating itself, contamination of the substrate, or inadequate surface preparation.

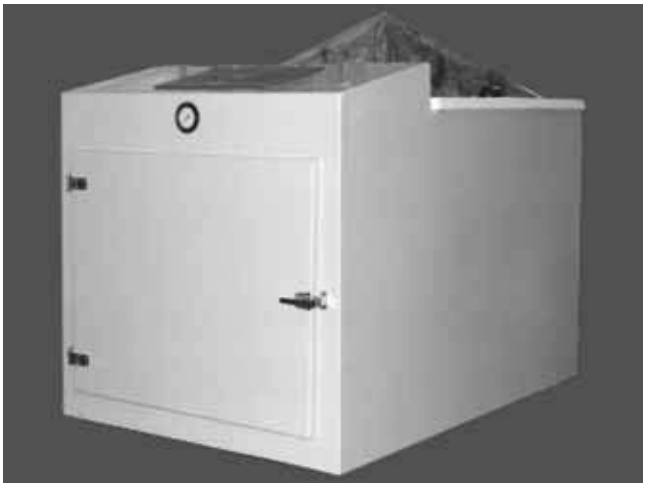

Fig. 4—Humidity Cabinet. (Reprinted by permission of Elcometer Inc.)

CONTROLLED CONDENSATION TESTING

Practice for Testing Water Resistance of Coatings Using Controlled Condensation (D4585) differs from D2247 in that the coated specimens are mounted with the uncoated face exposed to room temperature air. The apparatus (Fig. 5) consists of a test chamber in which the specimens form the roof of a chamber that is fitted with suitable water supply and controls.

Water vapor is generated by heating a pan of water at the bottom of the test chamber. The specimens form the roof or walls of the test chamber so that the reverse sides of the specimens are exposed to the cooling effects of room temperature air. The resulting heat transfer causes water

Fig. 5—Controlled Condensation Apparatus. (Reprinted by permission of Elcometer Inc.)

vapor to condense on the coated specimens as liquid water saturated with air. The temperature and amount of condensate forming on the specimens are controlled by the test temperature and room temperature.

The specimens are inclined so that the condensate runs off the test surface by gravity and is replaced by fresh condensate in a continuous process during the condensate cycle. Exposure conditions are varied by selecting the temperature of the test, the duration of the test, and periodic drying of the specimens. Failure may be caused by a number of factors including a deficiency in the coating itself, contamination of the substrate, or inadequate surface preparation. Any effects such as color change, blistering, loss of adhesion, softening, or embrittlement are observed and reported.

CYCLE TESTING

Test Method for Finishes on Primed Metallic Substrates for Humidity-Thermal Cycle Cracking (D2246) covers an accelerated means for determining the tendency of an organic coating to fail by cracking when exposed to humidity-thermal cycling. Although this method was withdrawn in 1992 without replacement it describes evaluation alternate exposure of prepared specimens in a cabinet maintained at 100°F (38°C) and 100 % relative humidity (with continuous condensation on the specimens), then in a cold box at –10°F (–23°C), allowing only a maximum of 30 s for transfer. Specimens are rated (using a grid overlay) by counting the number of grid squares within which one or more cracks is visible. Evaluation before and after exposure may be done for checking (D660 [11]), for cracking (D661 [12]), for erosion (D662 [13]), and sometimes for water beading (D2921 [14]).

ASTM test method for Humid-Dry Cycling for Coatings on Wood and Wood Products (D3459) was withdrawn without replacement in 2007 but describes a procedure for evaluation of coatings designed for use on interior wood and wood products by exposure alternately to low and high humidity at an elevated temperature. Test panels having a minimum area of 12 × 12 in. (300 × 300 mm) are exposed in 48-h cycles in exposure chambers maintained at 97 ± 2 % relative humidity and 122 ± 3.5°F (50 ± 2°C); the other chamber maintained at 50 ± 5 % relative humidity and 73.5 ± 3.5°F (23 ± 2°C). At each change of conditions during cycling, the panels are inspected under strong light for possible damage or change, which may be in the base material or in the coating. The 1998 version of D3459 is still available from ASTM.

Testing for the effect of water exposure combined with other exposures is not described in this chapter. Such testing includes light-and-water exposure apparatus using carbon-arc ultraviolet [15], Xenon-arc [16], and fluorescent UV [17]. It should be noted that UV or other weathering degradation (accelerated or natural) may impact coating water resistance characteristics. This is especially critical for substances that tend to be subject to dimensional instability (such as wood) or for coatings that are not opaque where the substrate can be affected by UV light.

ACCELERATED MECHANICAL EXPOSURE

In recent years efforts have been made to simulate real life conditions such as the effects of repeated automated washing of automotive paints. Such tests use a water, abrasive, detergent mix with rotating brushes to simulate the damage caused by worn, contaminated brushes to be found in automated car washes in commercial use.

The Car Wash Simulator (Fig. 6) is an example of such a test, utilizing a rotary brush, which can be set up using the same filaments that are used on commercial car washes.

WASHABILITY TESTING

Combination abrasion and scrub testing (D2486, D4213 and D3450) can be undertaken in wet conditions using individually controlled dosing units to introduce water between the abrasive brush or sponge to test paint on test panels or small components (Fig. 7).

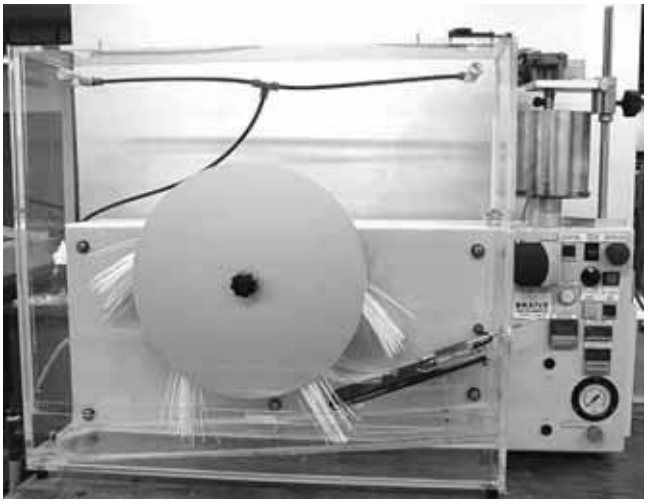

Fig. 6—Car Wash Simulator. (Reprinted by permission of Elcometer Inc.)

Fig. 7—Abrasion Scrubbing & Washability Tester. (Reprinted by permission of Elcometer Inc.)

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Part 13: Specific Product Testing

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Aerospace and Aircraft Coatings

Charles R. Hegedus,[1] Stephen J. Spadafora,[2] Anthony T. Eng,[3]
David F. Pulley,[4] and Donald J. Hirst[5]

ORGANIC COATINGS ARE PRIMARILY APPLIED TO aircraft for environmental protection and appearance. Reference [1] concludes, "The rate controlling parameter for the corrosion of aircraft alloys, excluding the mechanical damage factor, is the degradation time of the protective coating system." This clearly indicates the importance of the coating system's durability and its ability to control corrosion and erosion. Relative to appearance, commercial aircraft benefit from the aesthetic characteristics of the coating system, while military aircraft rely on camouflage properties to minimize enemy detection and tracking during mission operations.

To meet operational requirements, aircraft coating systems traditionally consist of a primer and a topcoat. Primers inhibit corrosion of the substrate and enhance adhesion of subsequent topcoats, while topcoats are applied for appearance and to enhance overall durability of the coating system. Self-priming topcoats, which perform as both primer and topcoat in a single coating, have recently been introduced [2,3]. In addition, specialty coatings are strategically applied to perform various functions such as protection against rain erosion, chafing, immersion in fuel, and high temperature. References [4–6] provide more detail on the formulation and properties of aircraft coatings.

A number of factors affect the performance of aircraft coatings, including the substrate material, the aircraft's operational environment, and flight conditions. Aircraft structures and skins are manufactured from numerous metallic alloys and polymeric composites with a variety of pre-paint treatments, thus complicating the adhesion and corrosion inhibition characteristics of the coating system. Environmental conditions also can vary dramatically (arctic, tropical, marine, industrial, desert, etc.). Skin temperatures during flight can range from –54 to 177°C (–65 to 350°F) while ground conditions may be relatively benign or highly corrosive. Aircraft type and mission also play important roles in coating system performance. A commuter aircraft that hops from island to island in the tropics sees frequent pressurization and depressurization along with high temperature, humidity, and salt water. In contrast, a military tactical aircraft may fly far fewer hours but will experience extreme structural loads during flight conditions. These flight conditions place environmental and mechanical stresses on the aircraft coating system. Therefore, selection of appropriate test and evaluation procedures is an essential component for determining acceptable coatings for aircraft application [7].

VISCOSITY

The viscosity of aircraft coating components, component mixtures, and raw materials is valuable to the formulator, manufacturer, and applicator for assessment of rheological characteristics. These characteristics affect paint application properties such as atomization, leveling, sagging, and brushability.

Cup Methods (Cup Viscometers)

In aircraft coating specifications and at application sites, Zahn and Ford cup viscometers are used for admixed paints because they are inexpensive, easy to use and maintain, and produce practical quantitative data. Although the stand-mounted, standard Ford cup is more accurate due to its stability, deeper capillary orifice, and larger volume, the dip-type Zahn cup is preferred since it is easiest to use and maintain. Zahn and Ford viscometers are described in ASTM Test Method for Viscosity by Dip-Type Viscosity Cups (D4212) and ASTM Test Method for Viscosity by Ford Viscosity Cups (D1200), respectively.

Brookfield and Stormer Methods

Brookfield and Stormer viscometers are rotation-type viscometers described in ASTM Test Method for Rheological Properties of Non-Newtonian Materials by Rotational (Brookfield) Viscometer (D2196) and ASTM Test Method for Consistency of Paints Measuring Kerbs Unit (KU) Viscosity Using a Stormer-Type Viscometer (D562), respectively. The Brookfield viscometer, which measures absolute viscosities in centipoises (cP) using a rotating spindle, is particularly effective in determining viscosities of non-Newtonian fluids due to its ability to measure shear stress (that is, torque of rotating spindle) at various speeds and shear rates. Since the cup viscometers described above offer relative simplicity and ease of use, the Brookfield viscometer is not used at application sites. However, it is frequently used as a research tool to characterize the viscosities of polymeric resin materials and dispersions.

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The Stormer or Krebs-Stormer viscometer uses a rotating paddle to measure relative viscosity expressed in Krebs units. It is designed to provide controlled, uniform, and relative data based on a paddle-stirring motion. This type of viscometer is rarely used in the laboratory or required in current specifications due to the ease of use and maintenance of cup methods and to the accuracy of the Brookfield method.

DENSITY

Wet coating density measurements provide a check on the theoretical density value and on the uniformity of the manufactured product. Determination of density by any convenient or suitable method in this Manual is acceptable; however, a weight-per-gallon cup is normally used due to the ease of use of this instrument. Typically ASTM D1475, Density of Liquid Coatings, Inks and Related Materials is followed.

FINENESS OF GRIND AND COARSE PARTICLES

Fineness of grind and presence of coarse particles are determined to assess the quality and uniformity of the pigment dispersion and coating finish. In order to produce a high gloss coating of good appearance, a paint should be free of coarse particles. However, the extremely low gloss requirements of some aircraft camouflage paints require relatively large particle sizes. Fineness of grind is determined by ASTM Test Method for Fineness of Dispersion of Pigment-Vehicle Systems by Hegman-Type Gage (D1210), commonly referred to as the Hegman scale. The coarse particle content is determined by the weight retained on a 325-mesh sieve as specified in ASTM Test Methods for Coarse Particles in Pigments (D185).

SOLID AND VOLATILE CONCENTRATION/ CONTENT

General

Several analysis techniques are used to determine the total solids, pigment concentration, and volatile concentration of aircraft coatings. This information can be used as a check on the coating composition when compared to the theoretical value as determined from the formulation. It can also be used to determine the quality of an as-received product and its potential surface coverage per volume of paint. In addition, restrictions on the volatile organic compounds (VOC) content of coatings increase the importance of determining the volatile concentration, and methods to determine this value are continuously being developed and refined. The following methods are currently used to determine these compositional properties for aircraft coatings.

Total Solids Content

The total solids content of a coating, often referred to as its nonvolatile content, is a measure of the combined polymer and pigment content in a paint. It is typically represented as the weight fraction or percentage of these "solid" components relative to the as-received "wet" coating. For aircraft coatings, this is determined by subtracting the volatile fraction of the coating from the total to determine the nonvolatile content. The method specified in ASTM Test Method for Volatile Content of Coatings (D2369) is used. A method that provides a volumetric assessment is ASTM Test Method for Volume Nonvolatile Matter in Clear or Pigmented Coatings (D2697).

Pigment Concentration

Three methods are available to determine the pigment weight concentration within a coating: ASTM Test Method for Determination of the Pigment Content of Solvent-Reducible Paints by High Speed Centrifuging (D2698); ASTM Practice for Separation of Vehicle from Solvent-Reducible Paints (D2372); and Federal Standard 141 Method 4021, Pigment Content (Ordinary Centrifuge). These methods use the fact that pigment particles, generally being more dense than the vehicle, will settle under centrifugal force. One distinction between these methods is the variation in rinsing solvent(s) used to separate the polymer from the pigment. Although each method utilizes a different solvent blend, it is common to deviate from the specified method by using solvents which are appropriate for the specific paint under analysis. All three methods result in a quantitative determination of pigment weight concentration in the paint; however, the latter two methods lend themselves to chemical analysis of the pigment sample after this determination.

Volatile Concentration

ASTM D2369 is a standard experimental method to determine the total volatile content of a coating. In contrast, ASTM Practice for Determining Volatile Organic Compound (VOC) Content of Paints and Related Coatings (D3960), offers a method of calculating the VOC using the nonvolatile content, the water content (if any), and the density of the coating. These latter values are predetermined using referenced ASTM methods, and they are subsequently used in the calculations to determine VOC of the paint. It should be noted that in solvent-borne coatings the VOC is the volatile content; however, water-borne coatings obviously have a nonorganic volatile component which must be taken into account when performing these calculations. The VOC is typically recorded in units of grams of organic volatiles per liter of paint with pounds per gallon used as an alternate.

Chemical Analysis

A variety of methods are used to analyze the chemical composition of aircraft coatings and their components. The specific technique that is selected is determined by the material being analyzed and the level of quantitative or qualitative data required. Some of the more common techniques to analyze polymer and solvent systems are gas chromatography, infrared and ultraviolet spectroscopy, and nuclear magnetic resonance (NMR). Atomic absorption and x-ray spectroscopy are common techniques for determining the chemistry of inorganic pigments. Table 1 provides some of the common ASTM methods used to analyze aircraft coatings.

TABLE 1—Analytical methods for aircraft paint components

Compound	ASTM Method
Ketones	D2804
Isocyanate	D3432
Water	D4017
Lead, cadmium, and cobalt	D3335
Chromium	D3718

Because of growing concerns over potentially toxic materials, restrictions are being placed on the lead and chromium content of many aircraft paints. These restrictions are in direct conflict with corrosion control requirements since chromate salts, such as strontium chromate, barium chromate, and zinc chromate, have been shown to be excellent corrosion inhibitors for many metals. Therefore, many specifications require analysis for these pigments to ensure either their presence or their absence. Specific methods to determine lead and chromate content are listed in Table 1.

STORAGE STABILITY

General

The effects of long-term storage on aircraft coating performance are a major concern. Long durations of time and extreme temperatures can have drastic effects on the chemical and physical nature of paints, causing them to have different properties than when they were originally manufactured. Since many aircraft manufacturing, rework, and maintenance activities have paint storage facilities that have only moderate environmental controls, determining the effects of these conditions is necessary. Of primary importance are chemical stability and pigment dispersion. These properties are assessed in the laboratory following long-term and accelerated storage conditions.

Long-Term Evaluation

Methods typically used for determination of stability of aircraft coatings are specified in ASTM Test Method for Package Stability of Paint (D1849), and Federal Test Method Standard (FTMS) 141 method 3022.1, Storage Stability (Filled Container). In these methods, the packaged coating is allowed to sit undisturbed at ambient conditions for an appropriate period of time. (One year is typical for aircraft coatings.) At that time, the coating is reevaluated to compare its physical and optical properties with those originally found for the as-manufactured material. Other methods may be used to evaluate specific aspects of the material at that time, such as FTMS 141 method 3011.2, Condition in Container; method 3021.1, Skinning; or method 4208, Evaluating Degree of Settling of Paint. In most cases, it is essential that (1) the paint be free from skinning, (2) the pigment has not reagglomerated or formed a compacted cake at the bottom of the container and it can be easily redispersed to form a consistent mixture, and (3) the applied coating has properties similar to when it was manufactured.

Accelerated Conditions

To speed the evaluation of a coating's behavior under storage conditions, methods have been devised to accelerate this behavior by subjecting the coating to extreme conditions. One common example is specified in FTMS 141 method 3019.1, Storage Stability at Thermal Extremes, which subjects the coating to 49°C (120°F) or –12°C (10°F) for 168 h, depending on the type of storage suspected. Methods involving cyclic exposure to high and low temperatures have also been used. With the development of high-performance water-borne coatings for aerospace applications, one major concern is the freeze-thaw stability of these coatings. ASTM Test Method for Freeze-Thaw Resistance of Water-Borne Coatings (D2243) is used to evaluate coating consistency and performance after 17 hat –18°C (0°F).

Another technique for predicting storage stability of coatings is by evaluating the settling properties of pigments under accelerated conditions. Aircraft coating specifications rarely contain this type of evaluation; however, centrifugation is often used as a research tool to evaluate the tendency of various pigments to settle and compact in specific vehicles. The centrifugal force and the duration are selected on a case by case basis to ascertain differences between systems.

FLASH POINT

General

The flash point of a coating is the minimum fluid temperature at which the solvent vapors are ignited by a spark or flame. It can be predicted roughly as the weighted average of the individual flash points for each of the solvents in a coating formulation. The closed-cup technique is generally preferred since container breakage during shipment and storage often leads to flammable vapors being trapped in a confined space. Naturally, these flash points tend to be lower than the corresponding open-cup values.

Pensky–Martens

The Pensky-Martens test is a closed-cup method that can be conducted on an admixed coating or on one of the separate components in the liquid (uncured) state. The material may be refrigerated to bring it to a temperature below the expected flash point. It is then placed in a closed metal cup, heated slowly while stirring, and periodically exposed to a pilot flame through a shutter mechanism. A thermometer immersed in the fluid measures the coating temperature. The flash point is the minimum temperature at which the solvent vapors ignite, yielding a large flame that propagates over the surface of the fluid. The procedure is covered in ASTM Test Methods for Flash Point by Pensky–Martens Closed Cup Tester (D93), Method A for clear coatings and Method B for pigmented coatings.

Setaflash

The Setaflash test uses an enclosed apparatus with automatic controls to determine the flash point. It is easier to operate than the Pensky-Martens tester and utilizes an electric heater for efficient heat transfer and greater accuracy. ASTM Test Methods for Flash Point of Liquids by Small Scale Closed-Cup Apparatus (D3278), Method B describes the test procedure.

Tag

The Tag tester is similar to Pensky–Martens, except that the cup is placed in a bath containing a mixture of water and ethylene glycol. Only coatings with no suspended solids (such as, fillers) can be evaluated. ASTM Test Method for Flash Point by Tag Closed Cup Tester (D56) is the applicable test method.

POT LIFE

Pot life is the length of time in which the flow properties (such as, viscosity) of catalyzed paints will not change within an acceptable range for application. Acceptable coating conditions can vary from no change up to gellation. Pot life requirements in the aerospace industry tend to be controlled by production limitations. Since a normal production work shift is 8 h, many paints have been required to

have a pot life spanning this period. More recently, restrictions on the volatile organic content compounds (VOC) of paints have resulted in high solids coatings that tend to inherently possess higher viscosity and shorter pot life (2–6h). Pot life of aircraft coatings is usually determined by measuring viscosity as a function of time after mixing the paint for application. Substantial increases in viscosity are an indication that the pot life is nearly expended.

It should be noted that the issue of pot life can be circumvented via the use of plural-component spray equipment, which is becoming more common in the production painting of aircraft. This equipment stores the various components of a multi-component paint separately and then mixes those components at the desired ratio immediately before or at the spray gun. This equipment not only negates pot life as a factor but also minimizes the amount of catalyzed multi-component paint that is wasted due to unused material. The only drawback is that the equipment is most effectively and efficiently used when large volumes of paint (5 gal or more) are used as opposed to small quantities (1 gal or less), which are typical of touchup maintenance operations.

DRYING TIME

ASTM Test Method for Drying, Curing, or Film Formation of Organic Coatings at Room Temperature (D1640) defines drying times of paint films. As many as eight stages of the paint drying process are recognized by coatings authorities. Determination of a particular set of drying properties is important for aerospace coatings due to the strict time and processing constraints placed on production and maintenance painting facilities. No particular drying time parameters are universal throughout the aircraft industry. Each paint facility has acceptable limits for these drying properties depending on their function, schedule, and climatic conditions. For example, set-to-touch time may be more important to a small parts shop where components are handled shortly after painting. In contrast, dry-hard times may be paramount at a production facility for painting entire aircraft that must be flown shortly after painting.

Set-to-Touch

A film is set-to-touch when it clings weakly to the finger under gentle pressure but none of the film transfers to the finger. This property indicates that the painted piece can be handled gently, but excessive contact will diminish the quality of the coating. This property may be considered important to shops painting small aircraft components which must be moved from the application area.

Tack-Free

Basically, tack is the tenacity of the film to cling to foreign objects. This component of drying is not considered of major importance in production painting; however, it may be used to ascertain the overall drying characteristics of a coating.

Dry-to-Recoat

This stage of drying is considered to be the most important for painting of aircraft because it is one of the major factors controlling the production rate. Dry-to-recoat is the time at which a second coat, or specified overcoat (such as, topcoat), can be applied without developing irregularities in the coating system, such as lifting, blistering, or loss of adhesion. If overcoated prior to the recoat time, these defects can be caused by a number of factors, one of which is the trapping of solvent in the original coat.

Dry-Hard

The most common technique is to squeeze or pinch the coated surface with the thumb and forefinger with maximum pressure. The dry-hard time is when this procedure can be performed without leaving a permanent mark on the coating surface. This drying stage is also important in production painting of aircraft since painting is usually the last stage of maintenance and the aircraft can be flown after the coating is dry-hard.

FILM THICKNESS

Aircraft coatings are developed and manufactured to be applied within acceptable thickness limits. Coatings which are applied outside of these limits will not exhibit their optimum performance properties. For example, thin coatings may not have the required tensile and shear strength, making them susceptible to cracking and chipping, especially around fastener heads and at panel seams. In contrast, coatings which are too thick may lack flexibility and can exhibit excessive internal stresses. Another important consideration is the excessive weight that coatings add to an aircraft, causing additional fuel consumption. Therefore, coating thickness is diligently controlled and measurements are performed in both the wet and dry states.

Wet coating films are checked for thickness during aircraft application processes using various wet film thickness gages according to ASTM Test Method for Measurement of Wet Film Thickness of Organic Coatings (D1212). A tooth gage is commonly used in the aerospace industry since it is simple to use, inexpensive, and can be used to obtain good approximations of dry film thickness. These approximations are made by multiplying the wet film thickness by the coating volume percent solids.

The thickness of cured aircraft coatings can be determined either destructively or nondestructively. Destructive methods involve the chipping or cutting of dry films from a substrate and subsequent measurement of the coating thickness with a gage. This approach is typically not taken for aircraft coatings since the coating-substrate bond must be destroyed. Nondestructive techniques include micrometer, eddy current, magnetic induction, and a magnetoresistor/ thermistor system. These are the most desirable methods of dry film thickness determination used in the aerospace industry, both in the field and in the laboratory due to their accuracy and ease of use. One problem encountered is that aircraft are constructed of a number of types of materials. Therefore, the method used to determine coating thickness may depend on the substrate material, especially if a nondestructive method is used. One method for film thickness testing is ASTM D7091, Practice for Nondestructive Measurement of Dry Film Thickness of Nonmagnetic Coatings Applied to Ferrous Metals and Nonmagnetic, Nonconductive Coatings Applied to Non-ferrous Metals.

OPTICAL PROPERTIES

General

The appearance of an applied coating is determined by a number of optical properties (color, gloss, opacity, etc.).

In the commercial aerospace industry, where public opinion is a consideration, these optical properties can strongly affect the initial impression of the aircraft and are considered to be important with respect to customer recognition. The optical properties of coating systems for military aircraft affect the detectability of these aircraft and thus effect their survivability in potentially threatening scenarios. In both the commercial and military sectors, optical properties are specified with strict tolerances and are closely monitored with instrumentation as well as with the naked eye.

Color

The colors used on commercial aircraft tend to be strong and vibrant for recognition and attraction. The colors of military aircraft coatings are empirically selected in order to achieve either theater-specific (desert, forest, arctic, etc.) or multitheater (world-wide) camouflage paint scheme requirements. In either case, paint color is considered to be important. In addition, color change is often used to assess the effects of environmental exposure (weathering, immersion in fluids, etc.) on aircraft coatings. Means of characterizing aircraft coating colors range from qualitative visual assessment to quantitative measurements with instruments, the latter providing the obvious advantage of consistent, numerical results. For the latter, ASTM Standard Practice for Calculation of Color Tolerances and Color Differences from Instrumentally Measured Color Coordinates (D2244) is followed, resulting in a color description in either the XYZ or Lab color coordinates. Color differences, as qualified by a delta E value, are determined by using these color coordinates as described elsewhere in this manual to determine delta E.

One additional note must be made with respect to color measurement of aircraft coatings. Colorimeters and spectrophotometers can both be used to quantitatively measure color. Colorimeters use a specified light source with defined radiation wavelengths and intensities, typically resulting in a direct output of XYZ and/or Lab color coordinates. Spectrophotometers measure light reflected from the coating surface over an entire wavelength region. (In the case of color characterization, this is the visible region of the spectrum.) Of the two, colorimeters are less expensive and easier to use. However, colorimeters do not account for metamerism. Metamerism is a phenomenon that occurs when an object appears to be different colors under different light sources. This effect is observed with some coatings for military aircraft, which use unconventional pigments to obtain camouflage properties. In order to confirm that two colors are the same, their total reflectance over the entire visible spectrum must match. These data are obtained using a spectrophotometer. In addition, spectrophotometers are frequently used for military aircraft coatings to determine their reflectance characteristics outside of the visible region, most commonly the infrared and ultraviolet regions.

Opacity (Contrast Ratio)

Opacity or hiding power is the ability of a coating to mask the underlying substrate. Opacity of aircraft coatings is usually quantified by its contrast ratio according to ASTM Test Method for Hiding Power of Paints by Reflectometry (D2805). In this method, the coating is applied over white and black substrates. (Contrast ratio or Leneta charts are typically used.) A colorimeter is used to measure the coating's luminous reflectance (Y) on the black and white surfaces. Contrast ratio is then determined by:

$$\text{Contrast ratio} = Y(\text{black})/Y(\text{white})$$

Contrast ratio is a function of coating dry film thickness. The method must define the coating thickness at which the contrast ratio is determined; 2.0 mils is common for aircraft topcoats. Applying a coating to a precise thickness is difficult and may require several attempts. An alternative approach is to determine the contrast ratio at several coating thicknesses and subsequently fit the data to a quadratic equation. This equation can then be used to determine the contrast ratio at the desired coating thickness.

Reflectance and Gloss

Incident light which is reflected from a surface has two components, specular and diffuse. Specular reflectance or gloss represents light that has been reflected off a surface when the angle of incidence equals the angle of viewing. Diffuse reflectance is light reflected in all directions other than specular. Specular reflectance data are usually obtained via glossmeters whereas diffuse reflectance data are obtained by the use of goniophotometers.

Gloss of aircraft coatings is measured by instruments that have been standardized to either 60° or 85° incident angles according to ASTM Test Method for Specular Gloss (D523). Commercial aircraft coatings have high gloss and are usually characterized at 60°. In contrast, many military aircraft are painted with low gloss coatings for camouflage purposes. In addition to gloss analysis at 60°, military coatings are also analyzed at 85° in order to minimize glare at grazing angles.

Directional reflectance represents the optical data that are obtained from analyzing reflected diffuse light. This type of data is normally obtained via goniophotometric equipment. Several methods describe procedures for these measurements, including ASTM Test Method for Color and Color-Difference Measurement by Tristimulus Colorimetry (E1347) and Practice for Goniophotometry of Objects and Materials (E167). The use of diffuse reflectance of aircraft coatings is typically limited to those for tactical military functions that require camouflage properties.

ADHESION

General

For aircraft coatings to provide maximum protection against degradation, they must firmly adhere to their substrate. Because of the complex nature of adhesion, various techniques have been devised to determine the adhesive characteristics of coatings. Since a coating's adhesion to its substrate can be significantly affected by environmental conditions, these tests are often performed after exposure to accelerated conditions such as immersion in water at elevated temperature. Common adhesion tests used to evaluate aircraft coatings are tape and scrape tests. Other techniques, such as mechanical peel, tensile, and shear tests, are used less frequently.

Tape Tests

Adhesion tape tests are described in ASTM Test Methods for Measuring Adhesion by Tape Test (D3359). These are

the easiest and most versatile of the adhesion tests because they can be conducted in both laboratory and field environments. Tape tests are performed by cutting through the applied coating, into the substrate. A variety of scribe patterns can be used. One common pattern (described in the "A" method of D3359), which is used to evaluate aircraft coatings, is two scribes forming an "X." An alternative pattern (described in the "B" method of D3359), is formed by scribing eleven parallel lines through the coating, followed by a second set of eleven lines which are perpendicular to the first set. These scribe lines create a matrix of 100 squares. Adhesive tape is firmly applied over the scribe area and is subsequently removed with a quick upward motion. Coating adhesion is then characterized using standard ratings for the amount of coating removed according to the ASTM method.

As mentioned above, the coated specimens can be subjected to a specific environment prior to testing adhesion characteristics. This practice is most commonly performed with the tape tests. A typical exposure for aerospace coatings is a 24 h immersion in water at 21°C (70°F). More severe exposures are becoming common as coating technology advances. One example is immersion in water at 65°C (150°F) for seven days. Immediately upon removal from the water, the coating is scribed and tested.

Scrape Adhesion Test

The scrape adhesion test is described in ASTM Test Method for Adhesion of Organic Coatings by Scrape Adhesion (D2197). Scrape adhesion is used to characterize the adhesive and shear strength properties at the primer-substrate interface. The instrument used for this test is the Gardner Labs Scrape Adhesion Test Apparatus (Model SG-1605). The specimen for this test has an area which is uncoated with the substrate exposed. The test is performed by guiding a weighted stylus at a 45° angle to the specimen along the exposed substrate into the coating system. The scrape adhesion value is recorded as the heaviest weight used without shearing the coating from the substrate. Typical scrape adhesion values for aerospace primers fall into the 3 to 5 kg range.

The scrape adhesion test is also used to determine the intercoat adhesion between a topcoat and a primer. When testing this property, a specimen with a section of primer exposed is used and the stylus is guided across the primer into the topcoat. Typical scrape adhesion values for aerospace topcoats also fall into the range of 3 to 5 kg. This test can also be performed after exposure to severe environmental conditions.

Peel and Tensile Tests

Peel test methods are rarely used for aircraft coatings. Instead, a modified version of an adhesive peel test is occasionally used. In this test, two thin metal strips are bonded together using the coating as the adhesive. One end of the specimen is left unbonded, and the metal strips at this end are separated to form a "T." They are subsequently pulled apart in a tensile machine, and the force needed to pull the two strips apart is recorded as the adhesive peel strength of the coating. The type of failure (adhesive or cohesive) is also recorded. An adhesive failure indicates that the coating strength exceeds that of the coating-substrate adhesive strength.

The most common tensile adhesion test used on aerospace coatings is a tensile pull-off test, also referred to as a button test. In this test, a flat head paten is bonded to the surface of the coating with an adhesive. A tensile force is then applied to the paten perpendicular to the coating surface until the paten is removed. The location at which the paten is removed from the surface must be carefully examined. In many cases, the adhesive which bonds the paten to the coating will fail or the coating may fail cohesively. In these cases, it can only be stated that the adhesive strength of the coating exceeds the tensile strength recorded. Only if the coating fails adhesively is the recorded tensile strength that of the coating-substrate adhesion.

FLEXIBILITY

General

Flexibility is an important property for aerospace coatings, particularly at low temperatures (–51°C), which is common for aircraft cruising at high altitudes. Cracking of coatings at skin joints and around fastener heads can lead to corrosion of exposed areas. Corrosion inhibiting epoxy primers used on aircraft tend to be brittle and exhibit poor flexibility, whereas the urethane topcoats are generally more flexible, especially at low temperatures. Sealant materials and elastomeric primers occasionally are used to improve the overall flexibility of the paint system.

Mandrel Bend

The flexibility of high-performance coatings is commonly characterized by the mandrel bend test method outlined in ASTM Test Methods for Mandrel Bend Test of Attached Organic Coatings (D522). This test is normally conducted at low temperatures such as –51°C and is performed by bending a painted specimen 180° around mandrels of various diameters with the coating aligned away from the mandrel. After allowing the specimen to return to room temperature, the coating is examined for cracking along the bend. The smallest (most severe) mandrel diameter that the coating can withstand without cracking is recorded. One standard military specification requirement for this test on low gloss coatings is a 2-in. mandrel bend while more flexible coatings can withstand mandrel bends of 1/8 to 1/4 in. at low temperatures without cracking.

Impact Tests

The most universal test for measuring impact flexibility of aerospace coatings is Method 6226 (G.E. Impact) of Federal Test Method Standard 141B. The test apparatus consists of a solid steel cylinder weighing 1.69 kg (3.7 lb), which has spherical knobs protruding from the end. These knobs are designed such that the coating system is subjected to elongations of 0.5, 1, 2, 5, 10, 20, 40, and 60 %. The impact is accomplished by allowing the steel cylinder to fall freely from a height of 1.05 m (42 in.) through a hollow cylinder guide, striking the reverse uncoated side of the specimen. The imprints formed from the knobs are examined, and the impact elongation is recorded as the highest deformation without cracking of the coating. A standard requirement for this test on aircraft topcoats is 40 % elongation.

Another commonly used test is the Gardner impact test specified in ASTM Test Method for Resistance of Organic Coatings to the Effects of Rapid Deformation (Impact)

(D2794). This test is performed in a similar fashion to the G.E. impact test described above; however, the weighted cylinder has a rounded end and is dropped from various heights. The weight of the impact cylinder and the highest height that causes no cracking or disbondment of the coating are used to calculate an impact strength, usually in inch-pounds. This test can be performed directly on the coated side of the panel or, like the GE impact test, on the reverse, uncoated side.

Tensile (Elongation) and Fatigue Tests

For aerospace coatings, free films of the coating generally 5 mils thick or greater are prepared and tested for tensile characteristics. Epoxy primers have relatively high tensile strengths (>2500 psi) but very poor elongations (<10 %), whereas flexible primers can have elongations exceeding 100 %. It should be noted that the rate of deformation has a significant effect on mechanical properties, including tensile, and this must be clearly specified as part of the testing procedure. For this reason, elongations obtained from impact tests cannot usually be directly correlated with those from tension tests.

Fatigue tests are not usually performed to study coating performance. However, fatigue testing of coated specimens with fasteners has been performed to study cracking of aircraft paints around fastener heads. In these studies, increased flexibility of the coating generally leads to less cracking and better overall performance. Isolated studies [8] have been reported in which coatings were used as a variable in fatigue testing of metal test fixtures. In these studies, a series of specimens were exposed to a corrosive environment to induce corrosion fatigue. In these cases, flexibility and corrosion inhibition are essential characteristics of the coating.

WEAR RESISTANCE

General

Aircraft coating systems can experience wear due to a number of causes and mechanisms. The most obvious of these is abrasion at leading edges of wings, antennas, and radomes caused by impingement of rain, sleet, dirt, and other debris. Since these leading edges are critical to flight dynamics, special wear-resistant coatings are often applied to these areas to protect the underlying substrate from damage. Another form of wear can be caused from the movement of adjacent parts such as flaps and stabilizers. In addition, internal parts such as bearings may be coated to prevent excessive wear. Since all of these types of wear cause different mechanisms of coating degradation, a number of varying tests are performed to simulate in-service conditions. For example, coatings that protect against rain erosion do not usually protect well against erosion from sand. Specifications for aircraft coatings (other than those for rain erosion) typically do not contain wear tests; however, development and selection of new aerospace coatings often require that characterization of wear properties be performed. Therefore, careful evaluation of wear mechanisms and selection of suitable evaluation methods is essential for these types of coatings.

Rain Erosion

There are a number of facilities throughout the United States that have built equipment to evaluate rain erosion. Some of these facilities are discussed in Refs. [9,10]. In general, coatings are applied to a small specimen that is subsequently secured to a test fixture arm. The test is performed by spinning this arm in a chamber with falling water droplets that impinge upon the coated surface. Parameters of the test include:

1. Substrate material, thickness, and geometry.
2. Coating type and thickness.
3. Water droplet size and falling rate.
4. Testing arm speed (specimen-water droplet impact).

Although attempts to correlate data from various test rigs have been unsuccessful at obtaining quantitative relationships, trends in coating performance have been observed. These trends generally agree with rain erosion performance on aircraft.

Taber Abraser

ASTM Test Method for Abrasion Resistance of Organic Coatings by the Taber Abraser (D4060) is a frequently used test throughout the coatings industry because it is well defined and relatively easy to perform. As such, it is often used for aircraft coatings to assess their wear characteristics. Care must be taken in interpreting Taber abraser results since reproducibility of data from lab to lab is not consistent.

HARDNESS AND MAR RESISTANCE

Pencil Hardness

The most frequently used test for hardness of aircraft coatings is the pencil hardness test, ASTM Test Method for Film Hardness by Pencil Test (D3363). Briefly stated, it is performed by guiding pencils of various hardness across a coating surface to determine the hardest pencil that will not scratch or mar the coating. The test is used on aircraft coatings for several reasons, including:

1. To assess coating cure and cure rate.
2. To evaluate the coating's ultimate hardness.
3. To evaluate damage caused by weathering and operational fluids (such as, by comparing coating hardness before and after exposure).

Shore Hardness

The Shore hardness test [ASTM Test Method for Rubber Property-Durometer Hardness (D2240)] is inappropriate for thin coatings (thickness <6.4 mm or 0.25 in.). However, for thicker coatings such as sealants, ablative, and intumescent materials it can be used to evaluate hardness, cure, and environmental effects.

Arco Microknife

Although the arco microknife test was originally designed to evaluate adhesive strength of coatings, it has been used to determine hardness. This can be performed by placing a specified weight on the diamond stylus and determining the number of scratch cycles required to cut through the coating. It can also be performed by determining the weight needed to get through the coating with a specified number of cycles.

Mar Resistance

Mar resistance is not usually considered a critical property for aircraft coatings. One method is the balance beam test that uses the scrape adhesion apparatus described in ASTM

Test Methods for Adhesion of Organic Coatings by Scrape Adhesion (D2197). The method determines the weight required to mar a coating surface with a stylus.

CORROSION INHIBITION

Salt Spray

Corrosion resistance is an important property for aerospace coatings, and numerous tests have been developed to evaluate the corrosion preventive properties of coatings, ranging from simple exposure studies to sophisticated electrochemical analysis.

Salt spray tests are commonly used as accelerated corrosion resistance tests for coatings. The two primary methods used for aircraft coating systems are the 5 % NaCl neutral salt spray test covered by ASTM Practice for Operating of Salt Spray (Fog) Apparatus (B117) and the acidified SO_2/salt spray test covered by ASTM Practice for Modified Salt Spray (Fog) Testing (G85—Annex 4). Specimens coated with an aircraft finishing system are usually scribed with an "X" through the coating into the substrate and then exposed for various times (usually 2000 to 4000 h for ASTM B117 and 500 to 1000 h for ASTM G85—Annex 4). Exposure periods for coatings vary for different substrate materials and can be selected either as a specified duration or as the point where significant differences in finishing system performance are observed. After exposure, the panels are inspected for corrosion in the scribe area and blistering or uplifting of the coating across the specimen. Subsequently, the coatings can be carefully removed from the surface without disturbing the underlying substrate by using a chemical stripper, and the specimen surface can be examined for evidence of corrosion.

Standard aircraft epoxy primer/polyurethane topcoat systems perform well on aluminum substrates in the neutral test, normally exhibiting no significant corrosion products in the scribe or any blistering of the coating after 2000 h. These materials may last up to 4000 h without any evidence of corrosion. The SO_2/salt spray environment simulates stack gases, such as those found in industrial areas and on diesel-powered aircraft carriers, and aircraft engine exhausts found on the flight deck of all aircraft carriers. It is an extremely aggressive environment, and aircraft systems exposed to this environment tend to fail at much shorter times than in the neutral test. A system exhibiting no significant corrosion products or blistering after 500 h is normally considered acceptable in this acidified environment.

Because numerous materials are used in the construction of aircraft, the contact of dissimilar conductive materials is common. When this occurs, the potential for galvanic corrosion is high if the two dissimilar conductive materials are not insulated from each other. In many cases, organic coatings are applied to provide this insulation. Therefore, it is becoming common to assess the ability of aircraft coatings to inhibit galvanic corrosion by painting and exposing specimens containing dissimilar conductive materials. One example is a graphite-epoxy composite coupled to aluminum.

Immersion Studies

Total immersion corrosion tests can be severe depending on the immersion solution, duration, and exposure temperature. Again, blistering or uplifting of the coating or corrosion of the underlying substrate constitutes failure in this test. Although this type of evaluation is not typically performed on aircraft paints, coatings requiring a high degree of impermeability, like those used in or around aircraft bilge areas, galley, lavatories, and other areas where water can be entrapped, would be evaluated with this type of test.

Filiform Corrosion

Filiform corrosion occurs on painted aluminum, steel, and magnesium in a high-humidity and elevated temperature environment containing oxygen and chloride ions. Filiform initiates at points where the coating ruptures (commonly around fastener patterns or panel seams) and propagates as filaments under the coating. If unchecked, damage of the coating system can allow other corrosion mechanisms such as stress corrosion cracking, exfoliation, and crevice corrosion to ensue. Typical filiform corrosion tests involve exposing coated specimens to hydrogen chloride vapors and then placing them into a high-humidity (85 % to 95 % RH) and elevated temperature (85 to 140°F) environment for a specified duration such as 1000 h. It should be noted that this type of corrosion is prominent on pure aluminum. For this reason, the test is performed on aluminum clad specimens in lieu of aluminum alloy.

Electrochemical Analysis

Reference [11] provides a thorough review of electrochemical methods used to evaluate the performance of corrosion protective coatings. Of these methods, electrochemical impedance spectroscopy (EIS) is one of the most promising techniques because it provides both qualitative and quantitative information about the corrosion resistance properties of the coatings and the substrates to which they are applied. In addition, EIS can give insight on the nature of their interfacial adhesion. References [12,13] provide detailed descriptions of EIS and its application for analyzing organic coating/metal substrate systems. EIS measurements can be made using a system consisting of a computer interfaced to a frequency-response detector and a potentiostat/galvanostat. Test cells consist of a glass o-ring joint clamped onto a coated metal specimen [12]. Electrolytes used for specimen exposure can range from distilled water to neutral or low pH salt solutions.

For an EIS experiment, the test cell described above is filled with the selected electrolyte solution. A reference electrode (such as, Calomel) and a counter electrode (such as, platinum or graphite) are immersed in the cell with the metal substrate serving as the working electrode. The EIS cell is allowed to reach equilibrium as indicated by its open circuit potential or steady-state rest potential. Small excitation amplitudes, usually in the 5- to 10-mV range, are introduced to the system, and the response signal is measured. These data can be correlated to an electrical circuit consisting of resistors and capacitors. The information from this electrical circuit is a model depicting the electrochemical reactions occurring in the coating-substrate system. Because of the detailed quantitative information that is obtained from EIS analysis, its use as a tool to research high-performance aircraft coatings is growing. In many cases, attempts are made to correlate EIS data with results from other corrosion studies such as salt spray. This approach provides a detailed assessment of coating integrity, durability, and corrosion inhibition.

WEATHERING AND ENVIRONMENTAL EXPOSURE

Outdoor Exposure

Outdoor exposure tests are normally conducted over periods of one year or more. In an effort to produce timely results, these tests are not frequently performed on aircraft coatings. However, older specifications, such as MIL-C-83286, did require a one year exposure of coated panels on an outdoor test rack in Florida. It was specified that the panels must be at a 45° angle and facing south. After this exposure period, the coating is evaluated for changes in color, gloss, and flexibility.

The U.S. Navy has instituted a program to evaluate the exterior durability of coatings in its operational environment by placing exposure racks on aircraft carriers and other ships. Results of these exposures have resulted in identification of successful aircraft coatings. Details of this effort are provided in Ref. [14].

Accelerated Weathering

The components of outdoor natural weathering that have the most significant effects on coatings and other materials are ultraviolet radiation and water (humidity, condensation, rain, etc.). It has been proposed that these conditions can be simulated and that the resulting effects can be accelerated by subjecting coatings and other materials to high-intensity light (including ultraviolet wavelengths) and water.

The most common accelerated weathering methods used for aircraft coatings are the xenon-arc Weatherometer and the QUV accelerated weathering tester. The former method is described in ASTM Standard Practice for Operating Xenon Arc Light Apparatus for Exposure of Nonmetallic Materials (G155). Again, there is a number of test variables that have significant effects on coating performance, and various laboratories have adopted slightly different procedures and parameters. Since there are no precise correlations between natural weathering and any of the accelerated methods for aircraft coatings, it is especially important that the test variables are well defined. One common approach that is used in military and federal specifications (MIL-PRF-85285, Coating, Polyurethane, High Solids and TT-P-2756, Polyurethane Coating: Self-Priming Topcoat, Low VOC) follows ASTM G155 as a guideline. The exposure is performed in a 6000-W, xenon arc weatherometer with a continuous cycle consisting of 102 min of high-intensity light only and 18 min of light and water spray. The conditions in the chamber are as follows:

1. Black body temperature 60°C (140°F)
2. Relative humidity 50 %
3. Intensity of the arc wavelength 0.55 W per m^2 at 340 nm.

The exposure period is 500 h, and the coating is subsequently evaluated for changes in gloss, color, and flexibility.

The second common method for accelerated weathering is described in ASTM Standard Practice for Operating Fluorescent Light Apparatus for UV Exposure of Nonmetallic Materials (G154). In this case, specimens are subjected to periods of ultraviolet light and condensation, respectively. During the condensation period, the coating surface is exposed to 100 % relative humidity at elevated temperature, while the backside of the specimen is exposed to cooler air, thus producing water condensate on the coating. Exposure parameters include UV intensity, duration of exposure to each condition, and temperature of the chamber and condensate.

Humidity

Since high temperature and humidity can cause coating disbondment and substrate corrosion, extreme humidity exposure is often performed on aircraft coatings to evaluate their resistance to such environments. Again, exposure parameters vary and must be clearly specified for reproducibility and interpretation of results. ASTM Practice for Testing Water Resistance of Coatings in 100 % Relative Humidity (D2247) is usually followed. The chamber conditions are 49°C (120°F) and 100 % relative humidity with constant condensation on the coated panels. A typical exposure period can range from 30 to 90 days.

FLUID RESISTANCE

Aircraft coatings are frequently subjected to aggressive operational and environmental fluids. Several examples are hydraulic fluids, engine oils, fuel, de-icing solutions, and cleaners. In order to assess the resistance of aircraft coatings to these fluids, a number of exposure tests are performed. The exposure can range from a simple wiping action to long-term immersion. The temperature of the exposure is also a critical variable. Following exposure, the specimen is usually evaluated for degradation of the coating (discoloration, softening, blistering, etc.) and substrate (corrosion).

Water Resistance

Resistance to water is usually performed by total immersion. The severity of the exposure can range from 24 h at ambient temperatures to seven days at 65°C (150°F). Since water can play a significant role in coating disbondment [15], adhesion tests are frequently performed immediately upon removal of the coated specimen from water immersion.

Another technique is to measure the water absorption (up-take) of a coating as a function of immersion time. This is performed by simply weighing the coated panel (or free film) as a function of immersion time. Water up-take values for high-performance aircraft coatings can range up to 20 %.

A third technique to characterize the effects of water on a coating is to determine its water vapor transmission rate (WVTR). WVTR is a measure of the rate at which water will permeate through a coating. ASTM Test Method for Water Vapor Transmission of Organic Coating Films (D1653) describes two methods to determine WVTR. In Method "A," a free film of the coating is sealed to the open mouth of a cup containing distilled water. In Method "B," the free film is sealed to a cup containing desiccant. These fixtures are exposed to controlled environments (temperature and humidity), and they are weighed periodically to determine the rate of water vapor diffusion through the coating. Aircraft coatings must exhibit low WVTRs to maintain their adhesion and corrosion inhibition.

Organic Solvent Resistance

Resistance to organic solvents is usually performed by rubbing a coated panel with a cloth dampened with a specified

solvent. Since toluene and methyl ethyl ketone (MEK) are both harsh and have been frequently used in the aerospace industry, they are common solvents. After rubbing the surface, the coating is inspected for color change, dissolution, or any abnormality which may have been caused by the solvent. The cloth can also be inspected for residue which may be apparent by a color change.

Hydraulic Fluids and Engine Oils

Hydraulic fluids and engine oils are frequently used at elevated temperatures, and therefore their attack on aircraft coatings can be accelerated and more severe. Table 2 describes typical immersion tests using these fluids.

HEAT RESISTANCE

Aerodynamic heating can produce skin temperatures of 121°C (250°F) in level flight and 176°C (350°F) during high-speed maneuvers. Painted components adjacent to engines and exhaust tracks may experience unusually high temperatures. This heat may exceed the maximum service temperature of some organic coatings, which may cause darkening, embrittlement, and/or premature aging. The heat resistance of a coating is determined by subjecting a coated panel to a constant temperature for a specific period of time. For example, specification MIL-PRF-85285 requires that a polyurethane topcoat withstand exposure to a 121°C (250°F) oven for 1 h without a significant color change (maximum delta E value of 1.0).

Thermal Fatigue

Thermal fatigue refers to the resistance of a coating to stresses induced by rapid temperature changes. Often called thermal shock, this simulates the effect of take-off from hot (and sometimes humid) ground temperatures to the cold atmosphere at high altitudes and then back again. The MIL-C-81945 intumescent coating used on weapons must withstand 60°C (140°F), 95 % relative humidity for 24 h followed by –40°C (–40°F) for 24 h. The coating is then cycled between the two chambers for 28 days. Cracks extending deep into the coating indicate failure in this test. Method 503.1 ofMIL-STD-810 provides further guidance.

Thermal Conductivity

Stored weapons (bombs, missiles, etc.), including those used on military aircraft, must be protected from accidental fuel fires. This is accomplished with exterior, insulating coatings on those weapons that delay ordnance reactions and provide fire fighters sufficient time to extinguish the fire. The efficiency of these coatings is measured by a unique test, originally developed by NASA [16]. It uses a small furnace burning JP-4 or JP-5 aviation fuel to produce a constant heat-flux of 10 btu/ft²-s at a flame temperature of approximately 1800°F (982°C). A coated panel is mounted to an open port above the furnace, and the temperature of the uncoated backside is recorded as a function of time. The thermal efficiency is calculated from these data. It is expressed as the number of seconds/mil of coating thickness for the backside temperature to reach either 500°F (260°C) or 1000°F (537°C). (Most explosives and propellants react between these two temperatures.) Specification MIL-C-81945 requires that intumescent coatings have a minimum thermal efficiency of 2 s/mil to 500°F (260°C).

TABLE 2—Aircraft operational fluid immersion tests

Material	Duration	Temperature
Lubricating oil (MIL-L-23699)	24 h	250°F
Hydraulic fluid (MIL-H-83282)	24 h	150°F
Jet fuel (JP-5)	7 days	70°F
Jet fuel (JP-8)	7 days	70°F

STRIPPABILITY

Aircraft are periodically returned to depot maintenance facilities for inspection and overhaul. At this time, the aircraft's exterior coating system is removed by chemical and/or mechanical means. In order to ensure that this procedure can be adequately performed, strippability tests are conducted in the laboratory as part of the coating evaluation procedure. One common testing procedure is accomplished by applying a chemical paint stripper, such as MIL-PRF-81294, onto the surface of a coated specimen. After a specified period of time (usually 1 h), the panel is abraded with a stiff bristle brush and rinsed with water to remove loosened paint. Usually, 90 % removal of the coating from the substrate is considered acceptable. Other non-methylene chloride and non-phenolic strippers, such as TT-R-2918, will require up to four hours to remove similar amounts of coating. MIL-PRF-81294 is a methylene chloride based stripper TT-R-2918 is a benzyl alcohol based stripper.

CLEANABILITY

Low-gloss aircraft coatings, such as those used in camouflage schemes on military aircraft, become dirtier and are more difficult to clean and restore than high-gloss coatings. This is primarily due to the increased surface roughness of low-gloss coatings, which entraps carbonaceous and oily soils as discussed in Refs. [17,18].

The cleanability or the ease at which dirt and soil can be removed from a coating surface can be quantified by consistently soiling a coating and using a standard cleaner and cleaning motion in attempts to remove this soil. Measuring the color difference of the coating prior to soiling and subsequent to cleaning provides an indication of the coatings cleanability. The following is a detailed procedure for the evaluation of the cleanability of aircraft coatings. The soil in this procedure was generated using a hydraulic fluid. This soil is representative of that found on operational aircraft. Other soils can be derived from greases and lubricating oils.

APPARATUS REQUIRED

1. Test panels 7.62 by 15.24 by 0.05 cm (3 by 6 by 0.02 in.) of 2024 T3 aluminum alloy chromate conversion coated with materials conforming to military specification MIL-DTL-81706 to produce a coating meeting MIL-C- 5541.
2. One-liter, wide-mouth, glass jars.
3. Balance, accurate to 0.1 g.
4. High shear mixer.
5. Hog bristle brush (Gardner WG-2000-B).
6. Acid brushes.

7. Rubber roller, 2270 g (5lb).
8. Forced draft oven capable of 105°C (221°F).
9. Wear tester (Gardner Heavy Duty Wear Tester).
10. Template for positioning and holding test panels on the wear tester.
11. Cellulose sponge backed with nylon web (Scotch Brite 63).

PREPARATION OF SOIL

1. Place 50 g of carbon black (such as Raven 1040 manufactured by Columbian Chemical Company) in 500 g of hydraulic fluid meeting military specification MIL-PRF- 83282.
2. Homogenize the carbon black and hydraulic fluid mixture using a high shear mixer for 15 min. Prior to application of the soil to the specimen, thoroughly stir or shake the mixture to obtain a thorough dispersion.

PREPARATION OF THE CONTROL FORMULA CLEANER

1. Any desired aircraft cleaned can be used. However, the following is a control formulation meeting a common aircraft cleaner (MIL-PRF-85570, Type II) as listed in Paragraph 4.6.13.1 of the specification.
2. Mix the first five ingredients listed below, then neutralize the mixture to a pH of 8.0 with acetic acid. Mix the last two ingredients together and then add that to the initial mixture.
3. Igepal CO-630 (1) 10.0 parts by weight
4. Monamid 150 CW (2) 5.0
5. Dipropylene glycol methyl ether 10.0
6. Deionized water 71.5
7. Benzotriazole 0.5
8. Hostacor 2098 (3) 2.0
9. Morphaline 1.0
10. (1) GAF Corporation, or equivalent.
11. (2) Mona Industries Inc., or equivalent.
12. (3) American Hoechst Corp., or equivalent.

PREPARATION OF TEST PANELS

1. To the chromate conversion coated aluminum specimens described, apply a suitable primer for the desired topcoat. One such material is epoxy primer conforming to MIL-PRF-23377 Type I or II to a thickness of 15.2 to 22.9 μm (0.6 to 0.9 mil). Allow drying for 4–6 h at ambient conditions. Apply the desired topcoat to the intended thickness. Allow the coating to cure under the appropriate conditions.
2. After allowing the desired cure time and conditions, use a bristle acid brush to coat the painted surface of a test panel with the soil described in the "Preparation of Soil" section. Remove excess soil by covering the test panel surface with tissue and exerting pressure by rolling the tissue with the roller. Repeat this blotting three times using fresh tissue each time. Brush the soiled surface ten times in one direction only, parallel to the long dimension of the test panel, using the hog bristle brush. Bake the test panel at 105°C (221°F) for 60 min.
3. Measure the L, a, and b tristimulus values on a suitable colorimeter and record the values as L_i, a_i, and b_i, respectively.

CLEANING PROCEDURE

1. Dilute the control cleaner by one part cleaner with nine parts distilled water (by volume).
2. Clean the test panel within 4 h using the wear tester as follows. Cut the sponge with any texture "ribs" running perpendicular to the cleaning stroke. When the dry sponge is attached to the cleaning head on the wear tester, the combined weight shall be between 1350 and 1400 g. Place the soiled test panel in the template at an angle 45° to the cleaning stroke. Saturate the sponge and cover the test panel with the diluted cleaner. After 55 to 65 s, clean the test panel using 5 cycles (10 strokes) of the wear tester, then immediately turn the test panel 90° in the template and clean for an additional 5 cycles. Rinse the test panel under a flowing stream of tap water at room temperature for 2 min and allow to fully dry.
3. Measure L, a, and b values on the same colorimeter used prior to the cleaning procedure and record them as L_f, a_f, and b_f, respectively.
4. Calculate the change in color due to soiling and cleaning according to the following equation.
5. A minimum of three replicates should be tested for each coating at each condition.

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Architectural Coatings

Neal Rogers[1]

INTRODUCTION

ARCHITECTURAL COATINGS ARE THE PAINTS AND coatings used to coat buildings and homes. Most are designated for specific uses such as roof coatings, wall paints, or deck finishes. No matter its use, each architectural coating must provide certain decorative, durable, and protective functions. Different test protocols may be applied in the evaluation of an architectural coating depending on its intended end-use.

For the purpose of this testing manual, the definition of the term *Architectural Coating* is most distinctly stated by standards ASTM D5146-10 and D5324-10 [1]. These two standards share the following definition of architectural coatings: "Organic coatings intended for on-site application to interior or exterior surfaces of residential, commercial, institutional, or industrial buildings, in contrast to industrial coatings. They are protective and decorative finishes applied at ambient temperatures." Although factory-applied coatings for building products such as vinyl siding or aluminum window frames may ultimately be used for architectural end-uses, these coatings will not generally follow all of the testing schemes described herein.

Substrates

The substrate that a paint is applied to determines the needed testing scheme. Here are several examples. First, painting over fresh stucco or masonry surfaces requires a paint that has resistance to the alkaline nature of the substrate. A tinted paint with marginal alkaline resistance may show quick color fading. Second, a paint designed to be applied to drywall should efficiently seal the surface to allow for the second coat to be nice and uniform. Finally, a coating that is designed for application directly over wood must be able to block tannins and extractives in the wood from bleeding through into the coating. Table 1 shows examples of common substrates for architectural coatings.

Because substrate conditions can affect end performance of a coating, development of an architectural coatings test program should take substrate differences under consideration. For instance, freshly milled wood panels that are used as test surfaces for coatings will behave differently than wood that has been exposed to natural elements before being painted. The natural processes of sunlight, moisture through humidity and precipitation, and temperature change causes the surface of wood to degrade. These differences in wood substrate can affect both short and long term adhesion performance of a coating.

Many tests for coatings are conducted on very uniform substrates such as lacquer-sealed paper charts or glass plates. These tests can help distinguish performance differences between several similar coatings, but may or may not be predictive of performance when applied on a real-world substrate. Application of a paint to real-world substrates is critical to identify performance differences from laboratory work in drying characteristics, adhesion, and film durability.

DO-IT-YOURSELF PAINTERS VERSUS PROFESSIONAL PAINTERS

The do-it-yourself (DIY) paint industry grew significantly in the late 20th century with the emergence of big box hardware chains who distribute their own high performance paint lines. DIY'ers are typically concerned with decorative aspects but also require some performance durability as well. For instance, a homeowner who wishes to change the color of a room may simply paint a new color but they still want the finished paint to resist color and gloss change with aging or abrasion. In order to get this performance level with the appropriate color, the DIY painter may be willing to trade off easy application if they are not as experienced as a professional painter to recognize the best application qualities and are happy with the finish when the job is complete.

Professional painters tend to be most sensitive to the application characteristics of a paint. It is important for the paint to have a certain open time so a painter can easily repair brush or drip marks during application. It is more critical for a professional painter than a DIY painter to have ease of flow and wetting from the application tool to the surface. Poor flow or wetting can cause additional effort to achieve a uniform appearance. A professional painter would not likely continue to recommend or select a paint with poor flow and wetting for future projects.

Architectural Coating Categories

The general class of architectural coatings can be broken down into a number of categories depending on a coating's end application. Each category calls for a testing scheme of common tests that can be customized depending on what features are the most important for the coating to be tested. ASTM offers several standard testing guides that list and briefly describe test methods that are relevant to broad categories of coatings (Table 2).

The following is a brief description of some of the most common architectural categories.

[1] *Cook Composites and Polymers, 920 East 14th Avenue, North Kansas City, MO 64116*

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TABLE 1—Common Architectural Coatings Substrates

Interior	Exterior
• Drywall/gypsum board	• Stucco
• Wood—trim, doors	• Concrete/masonry
• Plaster	• Siding—wood, cement fiberboard
	• Composite building materials
	• Roofing tiles

- Interior wall paints—interior wall paints are typically used for coating primed or previously painted surfaces. High performance interior wall paints are tested for film toughness characteristics such as the ability to withstand scrubbing, ease of stain removal, and resistance to blocking.
- Exterior paints—exterior paint films are designed to resist elements such as sunlight, dirt pickup, and attack by mold and mildew. They typically need a certain degree of flexibility to withstand expansion and contraction fluctuations of the building products they cover.
- Primers—primers are basecoats used to prepare the surface for subsequent topcoats. They need to have good adhesion to their recommended substrates, good sealing properties, and other characteristics that will protect the topcoat.
- Floor paints—floor paints typically need good abrasion resistance characteristics. They also need to withstand fluid spills without discoloring or losing hardness.
- Wood stains and clear wood topcoats—although not all wood stains are film-forming coatings, the clear finishes that cover them typically are. Clear topcoats must have good hardness development and be resistant to wear and tear from handling or daily contact with people.
- Deck finishes—deck finishes must be resistant to sunlight and provide good abrasion resistance and flexibility over the deck surface. Deck finishes must also prevent wood tannins from migrating through the finish and affecting appearance.
- Faux finishes and metallic/specialty finishes—these coatings are typically decorative in nature and have limited expectations of durability. Like wood stains, they often require a subsequent clear topcoat to achieve a more protective finish. Finishes that are intended to be durable without an additional topcoat require similar characteristics to the interior and exterior paint categories.

TABLE 2—ASTM Standard Guides for Architectural Coatings [1]

ASTM D3730-10	Standard Guide for Testing High-Performance Interior Architectural Wall Coatings
ASTM D5146-10	Standard Guide to Testing Solvent-Borne Architectural Coatings
ASTM D5324-10	Standard Guide for Testing Water-Borne Architectural Coatings
ASTM D6763-10	Standard Guide for Testing Exterior Wood Stains and Clear Water Repellents

PROPERTIES OF LIQUID COATINGS

Density

Density measurements are commonly used in quality control laboratories of paint manufacturers to ensure consistency of the finished paint. Density is typically measured by a type of pycnometer called a weight-per-gallon cup. In the United States, a weight-per-gallon cup is usually found as a stainless steel cylinder with a volume of 83.45 mL so that the weight in grams required to fill the cup divided by 10 is the density of paint in pounds per U.S. gallon.

Viscosity

Like density, viscosity is a second characterizing test commonly used in quality control laboratories of paint manufacturers. Viscosity for architectural coatings is typically measured by Stormer viscometer and/or a cone and plate viscometer.

The Stormer viscometer has a paint paddle that turns at a fixed rotational velocity in a paint. The instrument measures resistance to the rotation and provides a viscosity value in Krebs Units (KU). Most Stormer viscometers in service today have digital readouts, however older models have a falling weight attachment that uses gravity to provide power to spin the paddle. For these older models, the test technician uses a stopwatch to time how long it takes for the weight to drop a certain length and charts provided by the instrument manufacturer are used to calculate the KU viscosity measurement. Interior and exterior house paints typically have Stormer viscosities in the range of 90–110 KU. Stormer viscosities are considered a low shear rate viscosity. It can be thought of as the feel of the liquid paint as it is stirred in the can before application.

The cone and plate viscometer, often referred to as an ICI viscometer, uses a cone spindle and a flat plate to measure viscosity at a higher shear rate. The test paint is placed on the plate and then the spindle is pressed onto the plate and prompted to spin. The resulting shear force on the spindle determines the viscosity measurement. In architectural coatings, cone and plate viscosity is often suggested as an estimation of the brush drag of a coating. When a fully-loaded paintbrush is applied to a surface, the painter feels resistance to the flow of paint from the movement of the brush. Solvent-borne alkyd based paints often have ICI viscosities in the range of 4–7 Poise; water-borne 100 % acrylic latex paints have ICI viscosities typically below 2.5 Poise.

A rheometer is a more sophisticated rheologymeasurement instrument that measures fluid response over a range of shear rates. With experienced technicians, this type of instrumentation can be used to predict settling or separation of a paint when it is still in a liquid state. It can also be used to estimate how thixotropic a paint is. A thixotropic fluid displays a decrease in viscosity over time at a constant shear rate. Some thixotropy can be desirable for a coating, especially if it may be applied by spray in the field. Complete rheometric analysis is more often used as a development or stability investigation tool.

A more complete explanation of theory behind the use of rheometric and flow characterization of liquid coatings

can be found in Chapter 33 of this manual [2], "Rheology and Viscometry."

Stability

Stability of a liquid paint is often associated with physical phase separation or settling of solid components of the paint itself. Stability of the liquid paint is typically tested under one of three conditions: hot (oven stability), cold (freeze-thaw stability), or standard room temperature (shelf stability). Stability observation intervals vary with the test. For oven stability, observations are typically made at weekly intervals up to 4 weeks; for freeze-thaw stability, observations are often made after a 16-hour freezing cycle followed by 8-hour thaw cycle.

The key observation factor in a stability test is whether or not the paint fluid maintains its uniformity when stirred back together. Acrylic latex paints that are not freeze-thaw stable will develop a gelled structure and will not be able to be stirred back into a uniform liquid state. Paints appearing to have a uniform consistency in the liquid state might also be evaluated for the presence of grit or gloss changes in a film drawdown, viscosity changes, or pH changes. Long term-storage may also effect the persistency of some defoamers used in paint formulations making evaluation of foam on application testing another possible criteria by which to judge stability. ASTM D1849-95 (2008), Standard Test Method for Package Stability of Paint [1], and ASTM D2243-95 (2008), Standard Test Method for Freeze-Thaw Resistance of Water-Borne Coatings [1], provide methods for evaluating uniformity of liquid samples after storage at a wide range of potential temperatures.

Syneresis or settling may form during the course of a stability evaluation. Both properties are judged by assessing physical character of the liquid paint. Syneresis is a liquid/liquid separation normally characterized by a clear liquid layer at the surface of the liquid paint. The depth of a syneresis layer may be measured and compared with other samples. Settling is a solid separation where solid material from the paint settles to the bottom of the container. Observations of any grits or caked material at the bottom of the can are conducted by dipping a spatula into the paint and stirring gently. ASTM D869-85 (2011), Standard Test Method for Evaluating Degree of Settling of Paint [1], provides descriptions and rating scales for reporting the degree and type of settling found in a liquid paint sample.

Fineness of Dispersion

The fineness of pigments dispersed in a paint film are an important characteristic especially for semi-gloss to high gloss finishes. The most common method employed to assess fineness of pigment dispersion is by using a Hegman-type gage. The Hegman gage is a steel block with a path machined out such that the path is tapered uniformly in depth lengthwise from about 100 μm at 10 mm from one end to zero depth at the other end. Because a Hegman gage is often used in paint manufacturing during the pigment dispersion, or "Grind," process, the Hegman test is often referred to as a Hegman Grind or simply a Grind check.

ASTM Standard Test Method D1210-05 (2010) [3] describes the proper use of the Hegman-type gage to evaluate fineness of dispersion. Semi-gloss to high gloss coatings typically require Hegman Grind ratings above 6. For matte to satin coatings, the need for the Hegman tool to define the fineness of dispersion is not as critical, however, it can be used to confirm the consistency of a pigment dispersion for multiple batches.

Colorant Compatibility

Colorant compatibility with a tint base paint system is a key feature to ensure a formulation will retain its appearance properties when tinted with colored pigment dispersions, or "Colorants," at the point of sale. ASTM D5326-94a (2009) [1] provides a test method for assessing the effectiveness of color development in tinted latex paints. In this method, a film drawdown of uniform thickness is brushed into with a hand-held paintbrush. The higher shear forces of the brush can affect color development. If there is a tendency for a dark colorant to agglomerate or flocculate in a liquid paint system, colors may appear darker if the higher shear application forces of the brush cause more of the pigment to de-agglomerate. Similarly if a white pigment such as TiO_2 is flocculating, the color upon higher shear application would appear lighter.

Another way to simulate high-shear forces on a drawdown is by gently rubbing the uniform thickness drawdown with a finger. The most effective time to conduct this "rub-up" test is as the drying stage of solvent evaporation advances. As solvent initially evaporates from the paint film during the first stage of the drying process, a rub-up will not produce much shear on the paint except for pigment particles that are crushed by the rubbing finger. By allowing the paint to begin to dry, a gentle rubbing action will generate more stress and strain applied to the paint film.

Aside from color variation, viscosity differences may also develop when tinting a base paint, especially for accent and deep base tint systems that may require up to 8–10 % of colorant by volume to achieve the desired end paint color. At the time of writing this chapter, there were several rheology modifier product lines being promoted as polymer-based thickeners that are developed specifically for the benefit of maintaining viscosity and preventing viscosity loss upon tinting.

Volatile Organic Contents (VOC)

VOCs for architectural coatings in the U.S. are typically reported in terms of grams volatile organic compounds per liter of liquid paint less water and other exempt solvents. The definition of VOCs in other parts of the world have different definitions or different methods by which to judge VOC of a liquid paint. In the European Union zone, for instance, common coalescing solvent 2,2,4-trimethyl-1,3-pentanediol-1-monoisobutyrate used in acrylic emulsion paints is exempt because of its high boiling point of around 255°C compared to other glycol ethers and solvents used as coalescing agents.

A complete discussion of volatile organic content measurement related to paints, is found in Chapter 1 of this manual [2], "Regulation of Volatile Organic Compound Emissions from Paints and Coatings."

FILM-FORMATION PROPERTIES

Drying Times

In general, drying time assessment of a paint system is critical to understanding its performance. However, for most acrylic emulsion-based architectural paints, drying profiles tend to be very similar. Set to touch times are typically less

than 20–30 min with through dry achieved in less than a few hours. Many acrylic emulsion paint systems are ready for subsequent topcoats in under 2 h of drying at standard conditions of 75°F and 50 % relative humidity.

With solvent-based alkyd paints, dry time assessment can be more critical to predict early film performance. Alkyds rely on an internal oxidative cure mechanism to build molecular weight through cross-linking between polymer chains. Additives used to catalyze the oxidative cure reactions can alter the drying performance of an alkyd based paint. Typical long-oil alkyd trim enamel paints applied by natural spread rate have dry set to touch times in the range of 45–120 min and maintain a good flow and leveling profile during these early stages of dry. This flow profile helps alkyd paints achieve better open time than acrylic latex paints during early stages of dry. However, the slower oxidative drying character of an alkyd paint can cause slower development of film toughness properties such as block resistance and hardness.

The most common methods of dry time testing for architectural paint films are by dry time recorder or by finger touch methods. Although both types of testing are used often in practice, most laboratories have a preference on which method to rely. Laboratories that use dry time recorder methods typically run dry testing very frequently and become very good in the art of comparing and interpreting dry time recorder results. Laboratories that insist on running dry by finger touch methods often believe the touch methods are more sensitive to slight differences in dry that might go undetected by interpretation of a dry time recorder result.

Both dry time methods are valid, however, one must be aware that they may give different interpretations of a coating's drying profile. It is typically not valid to compare Dry Hard time as measured on a dry-time recorder compared to a thumb-imprint judgment of Dry Hard.

Although there are surely many others, here are a few resources that can be used as guides in the assessment of drying times and film-formation processes in coatings. A few suggestions are as follows.

- Paint and Coating Testing Manual, Chapter 36, "Cure: The Process and Its Measurement" [2].
- Paint and Coating Testing Manual, Chapter 39, "Drying Time" [2].
- ASTM D1640-03 (2009), Standard Test Methods for Drying, Curing, or Film Formation of Organic Coatings at Room Temperature [3].

Holdout

Holdout is a property that indicates the ability of a paint to seal a surface to allow subsequent topcoats to maintain their ideal appearance. Typically, holdout of a paint is related to developing the desired gloss level for an enamel topcoat. If a gloss enamel paint is applied directly to a porous surface such as drywall, or a porous flat paint finish, its gloss potential could be significantly diminished. Because of this, a primer with good holdout properties is often selected to be a basecoat for a gloss enamel paint.

There are two methods typically used to assess holdout. The first method is by simple gloss measurement. In this method, the test paint is applied to the substrate or surface where holdout properties are of concern. A separate film application of a topcoat paint is made to a well-sealed surface to determine its full gloss potential. Finally, the topcoat paint is applied to the test paint using the same application method used on the well-sealed surface. Gloss is measured for each of the two topcoats and the holdout result is reported as a percentage of gloss over the test paint system relative to gloss over the well-sealed substrate.

Holdout can also be assessed by measuring porosity of a topcoat paint applied over a test paint compared with the porosity of a topcoat paint over an ideal surface. Porosity measurements are discussed in the following section.

Porosity

The porosity of a coating impacts film toughness properties such as stain resistance, washability, and abrasion resistance. For instance, the less porous the coating surface, the more difficult the coating will be to stain. Accurate measurement of porosity can thus give an indication of ultimate film performance.

Porosity testing can be an indication of good film formation. Even if film formation visually seems complete, a porosity test has the potential to identify differences in film formation. The uniformity of a substrate also affects porosity of a topcoat finish. Although a film may appear uniform, a porosity test on the substrate of choice can indicate ultimate porosity.

There are two key test methods for evaluating porosity of paint films, one that involves staining of the surface, and one involving weight gain. The staining test method is presented in ASTM D3258-04 (2010), Standard Test Method for Porosity of White or Near White Paint Films by Staining [1]. A test paint is first applied as a uniform film to a non-porous surface, such as a lacquer-sealed paper drawdown chart. When dry, a dark staining medium is applied on the test paint and allowed to stand for a specified time interval. The staining medium commonly used is compatible with Mineral Spirits. This allows the stain to be rinsed away with a solvent that is not expected to significantly affect the surface film. After the staining medium is rinsed away, the panel is allowed to dry and reflectance measurements are taken between the stained and unstained areas. The porosity of the test coating is reported as the difference in reflectance between the stained and unstained areas.

The weight gain method presented in ASTM D6583-04 (2010), Standard Test Method for Porosity of Paint Film by Mineral Oil Absorption [1], is similar to the staining method but uses mineral oil absorption to achieve a weight difference rather than staining medium absorption to achieve a measurable visual difference. Mineral oil is applied to a dry uniform film-thickness coating over a non-porous substrate. Excess mineral oil is wiped off and the panel is weighed. The difference in panel weight before and after the mineral oil application allows the calculation of how much mineral oil was trapped in pores of the coating.

Penetration

Penetration is the ability of a coating to flow into and permeate the surface of its substrate rather than form a simple film at the surface. Penetration is a significant factor on porous substrates such as natural woods or some wood composites. A coating that penetrates in addition to forming a film at the surface often offers enhanced adhesion

characteristics. For wood finishes such as film-forming semi-transparent stains, improved penetration can also assist in enhancing water resistance and ultimate durability of the coated wood. These benefits are often most realized in exterior coatings applied to substrates such as chalky or previously uncoated weathered wood. Penetration into wood may be hindered if a paint film forms too quickly or if binder particle sizes are too large.

Although penetration is a significant consideration in designing an exterior wood coating system, there is not an abundance of standardized test methods available by which to evaluate penetration. One common laboratory practice involves using filter paper or blotting paper to represent a porous substrate. Several layers (5–10) of paper are stacked and the test coating is applied by a dropper to the top layer of the paper. As the coating migrates into the layers of filter paper, it can spread out within the layer or penetrate into successive layers. The end result is how many layers the coating penetrates. This test is most successfully used as a comparison between two similar coating systems.

A more challenging test method involves application of a test coating to its desired substrate. After the coating penetrates the surface and is allowed to dry, small cross-sectional areas of the coated substrate are cut and evaluated using standard microscopic techniques. By viewing several cross-sectional areas, a technician can judge the overall ability of a coating to penetrate into the substrate. This method can be difficult to judge depending on the coating system. In a clear system, the color differences may not be readily visible. Even for pigmented systems, if the pigment particles are inhibited from penetration and the binder penetrates more deeply, a false analysis may result.

Low Temperature Film-Formation

The ability of a paint to form a uniform defect-free film at low temperatures is an important characteristic of coatings that are designed for new construction or those designed for exterior application. These types of coatings are more likely than others to experience cold ambient air conditions or cold surface substrates during application. Low temperature film formation is usually assessed at temperatures just above the freezing point of water, 4°C (39°F), but may be tested as low as desired for the end application.

The test paint, substrate, and application tools are all pre-conditioned at the designated low temperature. If possible, the paint application is conducted at the same conditions, however, if the application tools must be removed from the cold environment to create a suitable sample for analysis, the sample should be immediately returned to the cold environment as soon as possible after the paint is applied. After several hours or other suitable dry time, the paint is removed from the cold chamber and assessed visually for any film defects or poor gloss development. An acrylic emulsion-based paint that does not have sufficient coalescing solvent for low temperature film formation will often crack when applied on a paper drawdown chart and placed in a 4°C temperature environment.

There are two ASTM methods for assessing low temperature film formation. ASTM D7306-07 [1] involves visual assessment of the film after testing and ASTM D3793-06 [1] requires a porosity measurement once the film is removed from the cold temperature conditions.

APPLICATION PROPERTIES

Liquid paints may be applied by brush, roller, or one of a variety of spray methods. The final appearance of a painted surface is a result of a combination of a paint's early drying profile, application tool selection, and flow and leveling characteristics of the liquid paint. The following sections describe test methodologies used to assess the application performance of a paint.

Rheology Effects on Application

Viscosity of liquid paints was discussed in an earlier section but this topic extends quite distinctly to application characteristics. For instance, a paint does not necessarily need a high ICI viscosity to have a good spray application profile. A paint ideal for brushing or rolling might have a moderate to high Stormer viscosity but still spread evenly on a given surface.

Ultimately, testing of real-world application techniques in a field environment or in a laboratory with substrates representative of field surfaces is necessary to completely assess application characteristics. It is possible to predict field application behavior based on rheometric analysis of liquid paints, but such correlation must be developed through an extensive study of real-world application techniques.

Anti-Sag Resistance

One of the benchmark tests in predicting flow characteristics of an architectural paint is assessing its tendency to sag when applied to a vertical surface. The most common way to do so is by using a specially designed film application bar called an Anti-Sag meter. The Anti-Sag meter creates a series of uniform films with increasing thickness that come from the drawdown clearance indicated on the bar. One common anti-sag meter, see Fig. 1, has drawdown clearances ranging from 4 to 24 mils clearance in 2-mil intervals. When a drawdown is made from this application tool and the panel is immediately hung in a vertical orientation with the thickest stripe at the bottom of the panel, a technician visually assesses and reports the highest drawdown clearance where the paint did not "sag" into the next stripe. Fig. 2 shows a finished Sag test drawdown. This type of Sag resistance determination is detailed in ASTM D4400-99 (2007) [1].

Sag may also be determined more subjectively on any vertical surface using any application tool such as a brush or roller. The laboratory test technician would take the base of a paintbrush, a spatula, or any other suitable tool to mark a horizontal or wavy line in the wet finish. This type of test results in a pass or fail result depending on how much of the paint sags across the line.

Fig. 1—Example anti-sag meter drawdown tool.

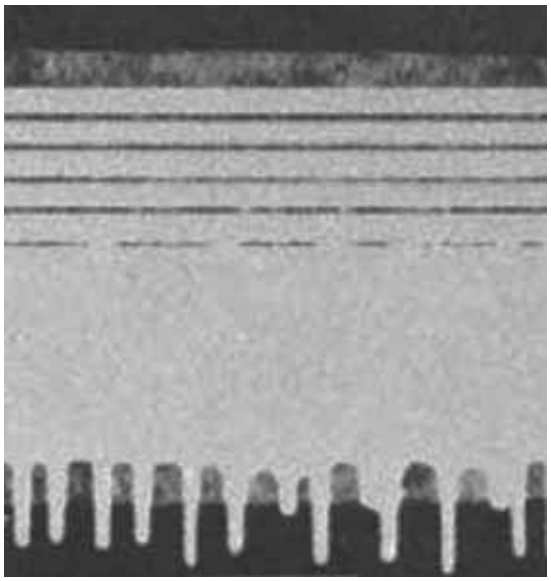

Fig. 2—Typical Sag pattern.

Fig. 3—Pocket wet-film thickness gage.

Leveling

The ability of a paint to level into a uniform finish is typically assessed on a horizontal surface. It is often more of a challenge for lower gloss and sheen finishes to level completely compared to higher gloss finishes which contain lower levels of pigment to inhibit flow-out of the polymer system.

A leveling evaluation may be done with any application tool other than tools designed to create uniform wet-film surfaces such as clearance drawdown bars. For a paint roller, the rheology and additives in a paint formulation and the nap size and construct of a paint roller will affect appearance in a rolled-out finish. The ability of the roller nap patterns to flow out into a smooth uniform finish represents the leveling capability of a paint. A paintbrush can also be used for leveling evaluation. Instead of nap mark patterns, the brushstroke marks must flow out smoothly to form a uniform film. When comparing multiple test paints for leveling, the same application tool should be used across different samples because different application tools may leave slight variations in film appearance.

There are a couple of specially designed paint-application drawdown bar tools that are used to assess leveling ability of a paint. The NYPC leveling bar applies five sets of two uniform stripes of paint to a test panel. Each group of two stripes is at a different drawdown clearance: 10, 20, 40, 80, and 160 mils. As the paint flows out, the gap between the stripes is overcome and the paint flows together. The rating is assigned based on what film thickness produces a result where one paint stripe is no longer able to flow into the stripe of its pair.

The second type of leveling drawdown bar that is used consists of a rounded bar that creates a pattern of uniform ridges across the drawdown area for a paint. This drawdown is rated by allowing the paint to dry in a horizontal orientation and then comparing the drawdown appearance to a set of levelness standards where 10 is completely smooth and standard number 1 shows very distinct ridges. Evaluations using this tool should be done in a controlled light environment and all test specimens viewed at the same angle or series of angles to ensure consistent interpretation and rating of results. Similar levelness standards may be used in practice to assess leveling resulting from paint brushouts.

Applied Spread Rate

Spread rate of an architectural paint is reported in units of area covered per unit volume of paint (sq. ft/gallon or sq. m/L). In some regions, spread rates are alternately reported in area per unit mass (typically sq. m/kg). The desired spread rate is set by paint manufacturers in order to achieve a certain dry film thickness that will give the end user of paint the durability properties needed for the paint to perform as it was designed.

Rather than target a spread rate, painters who apply by spray application methods typically assess spread rate in the field by using a wet-film thickness gage, see Fig. 3. This pocket tool quickly tells a painter if the speed of delivery of the liquid paint is sufficient to achieve the needed film thickness. Use of notch gages for measuring wet film thickness are detailed in ASTM D4414-95 (2007) [3]. A painter or laboratory technician can measure the spread rate applied to a test panel by measuring its area and the weight of paint applied. The weight applied can be converted to volume using the known density of the test paint and then area per unit volume can be calculated.

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Spread rate

Area of test panel = 20 by 30 cm = 600 cm^2 = 0.060 m^2

Weight of applied paint = 8.0 g = 0.0080 kg

Density of liquid paint = 1.3 kg/L

$$\text{Applied spread rate} = 0.060\ m^2 \div (0.008/1.3)L$$

$$= 9.8\ m^2/L \text{ or } 400\ ft^2/gal$$

Wet film thickness calculation (assuming uniform coverage)

$$\text{Volume applied} = (0.0080/1.3)L = 0.00615\ L = 6.15\ cm^3$$

$$\text{Area of test panel} = 600\ cm^2$$

$$\text{Wet film thickness} = (6.15/600)\ cm = 0.010\ cm = 100\ \mu m$$

For design of a laboratory test or field test of a given coating system, a laboratory technician must decide whether to control the spread rate by forcing the coating to be applied at a desired weight, or to apply the coating at a natural spread rate from a given application tool. If natural spread rate is selected, it is still considered a best practice for the technician to measure the amount of paint applied to the testing area at least for the first few samples to make sure the amount being applied is close to the desired result. Applying too much or too little paint to a test panel can greatly affect test results such as exterior durability, flexibility, and stain-blocking.

Applied Hiding Power

The ability of a paint to hide defects in the background can be a critical requirement. Very white or brightly colored paints sometimes do not have the pigmentation necessary to hide different or varying background colors they are intended to cover. Because of this, it is necessary to be able to assess hiding power using conventional laboratory methods.

ASTM D5150-92 (2009) [1] describes a method for evaluating hiding power for paints applied by roller. In this method, a standard sealed chart with varying degrees of light gray to dark gray to black stripes over a white background is used as the application substrate. Test paints are applied by roller and the result is visually assessed to judge which colored stripe is the last one to be barely visible under the topcoat. Although D5150 is for evaluation of roller-applied paints, the same type of panel can be used as a substrate for applied hiding power evaluation using any application tool such as a paint brush or airless spray equipment.

An alternate method for assessing applied hiding power differences between two paints is given in ASTM D344-97 (2004), Standard Test Method for Relative Hiding Power of Paints by the Visual Evaluation of Brushouts [3]. This method uses a black and white sealed chart as the substrate and requires the user to measure the amount of paint applied so it is applied at a known spreading rate. The method requires some practice of brushing technique because the visual assessment of hiding assumes uniform application across the entire brushout. In ASTM D344, the hiding power of the test paint relative to the control paint is defined as the spread rate of the test paint needed to achieve equivalent visual applied hide contrast divided by the spread rate of the control paint.

Hiding is often assessed on paints that are applied to achieve a uniform film thickness as with a drawdown method. This type of hiding assessment is described in the section on Appearance Properties.

Application Foam

Many architectural paints use defoamers as additive ingredients to suppress foam formation during manufacturing as well as during application. Foam can be particularly noticeable for application with a paint roller. As paint transfers between the roller and substrate, the fibers of the roller pull paint from the painted surface and back to the roller. The result of this repeated process can be foam in the form of un-popped bubbles along the path of the roller. In some cases the foam will pop before the paint is able to completely dry; however, in other cases the foam can be relatively stable and remain in the film after the surface has dried. This leads to an undesirable appearance. Foam can also be generated by brushing or spraying. Foam resulting from spraying applications may manifest itself as very small pinholes in the coating.

To test for application foam, a technician must simply choose the application tool and substrate of choice and then observe how foam develops after application. The final judgment of the presence of foam should be conducted after the surface of the film has dried. Microscopy may be used for verifying that the surface is free from foam, pinholes, or other defects.

Spatter Resistance

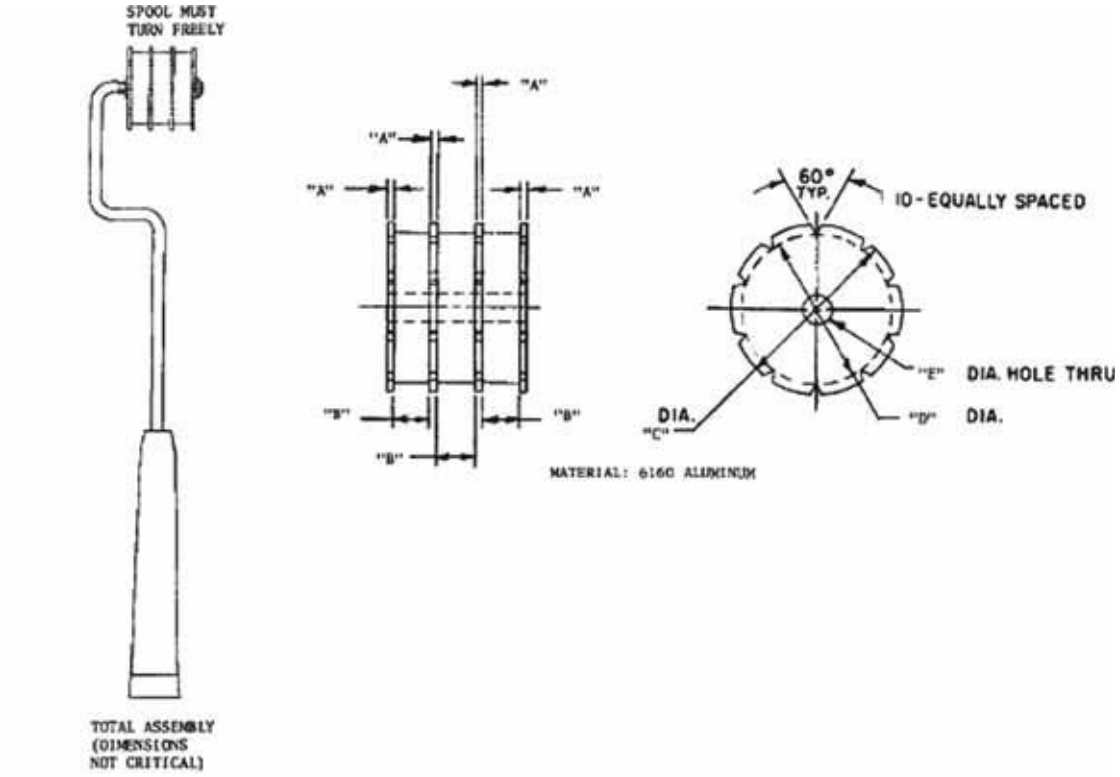
Spatter resistance is generally a property considered for interior wall paints. Although drop cloths are used in most painting scenarios to protect flooring or surrounding furniture, there is still a desire to prevent paint from spattering onto the person applying the paint. As with application foam, spatter resistance of a paint is most often associated with hand-held roller application tools. Spatter may be evaluated by choosing a substrate and application tool that will best represent what is used in the field.

ASTM D4707-09 [1] was developed to provide a systematic test method for evaluating and rating spatter resistance. This method calls for a specially designed "notch-spool" roller (see Fig. 4) to artificially generate spatter for any test paint selected. Each notch on the spool roller catches the paint and flings it downward during the application. The spatter is caught on a black panel (or a white panel for dark colors) and evaluated versus a set of visual standards also provided in ASTM D4707-09 to give a 0–10 rating scale. Even if the notch-spool roller is not used for the test, the visual standards are often used in rating spatter resistance using any suitable application tool.

Applying Uniform Paint Films for Testing

Much of the testing done on paint films in a laboratory environment requires the application of a uniform paint film. There are many ways to apply uniform paint films for testing which are detailed in ASTM D823-95 (2007), Standard Practices for Producing Films of Uniform Thickness of Paint, Varnish, and Related Products on Test Panels [3] (Table 3), as well as in Chapter 40 of this manual, "Film Preparation for Coating Tests" [2].

The most important of these standard practices for an architectural coatings laboratory are the blade film application practices. Spray application practices are occasionally used for architectural coatings projects, however, these techniques are much more common for application of industrial coatings to metal panels or other substrates. Architectural coatings manufacturers that do maintain



Dimensions			
		in.	mm
A	Flange thickness	0.063± 0.005	1.60 ± 0.13
B	Space between flanges	0.343 ± 0.005	8.71± 0.13
C	Total diameter	1.600± 0.015	40.16 ± 0.38
D	Diameter under notches	1.400 ± 0.015	35.56 ± 0.38
E	Hole diameter	0.281 ± 0.005	7.14 ± 0.13

Fig. 4—Notched spool roller and dimensions from ASTM D4707.

laboratory capabilities for spraying typically use these to assess characteristics using airless spray equipment that would be used by professional painters in the field.

Blade film applicators are more commonly referred to as "drawdown bars." They come in many dimensions, shapes, and have varying clearance gaps. Some are one-sided, some are two-sided (top and bottom have different clearance gaps), some are multi-sided (for instance, a square drawdown bar with four clearance gaps on one side and four clearance gaps on the other side), some are even adjustable to various clearances. The use of drawdown bar tools is quite simple—a test panel or substrate is affixed to a flat surface; a small amount of paint is placed at the top of the test panel just in front of the drawdown bar; and finally, the bar is drawn down leaving behind a uniform thickness of the liquid paint.

TABLE 3—Practices of ASTM D823-95 (2007) [3]

Practice	Description
A	Automatic Spray Machine Application
B	Motor-Driven Dip Coater Application
C	Motor-Driven Blade Film Application
D	Hand-Held Spray Gun Application
E	Hand-Held Blade Film Application

A common best practice to ensure a uniform film thickness drawdown on a sealed paper test chart is to use a vacuum plate as the flat surface beneath the test panel. The use of a vacuum will prevent the paper chart from having small bumps or bends which might lead to non-uniform film thickness in those areas. A representative vacuum plate is shown in Fig. 5. The nozzle attachment of the vacuum plate is connected directly to a vacuum pump.

Motor-driven drawdown bar film applicators are typically designed with a vacuum plate included. The potential advantage of using a motor-driven drawdown applicator rather than hand-held drawdown bar is that the speed of application is constant and there are no shakes or wiggles that could happen during a hand-held application. A practiced technician can become as good as a motor-driven drawdown applicator for producing consistent uniform films, but repeatability between different operators can cause minor differences.

One common type of drawdown bar is called a "Bird" bar. A 3-mil Bird bar is one of the most common pieces of equipment found in an architectural coatings laboratory. It is important to note that Bird bars are graduated differently

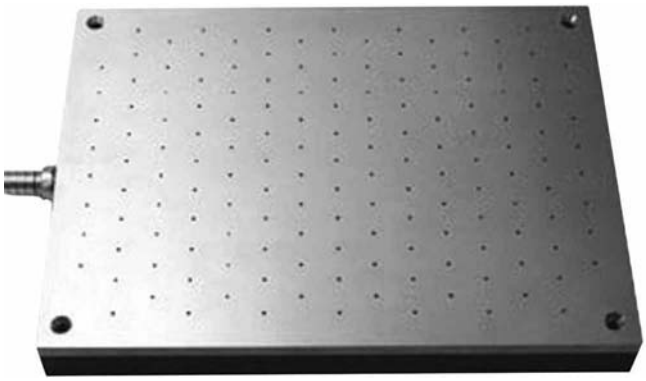


Fig. 5—Vacuum plate. (Courtesy of Paul N. Gardner Company.)

than standard clearance drawdown bars. A Bird film applicator labeled as 0.003 in. or 3 mils actually has a clearance of 6-mils. This is confusing to many paint technicians who do not recognize the distinction. The idea of the Bird bar when it was introduced was to allow a laboratory technician to apply a wet film of approximately 3 mils. The final wet-film thickness of the paint drawdown will vary depending on rheological character of the paint and the speed of the drawdown.

In the U.S., film thicknesses in the coatings industry are still typically reported in units of mils with 1 mil being equal to 0.001 in. Drawdown bar tools are also specified in units of mils. In the rest of the world, drawdown tools are typically specified in units of microns or μm. Because there are 25.4 μm per mil, a 100 micron drawdown bar is roughly equivalent to a 4 -mil clearance gap drawdown bar (Table 4).

Open Time

Regulatory pressures to formulate coatings at low solvent levels have caused open time to become an important property of interest for coatings formulators. Without consideration for solvent amounts or solvent selection, there are a broad range of ways to extend or reduce open time for a given coatings system. Restrictions on the use of solvents classified as volatile organic compounds have resulted in polymer design to play a much more significant role in how a coating behaves during early stages of dry.

In terms of brush application, open time is the amount of time after a coating is applied where the coating film can be re-brushed into without leaving any noticeable difference in the film appearance. After the additional brushing, the coating must still flow out to match surrounding areas in order to still be considered "open." This property allows a painter flexibility to return to an area already painted and repair any drips or marks left behind by the original coat. If a paint has a short open time and closes quickly, there are only a few minutes before the paint can be re-wet by brushing into it. After the open time has elapsed, re-brushing into the film adds an additional coat to the surface rather than repairing the original coat.

For interior and exterior paints, open time is tested in the laboratory by brushing into a uniform film at varying time intervals. For short open time paints, 2-min intervals are often used. For long open time paints, 10–15 min intervals are often more appropriate. To accentuate the appearance of open time, the initial film drawdown is disturbed by marking the surface which will be repaired by re-brushing into the film at the designated interval. The open time is the last time where the marks on the film surface are able to be re-incorporated into the film without being visible.

This same method can be extended to film-forming wood stain finishes by applying the coating directly to a wood substrate. At various time intervals, additional wood stain is applied on adjacent areas and lapped into the original application of stain. Here a laboratory technician is observing the visibility of overlap marks between adjacent areas. Open time for non-opaque wood finishes is often referred to as lapping time because the assessment focuses on the visibility of lap marks in the overlapping application areas.

TABLE 4—English Unit Approximation of Metric Drawdown Clearance Gaps

Metric	Equivalent in Mils	U.S. Drawdown Bar Equivalent
50 μm	1.97	2 mils
75 μm	2.95	3 mils; 1.5-mil Bird
100 μm	3.94	4 mils
150 μm	5.91	6 mils; 3-mil Bird
300 μm	11.8	12 mils; 6-mil Bird

Touch Up

Touch up is the ability of a paint to maintain its original appearance when a small area is re-painted with the same paint after the original coat has dried. This is an important characteristic because small imperfections are often found upon inspection of a newly painted wall or surface resulting in the painter wishing to repair them to improve uniformity of appearance for the overall paint job. In new construction, the ability to touch up paint is critical as there is a lot of traffic through a building or home while it is being completed for occupancy. Touch Up can be important for both interior or exterior paints but it is normally more important for paint on interior wall surfaces due to higher visibility at close distances.

To establish a laboratory test protocol for touch up, the field touch up scenario should be considered in selecting application tools and environmental conditions for the test. For a paint designed for a DIY consumer, roller or brush touch up over a roller base coat is the most common scenario. For professional painters, touch up with a brush or roller over a sprayed basecoat is common. Different application tools—which can cause a paint to experience varying shear stress during application—can cause differences in color development especially if surfactant and pigment loadings in the paint have not been optimally formulated. Environmental conditions can also change between the time of applying a basecoat and a topcoat. For example, during cold-weather months for new residential construction, the main paint application might be completed in cool conditions before heating systems in the new house are fully on-line. However, final touchups may be completed at the end of the construction process when environmental conditions would be normal room temperature.

A simple visual assessment is the most common observation criteria for a touch up test. ASTM D3928-00a (2010), Standard Test Method for Evaluation of Gloss or Sheen Uniformity [1], describes a laboratory procedure for providing a visual assessment rating for touch up by paintbrush of a paint sprayed on a test panel. Gloss and color measurements of touched up and non-touched up areas may be taken to assist a coatings formulator in differentiating performance of paint systems that appear visually similar.

APPEARANCE PROPERTIES

Color and Gloss

The measurement of color and gloss for architectural coatings is the same as measurements of color and gloss for other types of coatings. In an architectural coatings laboratory, film drawdowns over lacquer-sealed paper charts are typically used to assess color and gloss. In the production of architectural coatings, samples from paint batches are often force dried in an oven deemed suitable to speed the curing process without affecting assessment of the finished appearance. It is common for paints to be manufactured as white bases of varying strengths which are subsequently tinted using standard universal colorant dispersions based on standard recipes at the point of sale. To ensure accuracy of tinting across multiple batches it is important to measure and control the tint strength of the coating in production.

Tint strength is measured by adding a pre-determined amount of a specific colorant or blend of colorants to a white paint and measuring it against a standard. If the color matches within a pre-defined tolerance limit, the paint batch may be approved. The tolerance limit varies depending on what is the acceptable variation for the end customer. ASTM D3134-97 (2008)e1 [3] provides a standard practice for establishing acceptable color and gloss tolerances.

Gloss measurement for architectural coatings are important in order to define the finish for painters or consumers. Flat or matte finishes are measured for gloss using a higher viewing angle of 85°; mid-gloss paints, such as satin and semi-gloss, are measured at a viewing angle of 60°; and high gloss finishes are often measured at both 20° and 60°. A viewing angle of 85° is sometimes referred to as "sheen" instead of gloss.

A detailed discussion of color and gloss measuring instrumentation is found in optical properties sections of this testing manual such as Chapter 43, "Color and Light," or Chapter 44, "Gloss" [2].

Hiding Power

Hiding power is measured by comparing the color of a coating over a black background to the color of the same coating over a white background. This measurement is called contrast ratio and is often expressed as a percent. If a coating is completely opaque, the two colors will be the same and the contrast ratio will be 100 %. In practice, the contrast ratio is reported as the ratio of reflectance (Y-tristimulus) value of a white paint over black background to the reflectance value of a white paint over white background. Many lacquer-sealed drawdown charts are manufactured with white and black backgrounds in order to enable measurement from a single drawdown. Contrast ratio can be measured for any paint film thickness but in practice is often conducted over a 3-mil Bird drawdown.

Uniformity of Finish

Uniformity of finish is an important parameter for a coatings formulator. In a typical production environment, the uniformity of finish of a coating is expected to be perfect and is judged on a pass/fail scale. However, in a laboratory environment where modifications in additives or formulation parameters result in different film-formation characteristics, a 0–10 rating scale with 10 being a perfectly uniform film is often more useful. Film defects that result in non-uniformities of film appearance include things like cratering, orange-peel appearance, and pinholes. One key resource that offers a variety of examples of film defects is the FSCT Pictorial Standards of Coatings Defects Handbook [4].

DRY FILM PERFORMANCE PROPERTIES

Adhesion

An architectural coating system must be designed to have good adhesion on its intended substrate. Many architectural coatings are intended primarily for recoat of previously painted surfaces. Adhesion in this case is straightforward and can be easily verified using a simple cross-hatch adhesion tape-pull test as described by method B of ASTM D3359-09e2, Standard Test Methods for Measuring Adhesion by Tape Test [3].

Because previously painted surfaces can vary in porosity and compatibility with the topcoat, an architectural coatings laboratory often chooses to evaluate adhesion of a paint over an aged gloss alkyd enamel finish. Use of aged gloss alkyd enamels for an adhesion substrate became a standard for a couple of reasons when the first-generation of acrylic emulsion latex paints were emerging. First, the early acrylic emulsion latex paints were often used to paint over alkyd enamels because the alkyd enamels were the predominant paint used in construction at the time. Second, this was a challenging test for many of the acrylic emulsion paints to withstand. A practice for preparation of aged gloss alkyd panels can be found in ASTM D6900-10, Wet Adhesion of Latex Paints to a Gloss Alkyd Enamel Substrate [1].

Exterior coatings and primers often are subject to more challenging adhesion performance standards than interior wall paints. These coatings are subject to be directly applied to not only previously painted surfaces, but also to wood, masonry, and various metals such as steel, galvanized steel, and aluminum. Testing to these different substrates may also follow ASTM D3359 [3] or any other method as described in Chapter 50 of this manual [2].

Exterior coatings are often exposed to wet and humid conditions and must maintain their adhesive character when paint films are wet. One common laboratory practice for evaluating wet-film adhesion is to submerge the test panel in water or place a saturated paper towel or cheesecloth on the test area of the surface until the film is saturated. When the film is sufficiently wet, the coating can be tested using cross-hatch adhesion by tape methods. Another practice is described by ASTM D6900-10 [1]. In this test, the coating is applied to an aged gloss alkyd panel and allowed to cure at an agreed interval. The panel is then soaked, cross-hatched, and placed on a linear abra-

sion machine using a standard wet scrub brush attachment. After 100 or other agreed upon number of cycles, the percentage of squares removed is determined by visually examining the panel.

Scrub Resistance

The intent of a scrub resistance test is to demonstrate the ability of a coating to resist film deterioration and erosion during cleaning. Scrub resistance testing is considered most applicable to interior wall paints. It is generally not as important for exterior coatings because they are more likely to be washed down with water spray rather than with a scrubbing mechanism. Scrub resistance tests are typically done with a household cleaner or a laboratory-prepared cleaning solution. The cleaner selected may be abrasive or non-abrasive depending on the desired harshness of the test. The cleaner is applied to a wet bristle brush which scrubs the surface of the paint film. A linear washability machine tester is typically used to conduct the test.

There are two types of scrub resistance tests. In the first, the coating is tested to a failure point as described by ASTM D2486-06, Standard Test Method for Scrub Resistance of Wall Paints [1]. In this test method, the test paint is applied by drawdown to a uniform film thickness and allowed to dry for a week at standard conditions or at other agreed upon drying interval and conditions. A 12.7 mm by 0.25 mm shim is placed behind the test panel to create an artificial but consistent bump in the path of the scrub brush. As the scrub brush passes over the raised area during the test, the film will show failure here. A bristle brush is wet and applied with an abrasive scrub medium that speeds erosion failure of the test. In this method, it is often a best practice to conduct a comparative test between two coatings. This way any variability in setup of the test is minimized because the two coatings are scrubbed on the same machine simultaneously.

In the second type of scrub test, the coating is tested for a pre-set number of cycles and then measured to determine the amount of film that eroded during the test. Methods of this type include ASTM D4213-08, Standard Test Method for Scrub Resistance of Paints by Abrasion Weight Loss [1] and ISO 11998:2006[E], Determination of Wet-Scrub Resistance and Cleanability of Coatings [5]. In contrast with the scrub to failure methods which use a bristle brush with an abrasive scrub medium, this test requires use of an abrasive pad used with a non-abrasive medium. Additionally, no shims or raised area is necessary for this test. Instead, the coating to be tested is weighed before and after the test. The difference in weight is used to calculate the volume of film displaced or the amount of film thickness lost during the test.

Burnish Resistance

Burnish resistance is the loss of uniformity of finish when a paint film is rubbed during normal use. As with scrub resistance, burnish resistance is a test for interior wall paints rather than exterior paints. Flat and low sheen paints typically burnish more than semi-gloss or gloss paints and sometimes burnish resistance is not even evaluated for higher gloss finishes. The relatively high pigment content of flat paints makes them more susceptible to gloss increases due to burnishing.

In the laboratory, burnish resistance is tested using the same linear washability machine as the scrub tester. However, burnish resistance is typically evaluated under dry conditions. A dry abrasive pad may be used, or a cheesecloth-wrapped piece of wood is attached to the washability machine to provide the mechanism for burnishing. A test method for Burnish Resistance of Latex Paints is offered in ASTMD6736-08 [1].

For very low sheen paints, burnish resistance is typically reported as units of sheen increase. However, in the case of higher sheen flats or satin finish paints, a percentage of units of gloss increased may be more critical in differentiating two test paint systems in performance.

A preliminary assessment of burnish resistance differences between two test paints can be made by simply swiping the back of a fingernail across a drawdown of two test finishes while applying a little pressure. If one of the finishes shows the mark more, it will generally rate lower for burnish resistance. The end resulting panel from a wet-scrub test may also be used to estimate burnish resistance. Simply take gloss measurements on the panel in the path of the scrub brush and in the unscrubbed areas after the paint is allowed to dry.

Stain Resistance, Stain Removal, and Washability

The properties of stain resistance and stain removal are often confused during discussion of coating performance. Stain resistance is the ability of a coating film to resist staining from the specified medium. Stain removal on the other hand, is a rating of how easy it is to remove the stain once it is already present on a coated surface. Because semi-gloss and high gloss coatings tend to be relatively non-porous compared to flat finishes, they are inherently better at stain resistance. This often leads to a higher rating for stain removal because if the stain is trapped on the surface and not in the pores or crevices in the coating, a household cleaner will be able to more easily access the stain and wash it away.

The terms stain removal and washability are essentially equivalent. The term washability is often considered a more practical oriented test designed to mimic actual washing of an interior wall coating with a sponge and household cleaner. Alternatively, standard stain removal tests often have artificial removal methods such as scrubbing with a laboratory benchtop linear washability tester.

Stain resistance can be measured in a couple of different ways. The varieties of stains to use are highly dependent on the end application and what the person designing the test believes are the most critical stains to evaluate. A simple spot test can be used to assess stain resistance for any staining media. An effective test method is described in ASTM D1308-02 (2007), Standard Test Method for Effect of Household Chemicals on Clear and Pigmented Organic Finishes [3]. This method covers not only household chemicals, but also food items such as beverages, cooking oils or fats, and common condiments.

ASTM D1308 provides a wide latitude for an experimenter to choose the most critical parameters for study. Chemical spots can be covered or uncovered and allowed to stand on the test panel for any desired time interval before evaluating. At the end of the test, the stained film area is evaluated for staining or discoloration. Typically a rating scale (such as 10 = excellent, 0 = poor) is designed within

a laboratory to indicate relative performance. Alternatively, stains can be rated simply as pass or fail or, if the stained area is large enough, a color reading can be taken and reported as color difference versus an unstained reference area.

There are two primary ASTM methods that encompass methods used to assess architectural coating performance for stain removal and washability. ASTM D3450-00 (2010)e1, Standard Test Method for Washability Properties of Interior Architectural Coatings [1], utilizes a carbon black dispersion in mineral oil and odorless mineral spirits as the soil-ant medium. After the stain is applied to the test film, a scrub media solution is applied to a wet sponge and affixed to an attachment to the linear washability machine—the same machine used for scrub resistance testing. The sponge is allowed to pass over the soiled area for a set number of cycles. The final result is reported as the ratio of reflectance of the washed soiled area and the reflectance of the unsoiled dry film.

ASTM D4828-94 (2008), Standard Test Methods for Practical Washability of Organic Coatings [1], more closely represents a practical stain removal situation. In this method, soil and staining media include stains from common household items such as lipstick, ink pens, or crayons. The reporting method is a visual assessment and grading of the stain removal rather than a measured reflectance. Otherwise, the mechanics of this method are similar to ASTM D3450 both use a wet sponge with scrub medium and the linear washability machine for a set number of cycles.

Block Resistance

Block resistance is a test intended to measure the ability of a coating to withstand sticking to itself when under pressure. In a field environment, this is represented by a newly painted window and frame or a door and the surrounding molding. Most architectural trim enamel coatings are expected to stand up to block resistance at normal room temperature after only a day after being painted. Block resistance is not typically an issue for flat or satin finish paints—the higher pigmentation level of these classes of coatings usually enable good block resistance performance.

A block resistance test can be done in many ways in a laboratory environment but all block resistance tests follow the same basic procedure. Any two flat substrates, at least one of which is painted with the test paint, are placed face-to-face and a weight placed on top for a certain time interval. After the agreed upon time interval, the flat surfaces are separated from each other. The testing technician can rate the paint for any film separation that happens as well as how tacky the surfaces were to each other during attempted separation.

ASTM method D4946-89 (2008)e1, Standard Test Method for Blocking Resistance of Architectural Paints [1], gives instruction for one standard way to conduct this test. The ASTM method calls for a specific size rubber stopper (#8 stopper) and a 1-kg weight to be placed on top of each test sample. Each test sample consists of a paint drawdown that has been cut into square pieces with two squares placed face to face. The drawdown stays under the 1-kg weight block for 30 min, and then is allowed to rest at room temperature for an additional 30 minutes before separation. The separation is rated based on a 0–10 rating scale with ratings of 4–10 (no tack between samples) grading how tacky or difficult the separation, and the lower ratings of 0–3 (0 = complete separation) being reserved for paints where varying degrees of film sealing are observed.

Block resistance tests can be run at room temperature, but are often also run at elevated temperature of around 110–120°F. The elevated temperature makes a more challenging test and can simulate more challenging field conditions that coatings may face.

Print Resistance

Print resistance is related to block resistance, but instead of the coated paint sticking to another flat surface, another object is allowed to sit on the coated paint and evaluated for the imprint left on the painted surface. This would be tested most typically for high gloss enamel finishes. A typical print resistance test requires a cheesecloth to be placed on the surface and under a weight for a set time period. At the end of the time period, the weight and cheesecloth are removed. The tester then evaluates how much of the imprint is showing on the surface and does not recover. A detailed test protocol for print resistance is found in ASTM D2064-91 (2008), Standard Test Method for Print Resistance of Architectural Paints [1]. Examples of heavy, medium and slight print resistance are shown in Fig. 6 which can also be viewed in ASTM D2091-96 (2003), Standard Test Method for Print Resistance of Lacquers [1].

Architectural Primers and Stainblocking

Architectural primer coatings are designed to be recoated by durable topcoats, so they do not necessarily need to have the best scrub resistance, stain resistance, or high gloss appearance that are requirements for certain topcoat paints. Overall, primer performance is often judged based on properties of adhesion and holdout that were discussed in previous sections. One performance property that is a unique requirement of primers is stainblocking.

Stainblocking is the ability of a coating to prevent staining media present within or on top of a surface from penetrating into a subsequent topcoat. Stains that need to be primed originate from a variety of sources. Some of the more common sources are ink pens or markers on interior walls, water leaks on ceiling tiles, or tannins and other extractives that naturally occur in wood.

The basic steps for testing stainblocking are the same for all. Simply coat the stained substrate with the test primer, allow it to dry then topcoat it with a paint representative of the topcoat that would be used in a field environment. In order to ensure the stainblocking performance is a result of the primer, the topcoat that is chosen often has marginal inherent stainblocking on its own. The drying time of the primer system is a key variable in setting up the test; shorter dry times for the test primer can show more stainblocking performance differences than longer dry times.

For tannin blocking evaluation, wood boards being tested are typically exposed to a humid environment in order to stimulate the tannins within the boards to migrate through the primer. ASTM D6686-01, Standard Test Method for Evaluation of Tannin Stain Resistance of Coatings [1], provides a test procedure for evaluating tannin bleed-through.

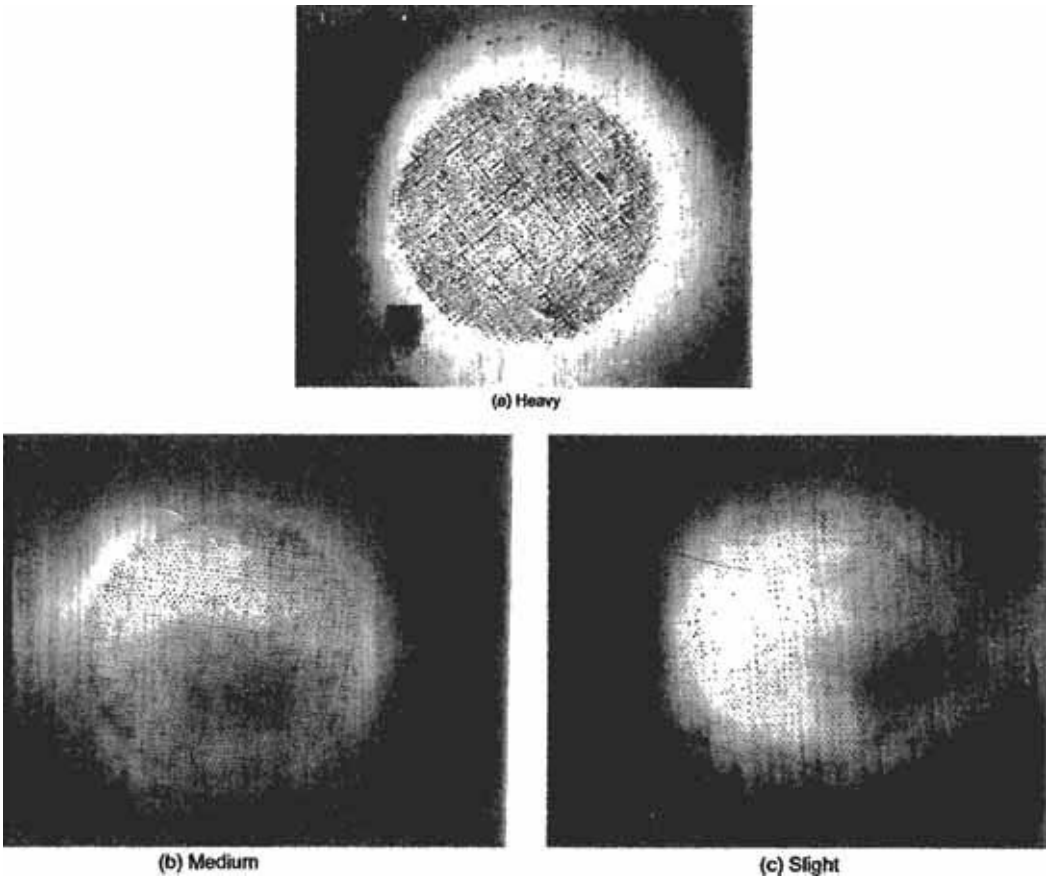


Fig. 6—Print resistance examples. Top panel represents heavy imprint (poor print resistance). Lower left panel represents medium imprint. Lower right panels represents slight imprint.

The results of a stainblocking evaluation are often evaluated by visual assessment and comparison of test primer versus control. For more differentiation, a spectrophotometer can be employed to measure the difference in color that the use of a stainblocking primer achieves. This allows for more precision in differentiating between multiple test systems.

Floor Coatings

Some architectural coatings are designed for application to wood or concrete floors. In general, floor coatings must be considered for their ability to withstand abrasion from light foot traffic. Abrasion Resistance is discussed in detail in Chapter 49 of this testing manual [2]. Any of the abrasion methods described there are applicable to architectural coatings; Taber abrasion or falling sand are most commonly used in practice.

Garage floor coatings have special requirements for testing such as the ability to resist automotive fluid chemicals and to withstand hot tires. Automotive fluid or other chemicals of interest can be tested in accordance with ASTM D1308-02 (2007) [1]. Additional detail on chemical resistance testing of coatings is also found in Chapter 55 of this manual [2]. Hot-tire pickup resistance of a coating can be simulated in a laboratory environment with a section of tire tread. The tire tread is heated to the desired temperature to simulate heat gained from road friction; the tire tread may also be heated while submerged in water to simulate a tire on a rainy day. The tire tread is then clamped to a concrete test panel that is coated with the test paint to generate a desired pressure. After a certain time period, the tire tread is separated from the test panel which is evaluated for film removal or disfigurement as a result of contact with the tire.

Deck Finishes

The architectural coatings category of deck finishes covers several types of coatings including paints, solid color stains, semi-transparent stains, and clear waterproofing coatings. Like floor coatings, deck finishes must also be considered for wear resistance and light foot traffic tests described in the previous section. Natural exposure to elements such as sunlight, temperature variation, and water/humidity are also critical for deck finishes. Because deck finishes on horizontal surfaces must hold up to standing water, they are often evaluated for water repellency. A discussion of water-repellent coatings and related test methods is included in Chapter 67 of this testing manual [2].

Environmental Effects

Many architectural coatings are designed for application to exterior structures. Each exterior coating must be able to withstand sun, moisture, and temperature variations in its designated environment.

For natural exposure, architectural coatings companies typically use a practice similar to ASTM D1006-01 (2008), Standard Practice for Conducting Exterior Exposure Tests of Paints on Wood [3], to evaluate exterior performance.

Although this test practice refers specifically to wood substrates, the basic principles of ASTM D1006 for exposure orientation, test fixtures, use of control or reference materials, application of paints, and inspection may be applied to any type of substrate. When D1006 was developed, wood substrates were once the most common siding material for residential construction, however, many other composite materials and finishing systems now predominate new construction markets.

For accelerated exposures, different methods can be selected. Three of the most commonly used accelerated methods for architectural coatings evaluation are:

1. UV-Condensation exposure—described in ASTM D4587-05, Standard Practice for Fluorescent UV-Condensation Exposures of Paint and Related Coatings [3].
2. Xenon-Arc exposure—described in ASTM D6695-08, Standard Practice for Xenon-Arc Exposures of Paint and Related Coatings [3].
3. Fresnel reflector rack exposure—described in Procedure C of ASTM D4141-07, Standard Practice for Conducting Black Box and Solar Concentrating Exposures of Coatings [3].

There are different reasons to select among these accelerated testing practices. Typical decision criteria on what accelerated protocol to use are decided by cost, ease of maintaining the test equipment and test fixtures, and experience as to which method most accurately duplicates natural exposure for the intended exposure environment. A detailed discussion of accelerated exposure testing for coatings is found elsewhere in this manual [2].

Inspection of coatings on exposure tests are related to maintaining the original appearance and integrity of the paint film. Common exposure evaluation criteria for architectural coatings include the following:

- Gloss and Color Retention
- Film Integrity: Cracking, Checking, Flaking, Erosion
- Chalking
- Mildew growth
- Dirt Pickup

Chapter 52 of this manual [2] describes general inspection practices for natural weathering tests and provides test reference standards to the items listed above.

CONCLUSION

This chapter has provided a broad review of test methods used for the assessment of architectural coatings performance. Sections of this chapter have described tests relevant to several subsets of architectural coatings as well as performance testing categories including liquid paint and film formation, application characteristics, appearance, dry film performance, and environmental effects.

Ultimately, an architectural coatings formulator must design test criteria that take into account changing regulatory requirements, various field application techniques and substrates, and environmental exposure factors. It is the author's intent that the contents herein prove useful to a formulator or testing technician to establish criteria, guidelines, and references for evaluating architectural coatings systems.

References

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[4] Sonntag, R. C., *Pictorial Standards of Coatings Defects,* Federation of Societies for Coatings Technology, Blue Bell, PA, 1979.
[5] ISO Standard 11998:2006[E]: Paints and Varnishes—Determination of Wet-Scrub Resistance and Cleanability of Coatings, ISO, Geneva, Switzerland, 2006.

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Artists' Paints

Benjamin Gavett[1]

INTRODUCTION

AS COATINGS, ARTISTS' PAINTS ARE DECORATIVE in nature and are intended to endure for decades or centuries under conditions of indoor storage and display. Relative to other coatings, they are highly loaded, most often with a single pigment. Thickness of application ranges from transparent washes to thick, textural builds. Typical tools used include the airbrush, paintbrush, and palette knife, but paints are also often applied by other means, such as rags, sponges, or with the hands. They are often modified at the time of application to change sheen, texture, color, flow, or other characteristics. The substrate used is usually paper or a cotton or linen duck stretched over an open frame, but may be almost anything else, including solid or compressed wood panels, paperboard, metal, synthetic fabric, glass, figurines, clothing, or walls.

Artists' paints are categorized according to their vehicle or binder. Most common are oil (alkali-refined linseed oil), acrylic (acrylic emulsion), and water color (gum arabic). Variations of these include several types of vegetable-based drying oils, such as cold-pressed linseed oil, safflower oil or stand oil, and acrylic emulsion copolymers. Other natural and synthetic materials that are in more limited current use are acrylic solutions, poly(vinyl acetate), casein, egg, wax, and various gums.

Although an artist will use almost any paint, those formulated for such use are expected, above all else, to be as permanent as possible. However, paint is only one element in the process of manipulating materials to transform vision and ideas into art. Stability of the finished work is a function not only of the paint used, but also of application technique, substrate, age, storage, handling, and ambient environmental conditions.

TESTING OF ARTISTS' PAINTS

Testing of artists' paints is done to ensure quality and consistency in their manufacture, as well as to determine the performance parameters a user should expect from the paint, such as flexibility, durability, and adhesion to various substrates. Some performance criteria, light fastness, for example, are similar among different types of paints. Others can be quite different, such as flexibility, or drying time. It is up to the manufacturer to perform tests necessary to ensure that the paints are of a quality consistent with or exceeding that which is expected and historically true for the type of paint being produced. The artist, through experience and education, must be aware of the particular limitations inherent with each type of paint. When new applications are explored, as is often the case with art, it becomes necessary to select and perform tests that will provide confidence that the finished artwork will have the desired physical integrity.

The tests described in this section have been found to be useful to quantitatively and qualitatively describe various characteristics of artists' paints. Acceptability of quality is determined between buyer and seller. In practice, it is largely dependent on what is considered characteristic of the particular paint type. Many of these test methods are ASTM standards that the reader should consult for further details. It is important to note that there are ASTM standard specifications for several types of artists' paints, including acrylic emulsion, watercolor, gouache, oil, resin-oil, and alkyd. These represent the current consensus, between producers, consumers, and other interested parties, of minimally acceptable performance characteristics and other criteria. Most of the following test methods were not developed for artists' paints in particular. Due to the wide spectrum of types of artists' paints and potential uses, this listing does not include all test methods that may be relevant, but several ASTM documents pertinent to artists' paints and not given herein are given in Table 1. Each method described is not relevant for all types of paint. Those included are of varying importance and applicability. They are grouped loosely into several categories: Shelf Stability, Working Properties, Film Properties, and Safety and Compliance.

SHELF STABILITY

It is common for art materials to languish for years on store shelves prior to being purchased. Once purchased, a container is typically opened and closed many times during a life cycle that may take months or years. Stability is evaluated to help ensure endurance of the product through foreseeable conditions of storage and use.

Appearance

The appearance of the undisturbed paint in the container creates an impression of quality, regardless of the ease of restoring it to a homogenous condition. Evaluations for appearance in the retail container are most accurate when based on true conditions of storage and use. However, this is not practical when developing new products. Potential failure may be more quickly realized by placing samples in a laboratory oven at a moderately elevated temperature. As the difference between normal and test temperature increases, accuracy in predicting potential problems may decrease because higher temperatures may exaggerate changes. In a study of latex paints published in the *Journal of Coatings Technology* [1], the authors concluded that an oven temperature of approximately 50°C most accurately predicted shelf-life performance. Items to note regarding

[1] *Golden Artist Colors, Inc, Bell Road, New Berlin, NY 13411.*

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TABLE 1—ASTM documents useful to artists' paints interests and not used in text

ASTM	Document Title
D1535	Standard Practice for Specifying Color by the Munsell System
D1968	Standard Terminology Relating to Paper and Paper Products
D3424	Standard Practice for Evaluating the Relative Lightfastness and Weatherability of Printed Matter
D3730	Standard Guide for Testing High Performance Interior Architectural Wall Coatings
D4236	Standard Practice for Labeling Art Materials for Chronic Health Hazards
D4941	Standard Practice for Preparing Drawdowns of Artists' Paste Paints
D5010	Standard Practice for Testing Printing Inks and Related Materials
D5067	Standard Specification for Artists' Watercolor Paints
D5181	Standard Test Method for Abrasion Resistance of Printed Matter by the GA- CAT Comprehensive Abrasion Tester
D5724	Standard Specifications for Gouache Paints
D6043	Standard Guide for Selection of Permanent and Durable Artists' Papers
D6801	Standard Test Method for Measuring Maximum Spontaneous Heating Temperature of Art and other Materials
D6901	Standard Specification for Artists' Colored Pencils
D7188	Standard Terminology for Printing Inks, Materials and Processes
E308	Standard Practice for Computing the Colors of Objects by Using the CIE System

appearance may include skinning, surface cracking, or separation. Parameters of acceptability will vary depending on expectations of the customer for the particular type of paint.

Color Change

Sometimes the color of a paint film produced from a container of paint changes during storage, for example, as can happen when a pigment is not compatible with the pH of the formulation. This may be determined by preparing a fresh batch of the paint to be tested and immediately preparing a drawdown from it. Subsequent drawdowns at the same thickness may be periodically prepared from the same batch after the paint has aged in the container. The subsequent drawdowns are compared against the original. Using a laboratory oven may accelerate the results obtained from this test.

Consistency

During storage and use, it is desirable that the paints maintain their intended texture and body. Evaluations are based on visual observation and workability with typical application tools. Items to note include mealiness, tackiness, elongation, and break. as well as other body characteristics. Conclusions may be drawn by comparing batches of the same formula, made at different times and that have been stored and otherwise similarly treated. It is useful to evaluate both full and partially empty containers.

Flocculation

To determine if the pigment is fully dispersed or has remained dispersed over time, a tint of the color is prepared with a compatible white. A drawdown is made and the excess paint is recovered and set aside until the drawdown is dry. Next, a small amount of the original wet mixture is placed on top of the dried paint film. This paint is then rubbed under pressure in a circular motion (a gloved thumb is suitable) in an effort to cause further dispersion of the pigment. If it has become more fully dispersed, the rubbed paint will appear as a stronger tint against the original drawdown.

Freeze-Thaw Stability

Shipping and storage often expose artists' paints to extreme temperature fluctuations. Water-based paints can be quickly ruined if not formulated for protection from freezing. ASTM Specification for Artists' Acrylic Emulsion Paints (D5098),in Volume 6.02 of the ASTM Book of Standards, describes the procedure used for testing acrylic paints. The same procedure is used for watercolors. To meet the requirements of the standard, the paints must pass five freeze-thaw cycles while retaining proper consistency.

Package Integrity

The expected life and use of the package containing the paints should be considered when designing appropriate tests. Consider, for example, how the container will be shipped or how many times a tube will be flexed. Potential interactions between the paint and packaging should also be evaluated. For example, solvents may migrate through the walls of plastic containers, causing them to become drawn inward. Real time evaluations are best, but potential failure can be accelerated by increasing temperature or solvent load.

Seeding

Over time, ingredient incompatibilities or reactive pigments may result in seeding, the formation of small, undesirable particles or granules in paint, varnish, or lacquers [2]. This can be readily observed by preparing drawdowns of the paint, as described in ASTM Practice for Preparing Drawdowns of Artists' Paste Paint (D4941) and examining the dried paint film. ASTM Test Methods for Coarse Particles in Pigments (D185) may also be used.

Settling

In low-viscosity formulations, it is common for pigments to exhibit some settling. Ideally this would not happen, but if it does, it is important that the pigments are easily remixed. Settling that occurs over time may be evaluated according to ASTM Test Method for Evaluating Degree of Settling of Paint (D869).

Spoilage/Putrefaction

It is necessary to protect against microbial contamination from raw materials and packaging or that may be introduced during manufacturing. Also, since artists' paints

are typically opened, used, and re-closed many times, it is important that they be formulated to resist microbial growth from contamination occurring subsequent to purchase by the consumer. ANSI Z356.5, American National Standard for Art and Craft Materials—Paints and Inks, Section 4.2, describes a test method for evaluating the effectiveness of preservatives used in paint formulations. Paints to be tested are inoculated with pieces of bread that have been covered with a sugar solution and allowed to mold. After 2 weeks, the paints are inspected for decomposition.

Viscosity Changes

Paint stability is quickly and quantitatively evaluated by monitoring viscosity. Viscometer type and method have not been standardized for artists' paints. If needed, a method may be agreed upon between buyer and seller. For most purposes, it is sufficient to ensure consistency of test conditions and equipment when doing periodic rechecks. Accelerated aging with the use of a laboratory oven is usually predictable of real-time viscosity stability of water-based paints.

WORKING PROPERTIES

Many attributes of importance to the consumer of artists' paints are difficult to measure and report with repeatability. This subjectivity is often coupled with varying preferences among users. An ideal paint for one artist may be lacking in certain qualities for the next. It is not as important to standardize these characteristics, as it is to determine them and transfer this knowledge to the buyer.

Brushing Characteristics

Paints are brushed out on standard substrates by experienced technicians and rated as being smooth, sticky, tacky, or fluid, as described in Section 6.6 of Commercial Standard (CS98) for Artists' Oil Paints [3]. This was the original quality standard for artists' paints and was the base from which the subsequent ASTM artists' paint quality standards were developed. It is also common to describe artists' paints for their tendency to flow and level or hold brush strokes and peaks.

Color Variation

If batch-to-batch constancy of color is desired, it may be determined by placing samples next to each other on a test card and drawing them down together using a thin film applicator. Comparisons of masstone, undertone, and tint are useful. For quantification and reporting, spectrophotometric measurements and CIE L*a*b* color difference may be obtained according to the practices described in ASTM Practice for Calculation of Color Tolerances and Color Differences from Instrumentally Measured Color Coordinates (D2244).

Drying Time

ASTM D5098, Specification for Artists' Acrylic and Dispersion Paints and ASTM Specification for Artists' Oil, Resin-Oil, and Alkyd Paints (D4302), specify drying time requirements. Dust-free drying time of these and other types of paints are determined by following the procedures described in ASTM Test Methods for Drying, Curing, or Film Formation of Organic Coatings at Room Temperature (D1640).

Fineness of Dispersion

Finely dispersed pigments are important for smooth brushing, realizing tinting strength potential, and maximizing encapsulation of pigment within the binder. ASTM Test Method for Fineness of Dispersion of Pigment-Vehicle Systems by Hegman-Type Gage (D1210) may be followed to measure this characteristic.

Odor

Evaluation of odor may be important in determining potential consumer acceptance of artists' paints. The different vehicles have characteristic odors and what is objectionable to some may not be to others. Formula variations may be rated, based on the acceptability of their odor, by a panel of intended users.

Opacity

Opacity is not standardized for artists' paints. It is expected to vary depending on the pigment and vehicle used. The artist benefits if opacity ratings are reported on the container or in manufacturers' literature. This characteristic is typically evaluated by applying a drawdown over a test panel that has adjoining areas of black and white. A scale is then established and colors are assigned values relating to a range from highly transparent to fully opaque.

Tinting Strength

The potency of a color is indicative of its value to the user, particularly when blending with white (absorption tinting strength). Depending on chemical composition, pigments are expected to vary accordingly in strength. Identically pigmented paints may exhibit differences due to degree of processing or loading. It would not be appropriate to critically compare paints of different vehicles because of differences in the loads they will tolerate. ASTM Standard Test Method for Determining the Relative Tinting Strength of Chromatic Paints (D4838) may be followed to arrive at instrumentally derived determinations of tinting strength relative to that of a standard or reference paint. Simple comparisons between paints can be made by using a white paint of standard composition and strength to prepare tints, which are then drawn down alongside of each other. The tints are most accurately prepared using a weight-based ratio of the standard white to the test color. A ratio based on volume, using syringes, may be useful if an accurate balance is not available or if it otherwise suits the purpose of the user.

Viscosity

Artists' paints are available in a wide range of viscosities, from pourable ink-like to heavy impasto. Oil paints are typically expected to maintain definition of the brush stroke, provide sharp peaks, and retain their shape as they emerge from the tube. Water-based vehicles are highly manipulative, and the desired viscosity is dependent on the intentions of the user and manufacturer. Viscosity, thixotropy, and dilatancy may be determined with the equipment and techniques described in ASTM Test Methods for Rheological Properties of Non-Newtonian Materials by Rotational (Brookfield Type) Viscometer (D2196).

FILM PROPERTIES

Adhesion

Intercoat and substrate bonding of artists' paints are extremely important. They become especially critical to

evaluate when determining surface preparation techniques for new or unusual substrates or when considering multi-media applications. There are many types of adhesion testing apparatuses, but a useful and inexpensive test involves cutting the paint films and attempting to lift them with pressure-sensitive tape. This is described in ASTM Test Methods for Measuring Adhesion by Tape Test (D3359).

Bleeding

Artists' paintings are typically created in a manner that results in overlapped or layered films. The tendency for color of an underlying dry paint film to migrate through to subsequently applied paint is an occasional but usually unwelcome occurrence resulting from the pigment exhibiting some solubility in the vehicle. The tendency for bleeding may be determined by applying an opaque white overstripe onto a smooth, dried paint film. The white is extended off the paint film and onto the uncoated portion of the test support. Discoloration due to bleeding will be readily apparent. This test is described as Test Method B of ASTM Test Methods for Bleeding of Pigments (D279).

Block Resistance

Artists' paintings are not typically produced, used, or stored in a manner that will cause them to come into contact with and stick to other surfaces. However, there are times when this does occur, such as in production situations or when there is inadequate storage space. If block resistance is important to the user, the paint in question should be evaluated because many artists' paints exhibit inherently poor block resistance. A case-specific test should be designed to simulate worst-case scenarios of pressure, temperature, and humidity fluctuations. Anticipated drying and storage times should also be considered in the test design.

Chemical Resistance

Resistance to the various liquids with which a painting may be expected to come into contact is an important characteristic. These include varnish vehicles, solvents used in varnish removal, and cleaning solutions that may be used on the paint film. Chemicals to be tested with a particular paint vary depending on the type of paint and what is expected of it. A procedure for designing appropriate tests may be based upon the Spot and Immersion Tests described in ASTM Test Method for Effect of Household Chemicals on Clear and Pigmented Organic Finishes (D1308).

Flexibility

Paints applied to flexible supports, such as stretched cotton or linen canvas, may be susceptible to potentially destructive forces. The different types of artists' paints vary in the degree they will flex without failure. Although there are no established standards, they have different thresholds of expectation and, therefore, acceptability.

During storage or shipping, paintings are often rolled up. ASTM Test Methods for Mandrel Bend Test of Attached Organic Coatings (D522) describes equipment and methods for determining and rating flexibility. Relevancy is increased by testing the coatings over the intended substrate and primer. Combined with the use of accelerated aging techniques, the mandrel test will help predict natural embrittlement of the paint film.

Paintings must also endure expansion and contraction of the fabric due to changes in environmental humidity and temperature. Sometimes these conditions become extreme, as when a painting is shipped during freezing weather. Failure will occur more quickly if the individual components of the painting have greater relative differences in their moduli of elasticity. Use of a temperature and humidity-controlled environmental chamber programmed to expose paintings to repeated cycles of extreme conditions will accelerate the failure that might be observed over time under normal conditions.

Another force of concern is mechanical impact against the film that may occur during handling. For example, when a painting is mounted on an open-back stretcher, fingers may inadvertently press into it as it is being carried. The risk of damage increases as temperature decreases and the glass transition temperature is approached. The rate at which external forces are applied also influences susceptibility to damage.

Gloss

Some manufacturers of artists' paints will add inert flatting agents to control the gloss values of the various colors so that they are similar within a line. Others will allow a color's gloss to be dictated by the characteristics of the colorant, i.e., tolerable load and particle size. Gloss values for artists' paints have not been standardized. It is a matter of preference and manufacturing philosophy. When required, gloss may be specified between the buyer and seller, with measuring parameters identified.

Lightfastness

ASTM Test Methods for Lightfastness of Colorants Used in Artists' Materials (D4303) describes three methods used to determine resistance to fading of acrylic, watercolor, alkyd, and resin-oil artists' paints. Included are conditions of exterior exposure under glass, artificial daylight fluorescent lamps, and xenon-arc apparatus. Prior to exposure, samples to be tested are tinted with white until they reach 35–45 % reflectance at their wavelength of maximum absorption, between 420 and 620 nm. With each method, exposure is continued until specimens have been exposed to a total radiant dose of 1260 MJ/m^2. To meet the ASTM standard specifications for use in artists' paints, the pigments must be tested under at least two of the three methods and exhibit a mean color change of less than eight color difference units (CIE 1976 L*a*b* color difference equation). These test methods are designed to predict performance of artists' paints displayed in typical household or museum environments. Results may not be indicative of performance if the intended use is more rigorous, such as in exterior mural applications.

There are also ASTM practices for determining the lightfastness of artists' materials by exposing samples indoors to sunlight filtered through window glass while simultaneously exposing a series of eight ISO Blue Wool Reference materials to control the duration of exposure. One half of each specimen and control is shielded from exposure during the test. This test takes longer to run, but it is relatively inexpensive. It is intended for artists' materials that are not specifically covered by other ASTM standard test methods. For details, see ASTM Standard Practice for the Visual Evaluation of the Lightfastness of Art Materials

by the User (D5398) and ASTM Standard Practice for the Visual Determination of the Lightfastness of Art Materials by Art Technologists (D5383).

Yellowing

While oil or alkyd paint vehicles may be expected to yellow to some degree, this may be considered a serious flaw if encountered in the newer generation of synthetic media. To determine the relative potential for yellowing of a vehicle, a standard titanium dioxide white pigment may be formulated into the test vehicle and into one of known stability. They are then exposed to the accelerated methods described in ASTM D4303, Test Methods for Lightfastness of Colorants used in Artists' Materials, and the amount of yellowing is determined with ASTM Practice for Visual Evaluation of Colors and Color Differences of Diffusely-Illuminated Opaque Materials (D1729) or Test Method D2244, Practice for Calculation of Color Tolerances and Color Differences from Instrumentally Measured Color Coordinates. It is also useful to subject films of the unpigmented vehicles to the same tests.

SAFETY AND COMPLIANCE

Flash Point

Solvent-based paints may require flash point determination for label warnings and to determine applicability of shipping regulations. The prescribed test method can vary depending on the authority. ASTM Test Methods for Flash Point of Liquids by Small Scale-Closed-Cup Apparatus (D3278) is usually applicable.

Toxicological Evaluation

The Federal Hazardous Substances Act (FHSA) requires all art materials to be evaluated by a board-certified toxicologist for potential to cause acute and chronic health effects. This law was incorporated into the FHSA with the Labeling of Hazardous Art Materials Act (LHAMA), the basis of which is ASTM Practice for Labeling Art Materials for Chronic Health Hazards (D4236). A wide assortment of test methods provides the information required for the toxicological assessment. These are not specified by the Standard Practice or LHAMA, but include all which are embodied in the field of toxicology as well as compositional analysis of the paints and their constituents. The evaluating toxicologist determines any testing that may be required to supplement the information that exists for the raw materials in a product. Appropriate precautionary label information is then assigned. The toxicologist must supply the criteria used in making these determinations to the Consumer Product Safety Commission, the enforcement agency of the FHSA.

One ASTM method developed to provide analytical data useful in a Toxicological evaluation is D5517, Standard Test Method for Determining Extractability of Metals from Art Materials. This method was adopted from the European Toy Standard, EN71-3. Test conditions are designed to simulate the acid potential of gastric juice, at body temperature.

Volatile Organic Compounds (VOC)

Artists' paints are sometimes applied to substrates that are covered by VOC regulations. Architectural, sign painting, and furniture application are examples. ASTM Practice for Calculating Formulation Physical Constants for Paints and Coatings (D5201) provides equations to calculate the theoretical VOC content of paints, based on the formula and exclusive of water and exempt solvents. EPA Test Method 24 is the standard analytical approach used to quantify VOC in coatings applied to architecture.

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Can Coatings

Joseph V. Koleske[1]

PREFACE

IN PREPARATION OF THIS CHAPTER, THE CONTENTS of the fourteenth edition of this manual were drawn upon. The author acknowledges the author of the chapter in the fourteenth edition, Martin B. Price. The current edition will review and update the topics as addressed by the previous author, introduce new technology, and include up-to-date references.

INTRODUCTION

The container industry is a major user of coatings with functional coatings used on the internal surfaces and protective, decorative, informative coatings used on the external surfaces. Internal coatings are often sanitary in nature and meet Food and Drug Administration requirements. In 2005, about 100 billion (also see Tables 1 and 2) cans were manufactured in the United States. Each can contains very little coating in a mass sense, but to point out the obvious, with a multiplier of ten to the eleventh power, very large amounts of materials are involved.

Cans are used to package a wide variety of materials including beverages (beer and soft drinks), food products (baby food, coffee, dairy products, fruit and fruit juices, meat and poultry, soup, vegetables, and others), pet foods, and nonfood products such as aerosols, automotive products, paint, and clear coatings. Beverage packaging is by far the largest user of cans with an annual usage of about 100 billion units in the USA and about 200 billion units worldwide. In a general sense, beverages are packaged in aluminum containers and food and other products in steel containers.

The majority of the cans are coated individually with most having different coatings on each side—i.e., internally and externally—and on the ends. These coatings provide corrosion resistance under a variety of conditions, compliance with strict food and taste requirements, and attractive, long lasting identification characteristics to each container. During storage, a long shelf life is required for internal beverage coating materials that are in contact with liquids that range from being quite alkaline to quite acidic in nature. The processes required for the efficient and economically acceptable manufacture of two- and three-piece cans and can ends involve complex engineering. Unique physical coating characteristics are required to conform to machinations of these complex mechanical systems that manufacture an article that is well known and broadly used at an extremely rapid rate and in large volume. A majority of the tests currently in use to ensure that all the requirements are met are discussed in this chapter. A brief description of the process for can production is included. Because it represents the largest volume of cans, most of the discussion will be directed toward beverage cans.

DESCRIPTION OF THE CAN INDUSTRY

Brief History of Beverage Cans[2]

The first flat top beverage can was made by American Can Company to contain Krueger's Beer.[3] The beverage went on sale on January 25, 1935 in Richmond, Virginia. When the year was over, 200 million cans had been sold. In the next year, the Felinfoel Brewery located in Wales, Great Britan sold canned beer outside the United States. The following year 23 breweries in the United Kingdom were marketing 40 brands of beer in cans. The Schmalbach Brewery became aware of the growing popularity of canned beer and introduced its first canned beer in 1937 using a three-piece can and a crown-cork closure rather than a flanged can end.

The early process for beer can construction was complicated and after a fast start in the mid-1930s, the technology did little until the early 1950s. Americans stationed in Frankfurt, Germany, became accustomed to using and liked the three-piece, tinplated-steel can, and in 1951 the German brewery marketed its export beer in this type of can. In addition, during WWII, beer was shipped to military personnel on overseas duty in steel cans. Even though the can required punching a hole with a special opener on the flat topped can, military personnel returning home brought a strong desire for this type of packaging and the metal-can beverage industry grew quite rapidly.

In 1959, Coors brewery became the first to introduce a two-piece, lightweight, aluminum can, but the special opener was still required. Later a pull-tap was devised, but it separated from the can and became an additional litter problem as well as a sharp item wherein people could be cut. Later, in 1963 Alcoa invented the easy open, pull-tab that stayed attached to punch a drinking opening in the can top and the litter and sharp hazard from the tabs disappeared. The two-piece aluminum can was here to stay in the United States, and it has grown to its current level of about a hundred billion cans with the volume about two soft drink cans to one beer can (Table 1).

Even with the new attached pull-tab, the aluminum can represented an environmental litter problem that would not

[1] *1513 Brentwood Rd, Charleston, WV 25314-2307.*

[2] Beverage can historical information can be readily found on the Internet at sites such as www.rexam.com, www.ballpackaging.com, and elsewhere.

[3] Gottfried Krueger Brewery, Newark, New Jersey.

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TABLE 1—United States production of beverage cans (number rounded to the nearest billion cans) [2]

	Billions of Cans					
	1980	1985	1990	1995	2000	2005
Beer Cans						
Aluminum	26	36	39	36	33	32
Steel	4	0.1	0.4	0	0	0
Total Beer Cans	30	36	39	36	33	32
Soft Drink Cans						
Aluminum	16	30	49	63	67	68
Steel	10	4	4	Nil	0	0
Total Soft Drink Cans	26	34	53	63	67	68
All Beverage Cans						
Aluminum	42	66	88	99	100	100
Steel	14	4	4	0	0	0
Total	56	70	92	99	100	100

go away by a rusting process. Cans were quite prevalent throughout the countryside. Further, aluminum, though abundant in nature as bauxite ore, was and is produced by a relatively expensive process and beverage can cost was and is important. To combat these problems, ways to decrease the amount of aluminum used in each can have been devised by using thinner and stronger designs. Since the early 1980s, aluminum cans have decreased in weight by about 30 %. By developing a good recycling program for the empty containers, the littering factor has been markedly diminished while obtaining overall cost savings for the industry. As described in Table 2, 63 % of beverage cans are recycled in the USA and in Japan 78.5 % are recycled. Elsewhere the number of cans recycled is less, but recycling is still growing in importance. During this time, internal and external coatings were developed to safely contain both beer and soft drinks and to present an attractive, decorative outer appearance.

The Can Coating Industry

The volume of coatings consumed by coating cans for food and beverages in the United States places the container industry among the highest users of finishes by all industries. However, the consumption has not been growing because the number of cans is relatively constant and there have been efforts through the years to increase formulation solids or to switch to essentially 100 % solid systems as represented by radiation-cure coatings. Although the United States is the largest user of cans and coatings for cans, the European market [1] certainly has a significant volume and manufactured over 38 billion units in 2005. South America is another growth area.

TABLE 2—Recent aluminum beverage can production in various countries [2,3]

Country	Year	~Billions of Cans	% Recycled
Australia	2005	3	. . .
Europe	2005	38	. . .
Japan	1999	17	78.5
United Kingdom	1999	7.7	31
United States	1999	102	63
World	2001	200	. . .

Can Production Process

Two-Piece Can Production

As late as 1990, about 400 million beer cans and 4 billion soft drink cans were made of steel in the United States (Table 1).[4] Five years later there were no steel beer cans and only a few soft drink cans made of this material. Currently, all of the beverage containers are constructed of aluminum and comprise what are commonly called "two-piece cans." Fig. 1 is a simplified schematic of the process used to prepare these cans from aluminum or steel. The can is manufactured by punch pressing cups from sheets or coils of either metal, though mainly from aluminum. The cups are then forced through a series of rings to "iron out" and form the domed bottom and to form a full-length can. At this stage, the product is a container with sides, a bottom, and an open-ended top that represent one of the two pieces of a two-piece can. The can lid, with pull-tab opener, is sealed and secured after filling and is the second piece of the can.

Decoration, identification, and, often, descriptive and informative consumer information are applied to the containers with exterior inks and coatings. Increased manufacturing speed and smooth movement on the production lines requires the proper lubricity of the coating. The containers and attendant coating require a high degree of abrasion resistance to maintain aesthetics and prevent can failure

[4] Annual production details for beverage and food containers can be found in Ref. [2].

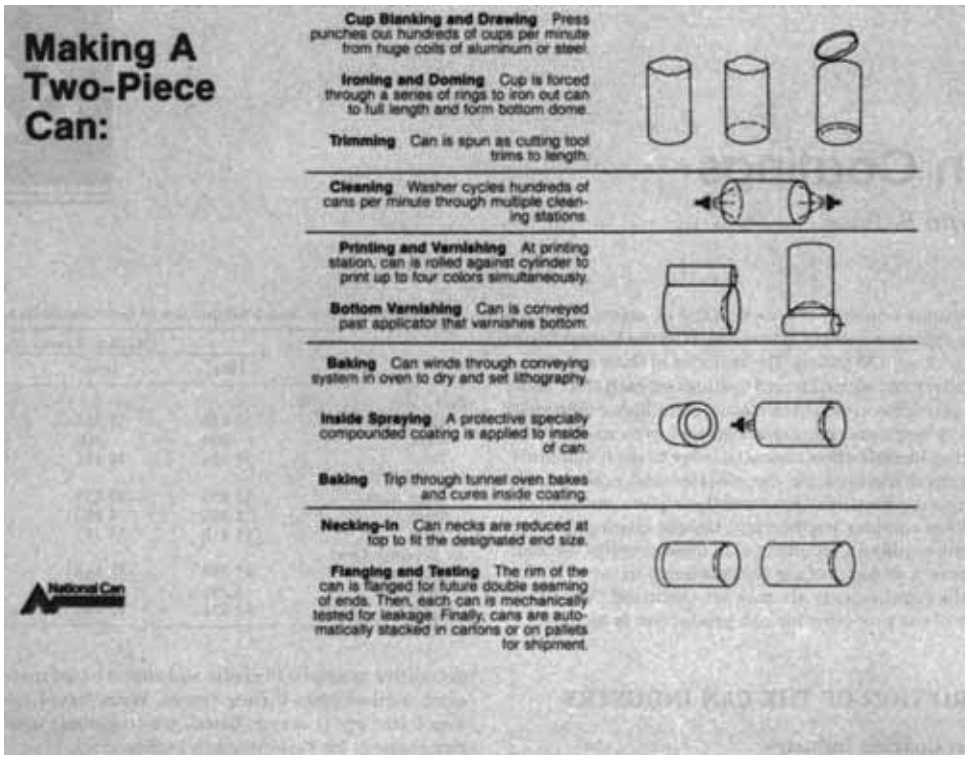

Fig. 1—Two-piece can production process.

during processing and shipping. Cans rubbing against one another during movement in any of the production process steps and shipping can cause scratches. These are often unacceptable for aesthetic reasons and, in extreme cases, can result in the actual rupture of the increasingly thinner stock from which the cans are manufactured.

In 1992, average aluminum cans weighed 16.55 g and by 2005 the weight had been decreased to 14.7 g—a reduction of 11.2 % [3]. Savings such as this, coupled with recycling, have reduced costs and made aluminum containers competitive. Cans are often so thin that filling before sealing is required to give the container adequate rigidity for the crimping/sealing operation. Further, the level of flexibility in the container and coatings must be inherently sufficient so that the severe crimping operation, which is critical to securing the lid onto the container, can be accomplished without coating failure or delamination.

Coatings are usually applied to the interior of these cans by spray techniques. Rapid application is obtained by using short bursts of airless spray from a lance positioned opposite the center of the open end of horizontally held cans. This process or a similar one is used when coating most food and drink containers. If the intended can content is acidic in nature, as is the case with most soft drinks, uncoated containers can corrode. Thus, an internal coating that presents an adequate barrier to this corrosion must be applied. Although beer is not strongly acidic in nature and corrosion is less a problem than with soft drinks, a major concern exists regarding taste-alteration potential due to contact of the beer with the metal container walls. Thus, the protective inner coating protects from metal contact and in itself must not alter the taste of the packaged product. To achieve this end, the coating must have a low level of extractables.

Coatings suitable for food and beverage use (a) must be Food and Drug Administration (FDA) compliant, (b) must pass subjective taste tests to ensure there is no adverse contribution of the flavor of the product, and (c) must meet demanding toughness and flexibility requirements. Both the interior and exterior coatings must pass most of these tests for production of the can to be acceptable. For a majority of the cases, after the can is packed and sealed, it is subjected to a thermal treatment to complete processing of the contents. Many of the commercial beer products require pasteurization that is normally carried out at 150 to 180°F (65.5 to 82.2°C). Higher temperature exposures are required for processing other food products in many packaging operations. Coatings on the crimped edges of the can that have survived the actual crimping and sealing procedure must maintain adhesion, clarity, color, and abrasion resistance after these thermal treatments.

Three-Piece Can Production

Fig. 2 is a simplified schematic of the three-piece can production process. In a typical manufacturing process for this type of can, a large metal coil is sheared into sheets. An "inside" container coating is placed on one side of these sheets usually by roll-coater application and the coating is cured. When an exterior can coating is required in lieu of paper or plastic labeling, the "exterior" or other side of the sheet is coated with the decoration and information as defined by the customer. This decoration is often overcoated with a clear coating and the sheets are cured for a second time to form the coated can body sheets. On low-rust potential metal when paper or plastic is the customer chosen labeling technique or when ultraviolet radiation cured coatings are used, the second oven-cure operation may not be required. (The ultraviolet radiation

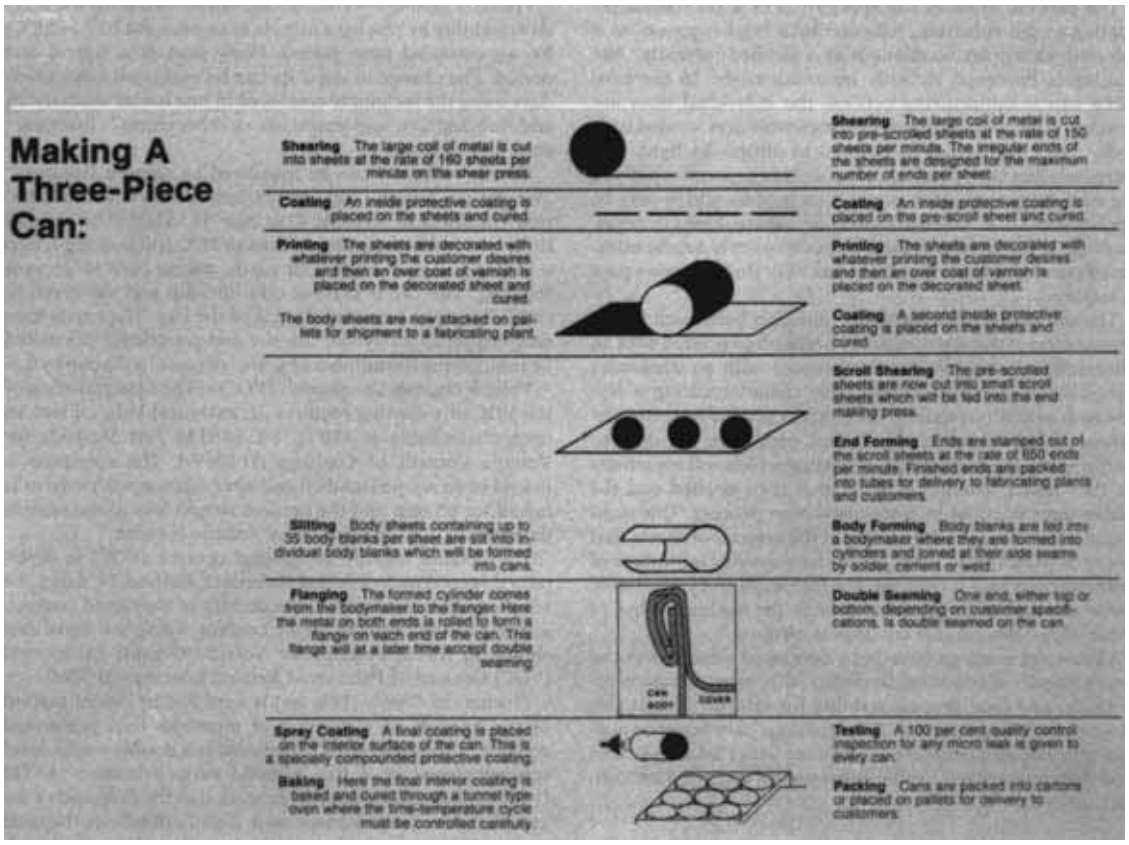

Fig. 2—Three-piece can production process.

curing process will be discussed later.) The coated sheets are stacked and shipped to the fabrication section or plant where they must easily slide over one another during the subsequent processing steps. To achieve the desired degree of lubricity, specific lubricants may be applied after the final baking process. The coated surfaces are often tested to evaluate the nonbonding characteristics of the sheets during stacking.

For can fabrication, the coated can body sheets are slit into individual body blanks. Usually about 35 body blanks are obtained from each sheet. The blanks are coiled into a cylindrical shape and flanged to permit formation of a seam. The seam is then welded, soldered, or cemented to form the can body. A coating is required to cover the seam, since the initially applied coating is usually destroyed or deformed during the seaming process. A coating, either liquid or powder, is applied to the seam and thermally cured or fused. This coating must have all of the requirements of the main body coating, including FDA compliance, and cause no detectable alteration to taste of the contained product.

Preparation of Can Ends

Can ends are stamped from sheets that are already coated on the side to be in contact with the packaged product. With some metals, the side destined to become the exterior will also be coated to impart corrosion resistance. Can-end coatings must have the proper combination of mechanical properties, particularly flexibility, to withstand the crimping necessary to secure the end to the top or bottom of the container. The coatings, including the crimped sections, must maintain their integrity through the elevated-temperature, food-processing steps as required for two-piece cans (Table 3).

Some can ends have been coated by the electrocoating or electrodeposition process. Early descriptions of the use of electrocoating process can be found in the literature in, for example, the United States Patent 3,847,786, "Roll-Through Method and Apparatus for Electrocoating Can Ends," Nov. 1974. The process provided for quickly coating the surface and, in particular, for covering any sharp

TABLE 3—United States production of food cans for human and pet consumption [2]

	Approximate Number of Food Cans (Billions)			
End Use	**1975**	**1985**	**1995**	**2005**
Dairy Products	1.90	1.25	0.97	1.93
Fruit and Juices	5.30	3.05	2.30	1.77
Meat & Poultry	1.60	1.49	1.70	1.79
Vegetables	10.70	8.34	9.27	9.92
Other[a]	11.00	9.65	9.88	7.46
Total Human Usage	30.50	23.78	24.12	22.89
Pet Foods	3.00	4.07	7.20	6.61
Total Food Cans	*33.50*	*27.84*	*31.31*	*29.49*

[a]Includes baby food, coffee, seafoods, soups, and other foods.

or raw edges from the forming process. More recently, in April 2007, United States Patent Application 20070080065, "Methods for Electrocoating Full Panels of Easy Open Ends," was filed by Oravitz and co-workers who applied for a patent that involved the electrodeposition process. The full panel of easy-open ends is essentially uncoated prior to electrocoating.

Ultraviolet Radiation-Cured Coatings

Ultraviolet radiation curing [4] is a relatively new technology that is being used to cure beverage can coatings [5–9] as well as in other areas of packaging [10]. The process has several distinct advantages over more traditional oven-bake systems. Among these are essentially the elimination of solvents and related volatile organic compound pollutants, improved production, efficiency, working conditions, low-cost plant installations as well as more rapid, simplified change-over from one decoration and set of colors to another. Presently, industrial production using this technique involves external clear and colored coatings.

This cure process involves the application of a formulated, photosensitive, low viscosity coating to a substrate followed by brief exposure to a selected ultraviolet wavelength range at a defined intensity. The coating is hardened or cured virtually instantaneously at high line speeds. In the two-piece manufacturing process, the individual cans are printed, often with ultraviolet radiation-curable inks, coated with a clear coating, and then exposed to the radiation. The extremely rapid cure permits the process to proceed rapidly to the next stage in the can production process, which may be application of a water-dilutable or solvent-based sanitary interior coating. Since this interior coating requires an oven bake, the radiation-cured coating is oven baked as well. Only one oven pass is required to achieve full cure.

The ultraviolet radiation cure technique has also been used in the preparation of three-piece cans. Sheets, often printed with a radiation curable ink, are overcoated with an ultraviolet radiation-curable overprint coating. After exposure to ultraviolet radiation, the dry-to-touch condition required for efficient production usually develops in a fraction of a second permitting the can-stock sheet to be flipped over to the reverse side. A coating that will eventually be the "inside" coating of the can is then applied and the entire sheet is cured by a standard oven process. This technique is also used for the coating of exterior sheets that are to be used for can ends. Again, the economic advantage of only one oven pass is realized. The importance of inclusion of some measure of the speed of cure in the quality control of these ultraviolet radiation-cured coatings is obvious.

Radiation cured coatings have been developed that meet the requirements of adhesion, flexibility, slip, gloss, abrasion resistance, and food process stability for exterior use. In general, these coatings are not used as interior coatings.

Testing of Can Coatings

Tests Conducted on Liquid Coating

Viscosity—As discussed in the previous section, speed of production is a critical aspect of an economically successful can production plant. The speed of application of paint required for the satisfactory coating of two-piece can bodies or of three-piece can sheets places unique requirements on the flow characteristics of the liquid coating. To ensure complete coverage with the standard thin layer of coating, outstanding flow must be assured. The usual means for viscosity determination is the use of a Brookfield Viscometer as described in ASTM D2196, Standard Test Methods for Rheological Properties of Non-Newtonian Materials by Rotational (Brookfield-Type) Viscometer.

Alternate methods for measuring viscosity include use of the Ford Cup or the Zahn Cup as described in ASTM D1200, Standard Test Method for Viscosity by Ford Viscosity Cup, and ASTM D4212, Standard Test Method for Viscosity by Dip-Type Viscosity Cups, respectively. These procedures relate flow to the length of time required for a test liquid to flow through a calibrated orifice at the tapered, bottom end of a cup. The Ford Technique is generally considered more accurate, though less convenient than the Zahn cup technique.

Viscosity Stability—The coating can be evaluated for long-term stability by placing a sample in an oven at 120°F (48.8°C) for an extended time period. Forty days is a typical test period. The change in viscosity can be evaluated every seven days using the technique employed to rate initial viscosity. In addition, settling, agglomeration, or other changes in appearance can be noted and taken into account when considering the evaluation.

Density—Density can be measured by using a Gardner™ "Weight per Gallon" cup as described in ASTM D1475, Standard Test Method for Density of Liquid Coatings, Inks, and Related Products. The process involves equilibrating the product at 25°C and pouring it into an appropriately cleaned cup up to the fill mark while taking care to prevent foaming. The cap is pressed onto the cup and the overflow is carefully wiped from the outside of the cup. The cup is then weighed on an analytical balance and pounds/gallon are calculated by multiplying the number of grams of coating in the cup by 0.1. When needed, the liquid coating thickness of an applied coating may be determined with ASTM D1212, Standard Test Methods for Measurement of Wet Film Thickness of Organic Coatings.

Volatile Organic Content (VOC)—The determination of the VOC of a coating requires an analytical balance and an oven controllable at 110±5°C, ASTM 2369, Standard Test Method for Volatile Content of Coatings. The liquid specimen is placed in an aluminum dish, and after dilution with a solvent is baked for 60 min at the indicated temperature. The percent weight loss of the sample is then determined as the percent volatile content.

The VOC is determined according to EPA Federal Reference Method 24, Determination of Volatile Matter Content, Water Content, Density, Volume Solids and Weight Solids, of Surface Coatings. This is done by using the weight percent volatile content, the density of the liquid coating, and the weight percent water content in concert with equations given in ASTM D3960, Standard Practice for Determining Volatile Organic Compound (VOC) Content of Paints and Related Coatings.

Fineness of Grind—This test is used to determine the fineness of dispersion of pigments in a pigmented coating. A Hegman Grind Gage with a double-wedge steel scraper is placed on a flat, nonskid surface as described in ASTM D1210, Standard Test Method for Fineness of Dispersion of Pigment-Vehicle Systems by Hegman-Type Gage. A sample of the coating is applied at the deep end of the groove on the gage surface so it slightly overflows the total groove. The

scraper is then drawn down over the entire length of the gage with sufficient pressure to clean the sides of the gage. A reading should be made at this point without delay. The reading consists of a visual observation made by viewing the side of the gage perpendicularly to the drawn coating: the point where the sample shows a definite speckled pattern is read from the numbers of the side of the gage. The quality of the dispersion is a measure of the effectiveness of the grinding operation in dispersing pigments for pigmented coatings or of additives, such as wax, for transparent samples.

Flash Point—The flash point of a coating is the minimum temperature at which vapor given off by the coating will ignite when exposed to a spark or flame. The Department of Transportation standards for shipment places a minimum flash point requirement for such coatings as these. A method to determine what is referred to as a "closed-cup rating flash point" involves use of a Seta Flash apparatus, ASTM D3278, Standard Test Methods for Flash Point of Liquids by Small Scale Closed-Cup Apparatus. For an open flash point, a tag open-cup method is often used, ASTM D56, Standard Test Method for Flash Point by Tag Closed Cup Tester. In both methods, the substance under test is heated at a controlled rate, for example 2°C/min, and a flame is passed over the surface. The flash point is defined as the temperature at which definite ignition is observed.

Cure Speed—A variety of methods have been devised for determination of this difficult to ascertain and even difficult to define characteristic of a thermoset coating. One practical definition of cure adequacy is the development of sufficient hardness in the coating that allows the can manufacturing process to advance to the next stage without marring the coating. Often, the customer and the coating supplier will agree on an empirical test to satisfy cure speed requirements. A simple technique may involve the use of cotton balls dropped onto the "cured" surface. Non-adherence of fine fibers or wads of fibers to the surface is often rated as an adequate cure because it relates to the ability to permit continuation of the manufacturing process. Frequently a higher degree of cross-linking than afforded by this empirical test is needed, especially for the development of resistance properties encountered by the coating at a later stage of its use. Rubbing the cured surface with a cloth moistened with a strong solvent is a method frequently employed. Determination of coating hardness using the pencil hardness test described later is a means of assigning a numerical rating to the relative degree of cure.

In the case of radiation cured coatings, ASTM D3732, Standard Practice for Reporting Cure Times of Ultraviolet-Cured Coatings, can provide guidance related to degree of cure and to cure speed attainable with such systems.

Tests Conducted on Cured Surfaces

Hardness—the hardness of a coating can be determined with the use of a series of pencils as described in ASTM 3363, Standard Test Method for Film Hardness by Pencil Test. The series of pencils have leads of various, known hardness—that is, lead with the following increasing harness—5B, 4B, #B, 2B, B, HB, H, 2H, 3H, 4H, and 5H. The cited test method describes the technique used to sharpen the leads and the way to perform the test. ASTM D1474, Standard Test Methods for Indentation Hardness of Organic Coatings, has other methods used for hardness determination.

Film Thickness—ASTM D7091, Standard Practice for Nondestructive Measurement of Dry Film Thickness of Nonmagnetic Coatings Applied to Ferrous Metals and Nonmagnetic, Non-conductive Coatings Applied to Non-Ferrous Metals can be used to determine film thickness of both steel and aluminum substrates. A variety of gages are described that are based on eddy current measurements. The information in this Standard Practice is meant to supplement and not to replace any manufacturer's instructions. As an example, a device may be calibrated with standard sheets of known film thickness placed on an uncoated surface of a similar substrate test section. After standardization, the head of the gage is placed on the coated sample and coating thickness is reported, usually in mils. The film surface is measured at several locations on the specimen and then averaged for the final, reported result.

A StrandGage® [11] is often employed in the metal decorating industry because it is easy to use when determining the thickness of very thin coatings (up to about 0.003 in or 0.076 mm) that are characteristic of the can industry. The device is calibrated to give results in milligrams or grams per area.

Film Continuity—Freedom from voids is a most important characteristic of beverage can interior coatings. Basically, the interior coating must be free of pinholes or other discontinuities. If such defects exist, they will lead to corrosion and contamination that will result in taste or color degradation and may result in destruction by rapid cathodic corrosion in certain instances. One of the accepted methods for evaluating the coating for such imperfections is an "enamel rater" instrument. Such devices electrically test the coating coverage and report an index of the amount of metal exposed.

One device for this purpose is the WACO Enamel Rater [12] in which a container such as a beverage can to be evaluated is filled with a conductive solution and placed on a platform. Electrical contact is made on a cleaned area of the can exterior, an electrode is placed in the center of the can's contents, and the amount of current flowing through the system is measured. The current flow will be impeded by the interior protective coating. Flaws, breaks, pinholes, or other defects in the coating are areas that will permit current flow. Suppliers and customers usually agree on a maximum acceptable value of current on time and result.

An alternative test technique for determining film voids is the copper sulfate solution immersion test. In this test, a sheet of coated metal is immersed in a solution of acidified copper sulfate for 2 to 4 min. After removal, a careful visual or magnifying glass examination of the coated metal will reveal copper-plated areas where inadequate coating protection permitted the copper to plate out onto the metal surface. The presence of such detectable flaws is an unacceptable condition for most commercial products.

Stability to Food Processing and Pasteurization Conditions—Many foods are packaged into containers in an uncooked state. Cans are sealed and the entire can is processed at an elevated temperature for the period required to complete the food processing. A characteristic test period is 1 h at 250°F (121°C) in an autoclave. Determination of the ability of a coating to withstand this treatment is often made by careful examination of a section of coated

substrate that has been mandrel bent [13]. The section so treated is then permitted to cool and next exposed to 100 % humidity at 100°F (37.7°C) for 16 to 24 h. After cooling, visual examination of the surface for discoloration, for film rupture, and for adhesion—especially in those areas where film extension has occurred—presents a useful appraisal of the ability of the coating to withstand food-processing conditions.

A less severe test is available for the pasteurization process. This process is required for some foods and for some beer packaging. The temperature used is 150 to 180°F (65.5 to 82.2°C) for 3 h. A similar visual examination of the surface of the coated steel or aluminum substrate is conducted for discoloration, blushing, adhesion loss, or film failure.

Abrasion Testing—A critical characteristic of an acceptable exterior film is its ability to protect cans from marring and scratching the decoration and identification. As mentioned earlier in the "Can Production" portion of this chapter, occasionally abrasion resulting from cans rubbing against each other—especially in shipping—can be sufficiently severe so as to cause metal rupture.

Various tests are employed to measure the coatings ability to resist abrasion. A simple technique involves rubbing the coated surface with a standard pencil eraser, counting the number of rubs or double rubs required to remove the coating, and reveal the uncoated surface. Often times an companies will devise proprietary, in-house techniques to test individual can, plastic bound can assemblies, and fully carton-packaged cans.

The TABER ABRADER TESTER™ is a commercial device in common usage for abrasion testing and preliminary evaluation of abrasion resistance [14]. In this test, coated panels are rotated under selected weighted abrasive wheels. The result value is usually reported as weight loss in "Milligrams/cycle × 1000."

Another abrasion test involves the use of the Gavarti GA-CAT device [15]. The instrument has a provision for mounting a limited number of specimens and can rapidly evaluate coated metal abrasion resistance. The device vibrates the cans or coated strips at a rate and for a duration that can be controlled thus emulating the abrasion received during transportation. The cans are visually examined after the allotted exposure time and rated according to individual company or customer defined standards.

Pack Testing—A requirement for the packaging of many food products is that no undesirable effects on the appearance of the container or the taste or color of the contents take place when the product is stored on a shelf for three years or more. An accelerated test to evaluate this characteristic involves the actual packaging of the substance in question in a test can. The can is sealed and exposed to the food processing conditions previously described, after which the product is aged at an elevated temperature for an extended period of time. Typical conditions for this test are 120°F (48.8°C) with a generally accepted estimate that one-month exposure at this temperature relates to one year of room temperature exposure. The coating product can be periodically examined by initiating several containers at zero time and withdrawing them selectively at one-month intervals. The test is useful for new product evaluation. A three-year actual test is usually required by most customers before they will accept a new product or a significant compositional change in a coating formulation. At the end of the test period, evaluations include can appearance, food taste, and vacuum testing. The latter is accomplished by piercing the container with a device such as a hand-held vacuum unit that pierces the can and seals a vacuum gage around the opening. Chemical reaction of the food product with coating or exposed container walls can result in a pressure change.

Adhesion Test—This test is similar to one used throughout the coatings industry. It involves pressing Scotch Brand™ Tape to the surface and examining the surface and the adhesive side of the tape after removal. The surface of the coating is scored with a razor in an "X" pattern or a crosshatch pattern before the tape is applied as described in ASTM D3359, Standard Test Methods for Measuring Adhesion by Tape Test.

Flexibility—A test known as the "T-Bend" test is commonly used throughout the metal coating industry [16]. The test evaluates the flexibility characteristics of a coating on a substrate by deformation of the coated substrate and subsequent evaluation of the adhered coating. A Zero-T (0-T) bend is a bend in a section of metal turned back on itself through a 180° bend. The examination after the bend can be visual, microscopic, or it can use Scotch Brand® tape adhesion or copper sulfate solution exposure for evaluation. This type of examination is usually dependent on a customer's stated requirements.

A second 180° bend around the bend already made represents a lesser level of flexure requirement. A coating that satisfactorily passes examination on this surface, and that already failed the 0-T test, will be considered a 1-T flexibility coating. A third bend represents 2-T, etc.

Another method of evaluating the flexibility of the coating involves the use of an impact testing device as described in ASTM 2794, Standard Test Method for Resistance of Organic Coatings to the Effects of Rapid Deformation (Impact). In this test, flexibility is evaluated by dropping a large, bullet-shaped weight from a measured height down through a cylindrical guide tube onto the uncoated surface of a test sheet placed on a die that has a depression analogous to the shaped weight. The test is termed a "reverse impact test." Microscopic examination of the impacted area is employed for evidence of cracking in the coating. The coating can be tested to the point of metal failure, a factor that depends on the thickness and strength of the substrate used. The test can also be carried out with the coated surface of the test sheet placed on the die. In this case the test is called a "forward impact test."

A test that is more specific to the can industry is the Erichsen Lacquer Testing Instrument. This device is a cupping and deep-drawing cup test machine that is used for testing coated ferrous and non-ferrous metals. In use, a cup is actually formed from a section of coated metal and the corners of the formed cup are examined for signs of inadequate flexibility.

Extraction Testing—Coating components capable of being extracted by the container contents must be below defined concentration limits. The Food and Drug Administration has established a series of limits and has defined certain liquids to be used for testing based on the planned contents of the container. These can be found in Code of Federal Regulations (CFR) 21, Section 175.300, Resinous and Polymeric Coatings. An extraction technique is also described in detail in this U.S.A. government publication.

Gloss Measurement—The specular gloss of a coated sample is measured using a 60° gloss meter as described in ASTM D523, Standard Test Method for Specular Gloss. The gloss meter should be equilibrated and calibrated against standard panels. The meter is placed over the panel to be tested, several readings are taken at different places on the panel, and an average of these readings is recorded. Care must be taken to control film thickness on test panels, since deviation in gloss level will be observed at varying thicknesses.

Color Measurement—Customers will assign an acceptable level of deviation of the final color or colors of the can-stock sheets or the cans based on a defined standard. Spectrophotometric analysis using appropriate ranges is reported. ASTM D2244, Standard Practice for Calculation of Color Tolerances and Color Differences from Instrumentally Measured Color Coordinates, describes techniques used for the analysis.

Blocking Resistance—Sheets of coated product are frequently stacked and stored before being transported to the next processing station. Such storage can often occur after an oven operation, which means that the sheets are stacked at an elevated temperature. As sheets are fed to the pile, the pressure imposed on the lower members of the stack can become considerable, and the sheets must resist adhering to each other. Efficient and rapid movement of these sheets individually for subsequent processing is essential to achieve an economical container-production rate. Simple tests are commonly developed between customer and supplier to evaluate the ability of coatings to resist this sticking phenomenon.

In one such test, a series of coated sheets or panels are stacked face to back. Pressure, usually imposed by means of a properly placed block of metal, is imposed on the top sheet or panel of the stack. The stack, which can be stored at controlled temperatures for defined periods of time, is examined after cooling for ease of separation. The weighted block of metal is usually of such physical dimension that the resistance to sticking can be determined and reported in appropriate pressure units.

Although there are a number of ASTM tests for blocking resistance, none are specifically designed for the can coating area. However, readers may be interested in reviewing ASTM D3003, Standard Test Method for Pressure Mottling and Blocking Resistance of Organic Coatings on Metal Substrates, which deals with the sticking of coatings applied to coil-coated substrates prior to fabrication.

GENERAL REFERENCE

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Testing of Industrial Maintenance Coatings

Dwight G. Weldon[1]

INDUSTRIAL MAINTENANCE COATINGS COVER A diverse range of coatings for use in a wide variety of industries. For example, coatings such as alkyds, acrylics, vinyls, epoxies, urethanes, polyureas, silicones, and silicates can be used to coat structures of such variety as bridges, railroad cars, chemical process vessels, elevated water tanks, and concrete floors. Therefore, it is obvious that because of the many different coating chemistries and the vast range of environments to which they might be exposed, the testing of industrial maintenance coatings can be a broad topic. Furthermore, a particular physical property which may be important in one application, such as temperature resistance for a stack coating, may be of little importance for a different coating in a different environment. Therefore, it is important to know not only what type of tests can be run, but to appreciate the relative importance of various tests, realizing that their ranking may change from project to project.

In broad terms, the testing of coatings falls into one of two categories: determining the properties of the liquid paint, and determining the properties of the dried film. The testing of liquid paint can involve not only determining compositional related parameters such as density or solids content, but also application related parameters such as dry time and sag resistance. Although dried films can certainly be subjected to a barrage of analytical techniques to investigate chemical composition, this would generally be considered a separate topic, and in the context of this chapter most of the testing on dried films is done to determine performance or physical properties, such as abrasion resistance or adhesion.

In the past, much emphasis, not only in testing but in specification writing, was placed on the chemical composition of the coating. In the last decade or so, the emphasis has shifted more toward performance based requirements. Although the performance of the coating on the substrate is certainly of more fundamental importance than which ingredients are in the can, the latter should not be ignored. Indeed, it is fairly common when screening coatings for a Qualified Products List (QPL) to base acceptance on their performance characteristics, but also to do some basic compositional testing of the specific batch which was submitted. The results of these compositional tests are then used to define the characteristics of any future batches which may be provided for specific jobs, to help insure that production batches have similar composition (and therefore hopefully similar performance characteristics) to the batch which passed the QPL testing.

TESTING OF LIQUID COATINGS

Density

The density, or weight/gallon, of a liquid coating is a rapid, inexpensive test which, when combined with a few other simple tests, provides a measurement indicative of the types and relative amounts of ingredients making up the coating. Indeed, a significant variation in density is a sign that a production error has probably occurred.

The density of a material is generally performed with a pycnometer, which is simply a device which has a specific, known volume at a certain temperature. In the paint industry, the pycnometer is known as a "weight-gallon cup," and the test is performed in accordance with ASTM D1475 (Standard Test Method for Density of Liquid Coatings, Inks, and Related Products). Briefly, a slight excess of material is placed in the cup, such that when the lid is attached the excess is forced out through a small hole in the center of the lid. This assures that the cup is completely filled. The cup and lid are weighed before and after, and the grams of liquid paint can then be used to determine the density of the paint, in lbs/ gal. Often, the density of the paint in lbs/ gal is simply the weight of the paint contained in the cup, in grams, divided by 10.

Solids by Weight

The percent solids by weight of a coating, often referred to as its percent nonvolatile by weight, is usually determined in accordance with ASTM D2369 (Standard Test Method for Volatile Content of Coatings). Basically, a liquid coating consists of four types of ingredients: resins or polymers, pigment, additives, and solvents. By determining the solids by weight, one is determining the combined amount of the first three ingredients. Since these are the ingredients left behind in the dried film, it is important that a particular production batch have the correct solids content.

Basically, the test method involves weighing a certain amount of liquid coating into a previously weighed thin, disposable aluminum dish, baking this in an oven for 1 hour at 105 to 115°C, and dividing the weight of solid material left behind by the initial weight of liquid material used.

The procedure is simple and straightforward, although the precision and accuracy for thick, high solids multicomponent coatings is not quite as good as for simple low solids coatings such as alkyds. In some such cases, these coatings contain curing agents which are volatile at the temperature of the test, meaning that they can evaporate in the oven before they get a chance to cross-link and become "nonvolatile." This possibility is recognized by ASTM, and

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for such coatings it is recommended that they be allowed to air dry for one hour after mixing and prior to placing them in the oven. Single component reactive coatings, such as moisture cured urethanes, are not specifically addressed by ASTM. However, it would seem logical to treat them in a similar fashion to the reactive two component coatings.

Volume Solids

The percent solids by volume of a coating, often referred to as its volume solids, is determined in accordance with ASTM D2697 (Standard Test Method for Volume Nonvolatile Matter in Clear or Pigmented Coatings). This is a somewhat more complicated test than either the density or weight solids tests described above, and indeed requires that these two tests be done in order to perform the necessary calculations. Essentially, the liquid coating is applied to small metal disks and allowed to dry. The disks are then weighed in air, and again while suspended in water, and the appropriate calculations are done to determine the percent, by volume, of the nonvolatile material in the coating.

Not only is volume solids an important property relating to the composition of the coating, but it has important practical significance. If the coating is supposed to be 70 % solids by volume and is to be applied at 10 mils wet, it will dry to a thickness of 7 mils. If a batch were low in solids, say 50 % versus 70 %, and if the applicator still applied it at the recommended 10 mils wet, he would only get a dry film thickness of 5 mils, rather than the expected 7 mils.

Viscosity

There are many ways to measure the viscosity of a coating. These include determining the time it takes for a coating to drain from a cup of known volume through an orifice of known size (ASTM methods D4212—Standard Test Method for Viscosity by Dip-Type Viscosity Cups, and D1200—Standard Test Method for Viscosity by Ford Viscosity Cup), the use of rotational viscometers using spindles, such as Brookfield viscometers (ASTM D2196—Standard Test Methods for Rheological Properties of Non-Newtonian Materials by Rotational (Brookfield type) Viscometer), and rotational viscometers using paddles, such as the Stormer viscometer (ASTM D562—Standard Test Method for Consistency of Paints Measuring Krebs (KU) Viscosity Using the Stormer-Type Viscometer). Brookfield viscometers can produce a much more accurate viscosity profile than a Stormer viscometer, because they allow one to obtain viscosity data over a wide range of shear rates. In contrast, a Stormer viscometer (Fig. 1) provides only a single data point, with the viscosity (expressed as Krebs Units, or KU) being determined under a single, low shear condition. Nevertheless, partly because of its simplicity, the standard quality control test for viscosity is done with the Stormer type viscometer.

When performing viscosity testing, it is important that the temperature requirements be observed, as this can significantly affect the results. It is also important to realize that the viscosity of a multi-component coating can change over time, and that viscosity should be determined as soon after mixing as possible.

Pigment Content

The weight solids test described above provides a measure of the total amount, by weight, of solid material in the liquid coating. It says nothing, however, about the ratio of pigment to vehicle, which can have a significant influence on the performance of the coating. The common procedures for determining percent pigment are ASTM D2371 (Standard Test Method for Pigment Content of Solvent-Reducible Paints) for solvent borne coatings, and ASTM D3723 (Standard Test Method for Pigment Content of Water-Emulsion Paints by Low-Temperature Ashing) for water-borne coatings. The first procedure involves using a centrifuge to separate the pigment from the vehicle and solvents, while the latter involves ashing a dried film of coating after first determining its weight solids. Once a sample has been analyzed for percent pigment and weight solids, the percent vehicle can be calculated simply by taking the difference between the two. The only error in this procedure, which is usually quite minor, is the inclusion of any additives as vehicle.

Fig. 1—Stormer viscometer used to obtain viscosity of coatings. (Photograph courtesy of Weldon Laboratories.)

Sag Resistance

Sag resistance provides a measure of how thick a coating can be applied to a vertical surface before it begins to sag. This is important, because if the coating is intended to be applied at 10 wet mils but sags at 5, it will have to applied in two coats rather than one.

Sag resistance is commonly tested in accordance with ASTM D4400 (Standard Test Method for Sag Resistance of Paints Using a Multinotch Applicator). This involves preparing a drawdown using a notched applicator (Fig. 2) which applies the coating in a pattern of stripes covering a range of thicknesses. The drawdown is then immediately hung vertically, with the thinnest stripe at the top and the thickest at the bottom, and subsequently evaluated to determine the heaviest thickness which does not sag into the stripe below it.

Fig. 2—A multinotch applicator used to evaluate sag resistance. (Photograph courtesy of Weldon Laboratories.)

Drying Time

How long it takes a coating to dry to touch, or dry hard, can be an important practical consideration. Furthermore, if the drying time of a particular batch is very much longer than expected, it could be an indication of a compositional problem. Drying time is commonly measured in accordance with ASTM D1640 (Standard Test Methods for Drying, Curing, or Film Formation of Organic Coatings at Room Temperature). The tests are simple but subjective, and involve such techniques as touching with one's finger to determine set to touch times, or using a twisting motion with one's thumb to determine dry to handle times.

Infrared Spectroscopy

Most of the above tests are rapid, require relatively inexpensive equipment, and provide a quick screening method to determine if a particular batch of coating falls within specification requirements. However, they essentially measure some type of bulk property which, although dependent to some extent on the specific ingredients of the coating, does not in any way actually identify these ingredients. A powerful tool for providing compositional information on paints and coatings, whether in the solid or liquid state, is infrared spectroscopy.

Infrared spectroscopy is described in great detail elsewhere in this volume. Simply put, it allows a material to be identified by measuring the amount of infrared light absorbed (or transmitted) at various frequencies. Indeed, a spectrum is simply a graph showing the amount of absorbed (or transmitted) infrared light as a function of frequency. Two examples of infrared spectra are shown in Fig. 3. Even without understanding the underlying theory of the process, it is obvious that the spectrum of the vinyl latex is much different in appearance than the spectrum of the

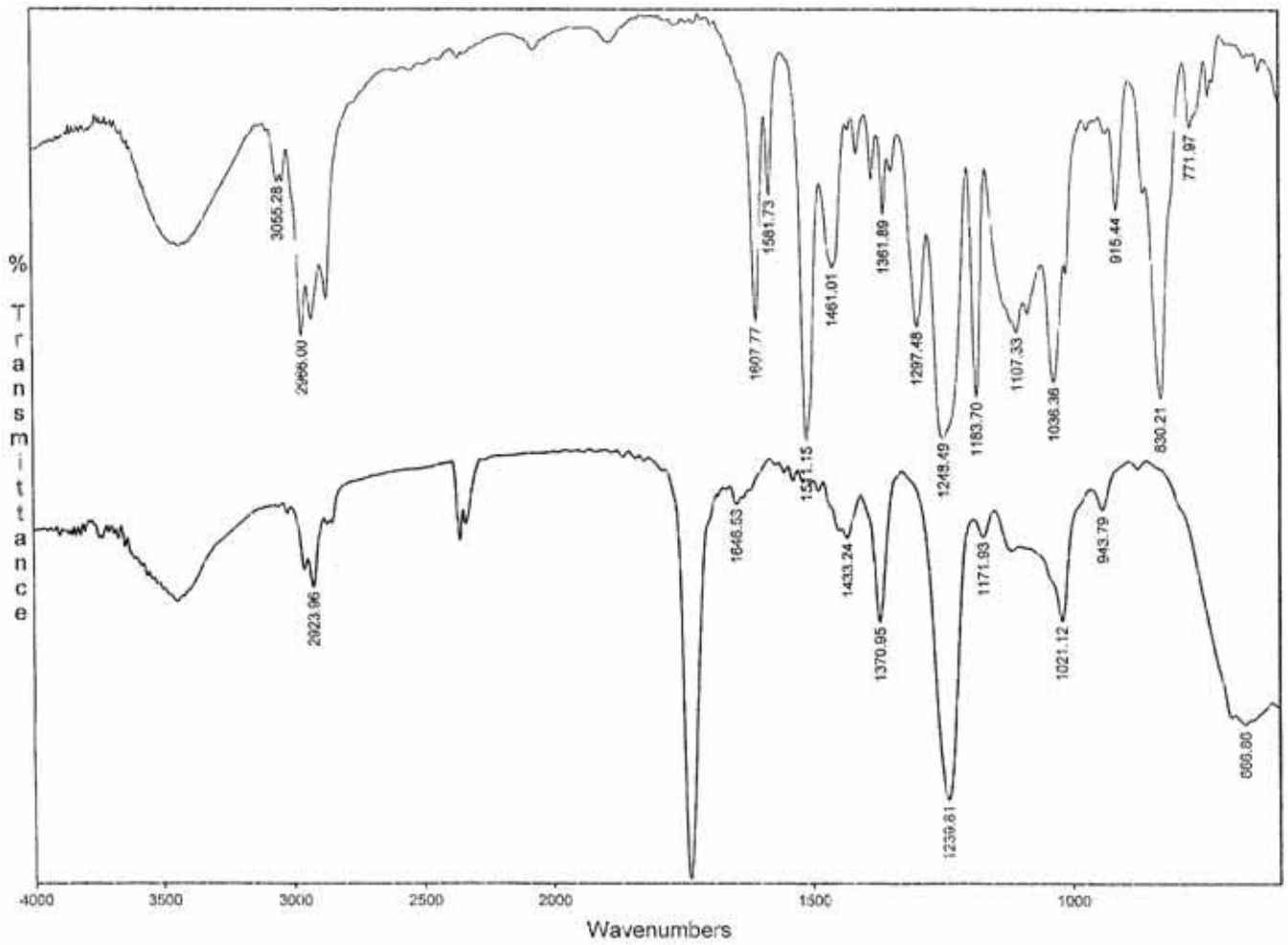

Fig. 3—Infrared spectra of an epoxy (top) and a vinyl latex (bottom). (Photograph courtesy of Weldon Laboratories.)

epoxy. The fact that different materials each have their own unique infrared spectrum has led to them being referred to as "fingerprints."

In recent years there has been a trend in product testing to obtain an infrared spectrum of the batch of coating submitted for testing. If the batch passes all the testing requirements and is approved, the spectrum is kept on file in the event that a problem occurs with a later, production batch of coating. If the spectrum shows a marked deviation in composition from the originally approved batch, it is likely that the problem is a coating one. On the other hand, if the various bulk properties are consistent, and the spectrum is a good match to the spectrum of the approved batch, it is likely (but not certain) that the problem lies elsewhere.

Although an extremely useful technique, infrared spectroscopy is not without its limitations. First of all, there is more than one way to actually obtain a spectrum of a sample, and the analyst must be consistent in his methodology in order to obtain reproducible spectra. Secondly, infrared spectroscopy generally cannot detect ingredients which are present at less than 4 % or 5 % unless they are somehow separated or at least partially isolated from the mixture. Therefore, a minor additive which might have a crucial bearing on the performance of a coating, such as an ultraviolet light absorber, would not even be detected by this technique.

TESTING OF APPLIED COATINGS

Because of the diversity of coating types, structures, and environments encountered in the industrial maintenance field, there are numerous tests which could be appropriate for a given situation. Because of this, the first question to ask when putting together a testing program, or evaluating the manufacturer's published literature, is "what is this coating going to be used for?." This simple question will help greatly in deciding which tests are appropriate, and how much emphasis to place on each test. The following is a list of many of the common tests which could be appropriate for evaluating the performance of an industrial maintenance coating. ASTM D6577 ("Standard Guide for Testing Industrial Protective Coatings") provides a good list of the many tests available.

Adhesion

Of all the physical and chemical properties of a coating, this one is arguably the most important. The best coating will offer little protection if it does not stick to the substrate. There are several methods to measure adhesion, including such subjective, "unofficial" techniques as prying with a hammer and chisel to rubbing with the edge of a coin. The three more widely used standardized ASTM techniques, however, include D3359, D4541, and D6677.

ASTM D3359 (Standard Test Methods for Measuring Adhesion by Tape Test) is often referred to as "tape adhesion." There are two methods to choose from, A and B, depending on the thickness of the coating. Method A is recommended for films greater than 5 mils thick, and involves using a cutting tool to scribe an "X" cut into the specimen, followed by the application of a special pressure sensitive adhesive tape. The tape is then rapidly removed, and the adhesion is assessed in accordance with the method's descriptive rating system. The ratings range from a 5 for no peeling or removal, to a 0 for removal beyond the area of the X. Method B, for thinner films, involves scribing a cross-hatch pattern into the specimen, again followed by the application and removal of tape. The ratings, which also range from 5 to 0, are assessed in accordance with pictorial representations of the percentage of coating removal.

The technique has the advantage of being quick, simple, and inexpensive, and can even be done on curved surfaces. However, occasionally problems can be encountered with the tape not adhering well to the paint, resulting in artificially good results. A more common problem, however, especially with thick, tough coatings, is not being able to scribe completely through to the substrate.

ASTM D4541 (Standard Test Method for Pull-Off Strength of Coatings Using Portable Adhesion Testers) is often referred to as "tensile adhesion." It involves using an adhesive to attach aluminum or steel dollies or stubs to the coating, and then using some sort of portable adhesion tester (Fig. 4) to measure the force required to pull the stub from the surface, hopefully taking the coating along with it. The result is reported in psi. A variation of this test is currently being evaluated for use on coated concrete.

The advantages of this method compared to D3359 include less subjectivity and less operator error associated with not cutting completely through the coating. It has several potential drawbacks, however, not the least of which is the fact that the various instruments on the market can produce widely varying results. Thus, it is critical, when performing the test, to report which instrument was used, and results between one coating and another should only be compared if they were tested using the same type of instrument. It is also not uncommon for the precision to be relatively poor, at least for certain types of instruments, so it is advisable to perform testing in duplicate or triplicate.

The method can usually not be used on curved surfaces, as this changes the degree of contact and hence the surface area tested, and, once the stubs are applied, it can take from a few hours to overnight before the adhesive has cured enough to test. Furthermore, some adhesives do not bond well to the surfaces of some coatings, resulting in glue failures rather than coating delamination. It should also be pointed out that it is not unusual for tensile adhesion and tape adhesion results to appear to be inconsistent. This is

Fig. 4—A type of commonly used portable adhesion tester. (Photograph courtesy of Weldon Laboratories.)

likely because tape adhesion applies a significant degree of shear stress to the coating, which is absent in the tensile testing. Thus, the coating adhesion, when assessed by tape adhesion, can sometimes appear to be worse than the tensile adhesion values would indicate.

A third, relatively new ASTM method for assessing adhesion, is D6677 (Standard Test Method for Evaluating Adhesion by Knife). This method involves using a knife to cut an "X" into the sample, and then uses the tip of the knife to pick or probe at the intersection of the cuts. There is a rating system based on the ease with which the coating can be removed. Investigators and inspectors have used similar methods for years in subjectively determining coating adhesion, and one of the main reasons for establishing D6677 was to try to standardize, at least to some extent, the various subjective methods in use.

Corrosion Resistance

When the structure being painted is made of steel, assessing the corrosion resistance of the coating is very important. By far the most commonly used procedure is the salt spray test, ASTM B117 (Standard Practice for Operating Salt Spray (Fog) Apparatus). The test involves placing the painted panels in a salt spray cabinet (Fig. 5), which essentially produces a fog of warm (95°F) saltwater (5 % sodium chloride). After an agreed upon period of time, such as 1000 h, the panels are evaluated for such things as blistering (ASTM D714—Standard Test Method for Evaluating Degree of Blistering of Paints), rusting (ASTM D610—Standard Practice for Evaluating Degree of Rusting on Painted Steel Surfaces), and undercutting at the scribe (ASTM D1654—Standard Test Method for Evaluation of Painted or Coated Specimens Subjected to Corrosive Environments), if the panels were scribed (an option) before placing them on test.

Fig. 5—An ASTM B117 salt fog cabinet. (Photograph courtesy of Weldon Laboratories.)

The procedure has been used for decades, and is firmly entrenched in many specifications. Over the last ten years or so, however, it has become somewhat controversial, and there is a body of evidence that salt spray results do not correlate very well with real world performance.

A second commonly used test procedure which has increased substantially in popularity over the last several years is what is known as Prohesion testing, which is described in ASTM D5894 (Standard Practice for Cyclic Salt Fog/UV Exposure of Painted Metal). The terminology, however, is somewhat confusing, as Prohesion testing refers to a procedure involving a cyclic salt fog test, which is only one component of D5894 (the other component being accelerated weathering).

In D5894, the test panels (either scribed or unscribed) are placed in a cyclic salt fog cabinet (sometimes referred to as a Prohesion cabinet), which introduces a fog of dilute salt water (0.05 % sodium chloride/0.35 % ammonium sulfate) at room temperature for one h. After one h, the cabinet is purged with warm, dry air for one hour, and the cycle is repeated. The panels remain in the cyclic salt fog cabinet (also described in ASTM G85, Standard Practice for Modified Salt Spray (Fog) Testing) for a specified period of time (typically one week), after which time they are manually transported to an ASTM G154 accelerated weathering cabinet, which uses ultraviolet light, heat, and moisture to weather the panels, again typically for one week. The panels alternate between the two cabinets, typically for a total duration of 1000 h, and are then evaluated in the manner described above for salt fog testing.

It is generally felt that D5894 gives better correlation to the real world performance of coatings than does B117. However, in both cases, and indeed with all accelerated laboratory test methods, it is extremely difficult to use the tests to actually predict the service life of a coating system. The tests are primarily used to compare one coating with another, allowing them to be ranked as to which can be expected to perform the best. There is also concern that D5894 gives artificially poor results for zinc-rich primers.

Accelerated Weathering

A commonly asked question of a coating is "how durable is it," or "how well does it weather." The best, but also the slowest way, to answer this question is to expose painted panels outdoors in an environment similar to what might actually be expected. As this can take years, there have been various accelerated laboratory test methods developed. All of these methods employ a combination of heat, ultraviolet light, and moisture to weather or degrade the coating. Broadly speaking, they fall into two categories, depending on the source of ultraviolet light: arc devices, and fluorescent tube devices.

Arc devices produce ultraviolet light by passing an electrical current through an electrode. Devices include enclosed and open-flame carbon arcs described by ASTM G153 (Standard Practice for Operating Enclosed Carbon Arc Light Apparatus for Exposure of Nonmetallic Materials) and D822 (Standard Practice for Filtered Open-Flame Carbon-Arc Exposures of Paint and Related Coatings), and

xenon arc machines described by ASTM G155 (Standard Practice for Operating Xenon Arc Light Apparatus for Exposure of Non-Metallic Materials). In all cases, water is sprayed intermittently onto the specimens as a fine mist, and exposure to light and darkness is alternated. A commonly used cycle is 102 min of light at 145°F and 18 min of light and water spray at 60°F. The xenon arc devices have become much more common than the carbon-arc devises.

Fluorescent UV bulb devices are described in ASTM G154 (Standard Practice for Operating Fluorescent Light-Apparatus (for UV) Exposure of Nonmetallic Materials), formerly known as ASTM G53. Briefly, they use fluorescent tubes to provide the ultraviolet light, and moisture in the form of condensation is produced by heating a trough of water located in the bottom of the instrument. Many different types of bulbs are available which have different spectral characteristics, although most fall into what is known as either the UV-A or UV-B region of the electromagnetic spectrum. The UV-B region is more aggressive and can produce results in less time, but the UV-A region is generally felt to be a more realistic test.

Regardless of which type of test is selected it must be kept in mind that it is very difficult, if not impossible, to predict an actual lifetime for a coating based upon accelerated weathering data. Weather varies dramatically from geographic region to geographic region, and even from year to year in the same region. Therefore, the primary use of accelerated weathering is to compare or rank one coating versus another.

Chemical Resistance

When one considers all the industrial environments that painted structures can be exposed to, as well as the fact that coatings are used to protect such things as waste water treatment plants, off shore oil platforms, secondary containments, and even the interiors of railroad tank cars and chemical process vessels, it is apparent that chemical resistance is an extremely important property. The two relevant test methods for determining chemical resistance are ASTM D1308 (Standard Test Method for Effect of Household Chemicals on Clear and Pigmented Organic Finishes), and ASTM C868 (Standard Test Method for Chemical Resistance of Protective Linings).

The title of D1308 is somewhat misleading, as the methodology can be applied to harsh industrial chemicals as well as mild household ones. The method is broadly written, and covers such possibilities as simple room temperature spot testing, where a small amount of chemical is applied to a test panel and covered with a watch glass for an hour or so, to high temperature immersion testing. The method does not go into much detail as to apparatus, time, or temperature, and basically leaves these decisions up to the investigator. Obviously, chemicals should be chosen which could reasonably come into contact with the coating, and realistic, although perhaps slightly elevated, temperatures should be chosen. Although in service the coating may be expected to perform for several years, laboratory testing is usually carried out for no more than a few months, with the panels being evaluated for such things as rusting, blistering, cracking, softening, or delamination. If the coating goes for a few months with little or no sign of deterioration, it is generally assumed to be acceptable for that chemical, even though it is not possible to predict the actual service life in years.

While D1308 involves immersion testing, C868 is often referred to as "one-sided" immersion testing, or sometimes "Atlas Cell" testing, even though there may be a number of companies which manufacture the equipment. A virtually identical test is described in NACE TM-01-74 (Laboratory Methods for the Evaluation of Protective Coatings and Lining Materials in Immersion Service). The apparatus used in C868 (Fig. 6) consists of a glass cylinder, typically 5 to 7 in. in diameter, fitted with ground glass take offs for such things as condensers, thermometers, or immersion heaters (one variety jackets the outside of the cell with a flexible heating element). The gasketed test panels actually form the two ends of the cell. The cell is then filled halfway to two thirds full with the chemical of interest, and the heating element set to maintain the desired test temperature. The test duration is typically from 3 to 6 months.

One of the main advantages to C868 testing is that, since the test panels are not immersed, there are no edge effects to worry about. Sometimes it is difficult to seal sharp edges, and failures can occur near edges which are more application related than coating related.

Another advantage to C868 testing, which depending on circumstances may be more perceived than real, is the belief that it mimics the "cold wall effect." The cold wall effect has been observed numerous times, and occurs when the outside, non-immersed surface of the steel is colder than the inner surface which is exposed to the contents of the vessel. This is a more aggressive condition than if the inner and outer temperatures are the same, and can more readily cause blistering of the interior coatings.

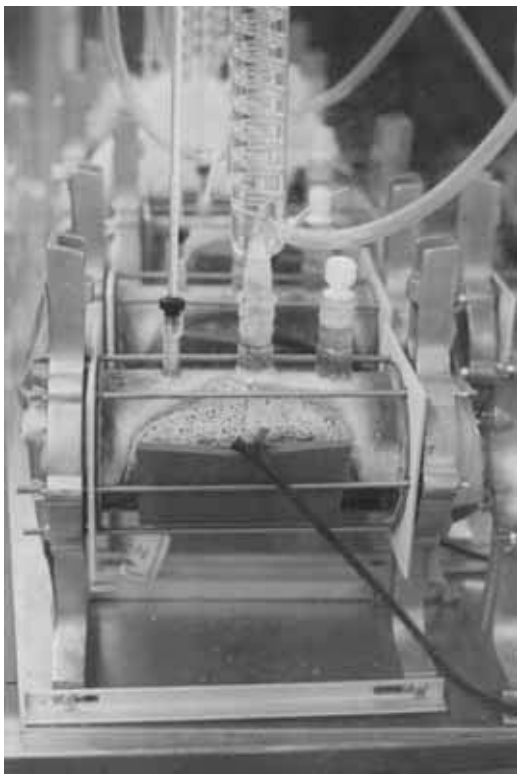

Fig. 6—An ASTM C868 chemical resistance cell. (Photograph courtesy of Weldon Laboratories.)

At first glance, this condition would appear to be simulated in Atlas Cell testing. However, unless the steel test panels are rather thick, there is actually very little difference in temperature between the inner and outer walls. A temperature gradient can be imposed by jacketing the outer surface with a cell containing circulating water, but in practice this is rarely done.

When doing chemical resistance testing, it is tempting to choose a temperature much higher than the actual, expected temperature, in order to accelerate the test. Care must be taken, however, not to choose too high of a temperature. If the coating is below its glass transition temperature when in actual service, but has been artificially raised above its glass transition temperature during laboratory testing, the possibility exists that it will have been made more permeable as a result. Thus, it could fail in the laboratory, yet in actual service it could perform very well.

Abrasion Resistance

Coatings used to protect handrails or used in areas subjected to heavy foot traffic need to be resistant to abrasion. By far the two most popular methods to evaluate abrasion resistance include Taber abrasion and falling sand.

Taber abrasion testing is described by ASTM D4060 (Standard Test Method for Abrasion Resistance of Organic Coatings by the Taber Abraser). The test panels, which are 4×4 in.^{2} with a hole in the middle, are mounted on a device called a Taber abrader. This is essentially a turntable with a pair of weighted abrading wheels which rest on the panel. As the panel rotates, the abrasive wheels turn along with it, resulting in removal of some or all of the coating. The panels are weighed before and after testing, and the result is usually reported as a weight loss per so many cycles (usually 1000 cycles). Coatings with better abrasion resistance lose a smaller amount of weight. When evaluating Taber abrasion results, it is important to know the number of cycles, the load on the wheels, and the type of wheels. CS-17 wheels are the most common, but wheels of lesser and greater abrasiveness can be used.

The falling sand test is described by ASTM D968 (Standard Test Methods for Abrasion Resistance of Organic Coatings by Falling Abrasive). Essentially, the test panel is mounted at a 45° angle beneath a tube which is attached to a hopper. A known quantity of sand is dumped into the hopper and impinges upon the test panel. The amount of sand required to wear through the coating is reported. On relatively thin, ordinary coatings such as an acrylic latex or an alkyd, the test is relatively simple to do. On a thick, high performance coating such as an epoxy or an elastomeric urethane the test can be extraordinarily time consuming, and requires large quantities of sand (an individual quantity of sand is to be discarded after a certain number of uses).

Impact Resistance

Examples of coatings which would require good impact resistance would include coatings for overseas shipping containers, and coatings for use on locks and dams. Most-impact resistance tests involve dropping a weight onto a coated panel and looking for cracking or disbonding. The most common procedure is ASTM D2794 (Standard Test Method for Resistance of Organic Coatings to the Effects of Rapid Deformation (Impact), where a hemispherical tup is rested on the panel, and a falling weight, housed in a guide tube, is dropped from varying heights to determine the greatest force, expressed in in-lbs, which will not crack or disbond the coating (Fig. 7). The procedure calls for the use of a thin gage steel panel which will deform under the conditions of the test, although many users prefer to use thicker steel representative of the actual article to be coated. If the weight is dropped on the coated face, the result is referred to as direct impact. If it is dropped on the back of the panel, it is referred to as indirect or reverse impact. Coatings nearly always have lower reverse impact than they do direct impact resistance.

Flexibility

A certain amount of flexing or movement is common with many structures. Electrical transmission towers flex and move in the wind, thin galvanized decking can flex when walked upon, and metal can change dimensions slightly upon freezing and thawing. Furthermore, instantaneous flexing can occur when a surface is subjected to a sharp impact. Indeed, it is difficult to imagine a case where flexibility would not be a desirable property of a coating. The fact that not all coatings are flexible is because to impart flexibility to a coating, one must often sacrifice other properties, such as chemical resistance or resistance to permeation.

Coatings are commonly tested for flexibility by bending a coated, thin gauge steel or aluminum panel over a mandrel and examining the coating for cracking, in accordance with ASTM D522 (Standard Test Methods for Mandrel Bend Test of Attached Organic Coatings). The method

Fig. 7—A variable impact tester used to measure the impact resistance of coatings. (Photograph courtesy of Weldon Laboratories.)

Fig. 8—A conical mandrel tester used to determine per cent elongation. (Photograph courtesy of Weldon Laboratories.)

describes two procedures, one using a conical mandrel, and one using cylindrical mandrels.

The conical mandrel consists of a metal cone, 8 in. in length, with a diameter of 1/8 ft at the narrow end to 1 1/2 in. at the wide end (Fig. 8). There are clamps for mounting the panel, and a rotating arm which is used to bend the panel around the mandrel. If the coating is being evaluated for percent elongation, it is bent slowly (over a period of 15 s). If it is being evaluated for crack resistance it is bent quickly (approximately 1 s). If cracking occurs, the distance which the cracking extends from the small diameter end towards the large diameter end is measured and used to determine the coating's percent elongation. If no cracking occurs, the percent elongation is greater than approximately 32 percent. When using cylindrical mandrels, one usually simply reports the smallest diameter mandrel over which the panel can be bent without cracking, although % elongation can also be estimated.

The mandrel testing described in D522 is usually sufficient for testing most industrial maintenance coatings. However, for very flexible elastomeric coatings it is of little use, since these coatings will have elongations of 100 % or more, far above the maximum 32 % which can be determined by D522. In such cases, it may be desirable to test such coatings using the so-called "universal testing machines," which essentially use clamps to hold free, unsupported films of coatings between the jaws of the machine. The sample is then stretched apart at a known rate and a stress-strain curve obtained. Such properties as percent elongation, tensile strength, and modulus (essentially the "stiffness" of the sample) can be determined. Applicable test procedures include D2370 (Standard Test Method for Tensile Properties of Organic Coatings) and D638 (Standard Test Method for Tensile Properties of Plastics). It is often difficult, however, to test very thin free film coatings by these methods, although coatings thicker than about 5 mils can usually be tested.

Moisture Resistance

A coating intended to line the interior of a potable water tank obviously requires good moisture resistance. While salt spray and accelerated weathering tests have a moisture component to them, they introduce other elements which the potable water lining would not be exposed to. Since water could certainly be considered a chemical, some type of water immersion test could certainly be carried out in accordance with the general chemical resistance testing previously described by ASTM D1308. However, water or moisture resistance is more commonly done in accordance with either ASTM D4585, D2247, or D1735.

ASTM D4585 (Standard Practice for Testing Water Resistance of Coatings Using Controlled Condensation) involves generating water vapor by heating a pan of water located in the bottom of the chamber. The test panels form the roof or walls of the chamber, and since their back side is exposed to the cooler air of the laboratory, condensation forms on the coated front surfaces. Although this sounds like a relatively gentle test, it is actually quite aggressive since the condensing water is relatively pure and it is conducted at a slightly elevated temperature. Coatings typically fail by blistering. ASTM D2247 (Standard Practice for Testing Water Resistance of Coatings in 100 % Relative Humidity), is somewhat similar, except that the cabinet is designed differently and the specimens are completely suspended inside the chamber.

Considerably different than the above methods is ASTM D1735 (Standard Practice for Testing Water Resistance of Coatings Using Water Fog Apparatus). This method uses a chamber similar to an ASTM B117 salt fog cabinet to expose the panels to an actual mist of water.

Hardness

Industrial maintenance coatings are commonly rated for hardness using the pencil hardness method described in ASTM D3363(Standard Test Method for Film Hardness by Pencil Test). In this method, a series of pencils is used to determine the hardest pencil lead which will not scratch or gouge the coating. The pencil ratings, from softest to hardest, are as follows:

6B-5B-4B-3B-2B-B-HB-F-H-2H-3H-4H-5H-6H

The test is somewhat subjective, not only because of operator variability, but also because of possible variations among different sets of pencils. ASTM lists a reproducibility of plus or minus one pencil.

For thick coatings, hardness is sometimes determined using some type of indentation tester. The two most commonly used are the Barcol (D2583) and Durometer (D2240—Standard Test Method for Rubber Property-Durometer Hardness) types. In both cases, hand pressure is used to drive a spring loaded indenter into the coating, and the ease of penetration is reflected on the scale (higher numbers indicate harder coatings).

Water Vapor Permeability

It is not surprising that a coatings resistance to the permeation of water vapor can have a significant bearing on its ability to protect the substrate. In many cases, this is tested in a very practical way by subjecting painted test panels to wet or humid environments, such as the salt spray, accelerated weathering, and humidity tests described above. A more direct way to actually measure the rate of water vapor permeation, however, is described in ASTM D1653 (Standard Test Methods for Water Vapor Transmission of Organic Coating Films). In this test method, free films of coating (or films attached to a thin, porous paper substrate) are sealed to the open mouth of a cup or dish, and essentially form the lid of the cup (Fig. 9). In Method A the cup

Fig. 9—A permeability cup used to determine water vapor transmission. (Photograph courtesy of Weldon Laboratories.)

contains a desiccant, and the assembly is placed in a humid environment. The cup is weighed periodically to measure the amount of moisture which has passed through the coating and into the desiccant. In Method B, which is the more common procedure, the cup contains water, and is placed in a dry environment. It is then weighed periodically to determine the amount of moisture which has passed through the coating and out of the cup.

Theoretically the procedure sounds very simple and straightforward. In practice, however, it is not quite so simple. It can sometimes be extremely difficult to obtain, as the method calls for, "smooth and completely continuous films of uniform thickness throughout the test area." Furthermore, if the coatings are very thin, or very brittle, it can be a frustrating task to remove them from the release paper or even mount them on the cups without tearing or fracturing them.

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Pipeline Coatings

Alfred Siegmund[1]

IN PREPARATION OF THIS CHAPTER, THE CONTENTS of the fourteenth edition were drawn upon. The author acknowledges the authors of the fourteenth edition. The current edition will review and update the topics as addressed by the previous authors, introduce new technology that has been developed, and include up-to-date references.

INTRODUCTION

Energy and its availability continue to drive the industrialization of nations. America uses a very large volume of energy based on fossil fuels. Many times, the usage point is a great distance from the source. Carbon-steel pipelines continue to be the most economical means of transporting fuel from the source to the consumption point. Many thousands of miles of pipelines crisscross the landscape. As with all carbon-steel pipe, corrosion is a major concern. Pipeline failures [1] always make big headlines, cost large amounts of capital to repair, and frequently disrupt needed service.

Building a major pipeline is a costly, time-consuming project. First, an abundant source of fossil or other fuel must be located and combined with a provider who will service an end user. Federal, state, and local permits must be obtained, rights-of-way purchased, and financing obtained. From start to finish, this can be a multi-year project. To protect the investment and to provide for safe operation, every possible means of protection must be considered over the life of the pipeline. The most economical means of protection continues to be a combination of cathodic protection and protective coatings. This chapter focuses on the role of coatings and their design, selection, and use.

MARKET

The United States Department of Commerce estimates that loss of steel due to corrosion costs in the billions of dollars each year in the United States alone. The market for pipeline coating products varies each year and depends on the number of permits issued. At about the turn of the twenty-first century, this market was estimated to exceed $350 billion per year—an amount that grows each year. The market is divided between repair and rehabilitation products and new construction products. There are five basic product groups available for such uses.

- Asphalt enamels and asphalt mastics . . . 7 %
- Coal tar and coal tar modified products . . . 14 %
- Fusion Bonded Epoxy (FBE) powder coatings . . . 32 %
- Polyolefins, including both bonded and extruded products . . . 17 %
- Tape products . . . 30 %

The distribution of product use size will vary from year-to-year depending on the active projects in particular areas as well as developments and improvements within the product areas. Table 1 contains a listing of some considerations that are pertinent for such coatings.

WHY USE COATINGS?

Control of steel pipeline corrosion is a complicated process that involves several different techniques. Internal corrosion protection may be accomplished with organic coatings and/or inhibitor coatings. External corrosion protection is almost always a combination of cathodic protection and organic coatings. Careful selection of the coating material in combination with proper application can result in many years of trouble-free service. In certain regions where permafrost is encountered, special considerations regarding the environment need to be made [2].

Coatings are required to provide a wide range of protective properties that vary from excellent mechanical characteristics to elevated temperature resistance. On a per-square-foot basis, coatings have proven to be the most economical corrosion control system for steel pipelines. The United States Department of Transportation (DOT) recognizes the protection provided by coatings. It is a DOT requirement that a bonded coating protect all new steel pipelines involved in intrastate commerce.

PRODUCT DEVELOPMENT, COMPARATIVE TESTING, AND QUALITY CONTROL

Product testing utilizing procedures or methods published by ASTM, NACE, SSPC, and others takes place in three distinct time frames. Several pipeline specifications, methods, and practices are given in Table 2. The technologist will use a broad spectrum of tests to learn everything possible about the product. The goal is to determine the strong points of the product and possibly to correct any product deficiencies. The basic properties of an external coating are resistance to cathodic disbondment, adhesion, impact resistance, flexibility, and resistance to moisture penetration. Such failure modes have been described in the literature [3]. Defining these properties will provide the technologist with information used to decide whether or not a potentially useful product is being considered. Many other properties must be defined to generate a product specification list.

The pipeline engineer will use a series of tests to choose between comparable products and will use some of these tests to establish an in-process quality program.

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TABLE 1—Considerations for repair and rehabilitation coatings	
Adhesion and compatibility	Time to pipe burial
Coating cure time	Two-component, cold-damp surfaces
Inspection	Transition to existing coatings
Materials and workmanship	Weather for over-the-ditch repair
Surface preparation	Weather, temperature, rock shields

The application, along with an outside quality team, will use a limited number of in-process tests to assure product quality.

INTERNAL PIPE COATINGS

Most of the information in this chapter refers to external pipeline coatings. Internal pipe coatings are used, but their use is far more complicated than the external coatings [4]. Internal coatings not only provide corrosion protection, they can impart minimized erosion, fouling, friction, and wear—all of which are dependent on what is flowing in the pipe. Thus, internal coatings can provide improved flow rates (~ 5 – 15 %) and greater productivity, factors that will result in decreased maintenance costs. The internal coating will be in contact with liquid or gaseous substances such as crude and refined oil, water, air, food products, oxygen, nitrogen, natural gas and so on. Three common systems used are two-component epoxy polyamide/amine combinations that cure under ambient conditions, fusion bonded materials that are thermally cured, and air-dried, field applied coatings based on either epoxides or urethane chemistry.

With this strong dependence on what is being carried in the pipeline, only this brief mention will be made of the coating technology for internal coatings. In a general sense, the topic is too complex for this particular chapter.

TABLE 2—Pipeline coating specifications, practices, and standard methods	
Test Designation	**Title**
API RP 5L2	Recommended Practice for Internal Coating of Line Pipe for Non-Corrosive Gas Transmission Service
API RP 5L7	Recommended Practice for Unprimed Internal Fusion Bonded Epoxy Coatings of Line Pipe
NACE RP T-10D	Recommended Application, Performance and Quality Control of Plant Applied Fusion Bonded Epoxy External Pipe Coatings
AWWA C203	Coal Tar Protective Coatings and Lining for Steel Water Pipelines—Enamel and Tape Hot Applied
AWWA C210	Liquid Epoxy Systems for the Interior and Exterior of Steel Water Pipelines
AWWA C214	Tape Coating Systems for the Exterior of Steel Water Pipelines
AWWA C215	Extruded Polyolefin Coatings for the Exterior of Steel Water Pipelines
AWWA C217	Cold-Applied Petrolatum Tape and Petroleum Wax Tape Coatings for the Exterior of Steel Water Pipelines

EXTERNAL COATINGS FOR REPAIR AND REHABILITATION

The existing pipeline infrastructure is aging. Many lines have 20, 30, or 40 years of service and are in need of repair and maintenance, which poses a unique set of problems [5–8]. First is that the pipeline will remain in service during the work effort. This can cause problems with temperature—hotter close to compressor stations and variable in other locations. Access to buried pipe is limited due to the confines of the associated ditch. This limits surface cleaning and can markedly affect the choice of coating and the long-term performance of the selected product.

Application techniques are limited to spray equipment that is tractor mounted and travels along the pipeline or traveling equipment that actually rides on the pipe. Weather conditions are a significant consideration in the selection and performance of the coating. Cold damp surfaces are not uncommon as well as hot days during summer and in desert areas. Cure time, or time to bury, becomes an important factor as maintaining an open ditch during certain weather condition can pose serious difficulties.

The previously mentioned concerns limit the coating that can be effectively utilized. Waxes, oils, and greases are still utilized as protection for elbows, valves, and other short runs. They are generally protected by a layer of Kraft paper or felt to allow them to be quickly buried.

Coal tar and coal tar modified products are well suited for rehabilitation and over-the-ditch applications. There is a wide choice of products that include but are not limited to modified epoxides, urethanes, and associated mastics and enamels [9]. The moisture resistance of these coatings along with their relative ease of application makes them a good choice for this service. Tests used for coal tar and related products are listed in Table 3.

TABLE 3—ASTM test methods for analyzing coal tar and related products (a partial listing)	
Designation	**Standard Test Method for**
ASTM D4	Bitumen Content
ASTM D5	Penetration of Bituminous Materials
ASTM D36	Softening Point of Bitumen (Ring-and-Ball Apparatus)
ASTM D71	Relative Density of Solid Pitch and Asphalt (Displacement Method)
ASTM D2415	Ash in Coal Tar and Pitch
ASTM D3143	Flash Point of Cutback Asphalt with Tag Open-Cup Apparatus
ASTM G17	Penetration Resistance of Pipeline Coatings (Blunt Rod)

Cold-applied tapes that are applied by equipment that rides the pipe are popular. Machines have been utilized that clean and coat the pipe in a short time span allowing for quick return of the pipeline to service.

Table 4 contains a listing of typical tests used to determine the acceptability of external pipeline coatings.

FACTORY OR PLANT APPLIED PRODUCTS

The majority of new pipeline construction projects use plant-applied coatings. This allows for thorough evaluation of the coatings before they are put in service. This involves a coordinated effort between the coating supplier, applicator, and end user. A comprehensive quality control plan can be implemented along with in-process quality checks. All of this leads to a project with a longer life before repairs are needed. A variety of coatings will meet such an effort to develop factory-applied products.

- Extruded polyolefins
- FBE powder coatings
- Multi-layer products
- Tape and wrap products

Table 5 is a listing of in-process tests that might be used to determine coating quality. It should be pointed out that some of the products can be field applied as indicated.

Tape and Wrap Products

These coatings mainly consist of polyolefins applied in tape form. They are comprised of an adhesive layer and an outer protective layer. In some instances, the two layers are co-extruded and applied as a single tape. Most tape and wrap products are cold applied, but there are some that are "heat fused" to bond the layers together. These coatings provide added moisture protection and resistance to handling damage.

Extruded Polyolefins

The next step in process improvement was to use a thermally extruded polyolefin as the outer layer of polyolefin and thus provide for a continuous protective outer film. This added even more moisture protection and handling damage control. As in the tape and wrap system, an adhesive prime coat comprised of a mastic, two-part epoxy, fusion bonded epoxy, or rubber-based material is employed [10–12].

Coal Tar Enamels

Coal tar enamels are particularly suitable for coating steel pipe. They are generally hot applied either in the yard or in the field. In use, they are virtually unaffected by long periods of water immersion, soil stress, punctures, or bacteria, and they provide a relatively high electrical resistance. These coatings work best in the temperature range of 1.1 to 82°C (30 to 180°F). The enamels are degraded by ultraviolet radiation and therefore should be wrapped with Kraft paper when exposed to sunlight. Coal tar enamels

TABLE 4—Typical starting point tests used to evaluate acceptability of external coatings

Test Type	Designation or Method
Abrasion	ASTM D4060, Standard Test Method for Abrasion Resistance of Organic Coatings by Taber Abraser
	ASTM G6, Standard Test Method for Abrasion Resistance of Pipeline Coatings
Bend	ASTM G10, Standard Test Method for Specific Bendability of Pipeline Coatings
	NACE RP0394, Standard Recommended Practice—Application, Performance, and Quality Control of Plant-Applied, Fusion-Bonded Epoxy External Pipe Coating
Cathodic Disbonding	ASTM G8, Standard Test Methods for Cathodic Disbonding of Pipeline Coatings
	ASTM G42, Standard Test Method for Cathodic Disbonding of Pipeline Coatings Subjected to Elevated Temperatures
	ASTM G95, Standard Test Method for Cathodic Disbondment Test Of Pipeline Coatings (Attached Cell Method)
Hot Water Soak	ASTM D870, Standard Practice for Testing Water Resistance of Coatings Using Water Immersion
	ASTM G9, Standard Test Method for Water Penetration into Pipeline Coatings
Impact	ASTM G14, Standard Test Method for Impact Resistance of Pipeline Coatings (Falling Weight Test)

TABLE 5—Coating quality tests and related methods

Test Type	Designation or Method
Abrasion	ASTM D4060, Standard Test Method for Abrasion Resistance of Organic Coatings by Taber Abraser
	ASTM G6, Standard Test Method for Abrasion Resistance of Pipeline Coatings
Cathodic Disbonding	ASTM D6676, Standard Test Method for Cathodic Disbonding of Exterior Pipeline Coatings at Elevated Temperatures Using Interior Heating
	ASTM G8, Standard Test Methods for Cathodic Disbonding of Pipeline Coatings (short time test)
	ASTM G80, Standard Test Method for Specific Cathodic Disbonding of Pipeline Coatings
Defect	ASTM G62, Test Method for Holiday
Determination	Detection in Pipeline Coatings
Film Thickness, Total	ASTM G12, Standard Test Method for Nondestructive Measurement Of Film Thickness of Pipeline Coatings on Steel
Impact	ASTM G14, Standard Test Method for Impact Resistance of Pipeline Coatings (Falling Weight Test)
Preheat Temp.	Standard Temperature Measuring Devices
Surface Prep.	NACE and SSPC Specifications

frequently are reinforced with a fiberglass mat or embedded with a felt mat as a means of protection. The products do provide for many years of service and were the first commonly used external protective coatings.

Coal Tar Mastic

Coal tar mastic is heavily filled with clays, silica, fiberglass, or similar materials. The resultant material is a highly viscous mass that is cold applied to a thickness of 1.27 to 1.6 cm (1/2 to 5/8 in.). Coal tar mastic can be applied as a hot extrusion, seamless coating. The material can be applied to a wide range of pipe diameters for buried pipeline service.

Coal Tar Epoxides

Coal tar epoxides are two-component materials that require mixing just prior to application. Coal tar plays two important roles in this type of coating: (1) cost reduction and (2) improved water resistance. The two components are designed to air cure and provide a harder film than neat coal tar products. Excellent adhesion is provided by the epoxy component if optimum cure is achieved.

Coal Tar Urethanes

As with coal tar epoxides, coal tar is used primarily as a cost reducing material. With the coal tar urethanes, the base components are polyols and multifunctional isocyanates. The systems can be spray applied to yield very rapid cure speeds. This feature reduces out-of-service time for the pipeline.

These coatings have the advantages of lower cost, excellent water resistance, a wide range of application techniques, and long proven service lives. They can be plant applied or over-the-ditch applied. They comprise one of the largest group of coatings used for repair and maintenance of existing pipelines.

In general, coal tar products have limitations in protection when combined with cathodic protection. Temperature service is limited to 66°C (150°F).

Fusion Bonded Epoxy Powder Coatings (FBE)

This relatively new technology now is dominant in the United States new pipe-construction protective-coating market. Refinements in this technology have taken place over the past 35 years as it grew in popularity. Drawbacks to this coating technology are moisture absorption by the basic epoxy powder and transportation damage due to the film thickness specifications for this product line [13–17].

Specialty products have been formulated within this coating type. Abrasion resistant products exist for pulling pipe under roads and rivers. Surface texture products with improved adhesion of heavy weight cement coatings are available [18]. In many instances, a combination of two coats of the powder coating applied dry-on-dry are used to gain the desired combination of end-use characteristics.

There are three levels of temperature performance products within the FBE product type. The "standard" FBE is rated for 66°C (150°F). A second generation of the coating provides for resistance to 82°C (180°F) is available, and a third generation that is rated for 93°C (200°F) has been qualified.

Multi-layer Products

The multi-layer or three-coat systems currently dominate the external pipeline coating market outside the United States [19–21]. The system was designed to take the best properties of each system and combine them into one product. The product normally consists of an epoxy primer followed by an adhesive tie-coat and then a polyolefin topcoat.

The epoxy primer provides for excellent adhesion to the metal surface and gives excellent cathodic disbanding resistance. The epoxides coating can be either in the form of a liquid or an FBE powder, but the trend is toward a powder application and thermal curing. The adhesive tie-coat is designed to adhere to both the epoxy primer and the polyolefin topcoat and thus provide the tie between the coatings. The outer polyolefin topcoat gives excellent resistance to water penetration and mechanical damage during transportation and installation. Application of the outer layer is by extruder, which will effectively increases the cost of the overall system.

Specialty Coatings

By definition, specialty coatings are those that have been developed and successfully applied to meet specific needs. They have not generated sufficient business/use to determine their survival rate or their place in the market. There are three specialty products with sufficient merit to mention.

The first of these coatings is a three-layer system based entirely on powder coating products. The outer layer is a polyethylene powder that depends on residual heat to thermally fuse and flow the powder into a continuous film. This limits the total film thickness that can be applied, but it meets all of the other characteristics of a multi-layer product.

The second product uses thermal sprayed aluminum with a seal coat as the applied product. This system has been applied to several offshore pipelines. The product has an estimated life of more than 35 years. This is a totally different coating system that utilizes sacrificial metals for protection as opposed to the normal practice of using a barrier product.

The third specialty system is designed for hot product lines that operate between 93°C (200°F) and 149°C (300°F). The desire is to provide protection on hot product lines in areas close to compressor station where elevated surface temperatures are encountered. The system is based on an epoxides base coating with a composite inter membrane and is applied as a multi-layer wrap.

Girth-Weld Products

All pipelines have connections at the welds and at other components that cannot receive coatings at the plant [8]. They must be protected after the pipe is welded together to form a pipeline. These are the weakest links in the system. The coating that is on the body of the pipe may not be the best choice for field application to the weld areas.

The most popular girth-weld products are based on two-component epoxy products or heat-shrink sleeves. All of the products have a corresponding girth-weld material. Logistics, weather, and cost may prevent them from being the product of choice for the girth-welds.

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Sealants

Saul Spindel[1]

SEALANTS ARE PRODUCTS INSTALLED INTO AN opening to prevent the intrusion of air, water, dust, heat, cold, and other materials such as gases, e.g., radon. The liquid-applied sealant is installed into the opening by gun or knife. It is then expected to function even though the space (joint) it occupies is stressed because of movement of the joint to which the sealant is applied due to expansion and/or contraction due to temperature changes, thereby placing significant strain upon the adhesive forces that bond the sealant to the substrate to which it is attached. The sealant is also expected to function regardless of whether it is applied to a horizontal opening or a vertical one or whether it is applied to a building facade subject to rapid expansion and contraction or to a plaza or deck where it is subject to puncture by spiked heels.

The opening, or gap, into which a liquid-applied sealant is installed is usually called a joint. The sides of the joint (substrates) may be made of similar or dissimilar materials, generally varying in width from 0.250 to 2.00 in. (0.64 to 5.08 cm) with the depth of the installed sealant usually about one half the width. When required, sealant backing (preformed joint fillers) made of materials such as open or closed cell rubber or polyurethane foam are installed to control the joint depth. Primers are sometimes used to improve adhesion of the sealant to the substrate.

Typical building materials that sealants are used with are glass, steel, concrete, mortar, granite, marble, aluminum, various painted or coated surfaces, or wood. When the sealant is installed into the joint, the surfaces the sealant contacts must be clean, dry, sound, and free of contaminants or loose particles to provide an opportunity for the sealant to perform as intended [1].

Caulks or sealants are fomulated based on oils, latex polymers, butyl, acrylic and blocked styrene solvent-release polymers, and polysulfide, polyurethane, and silicone elastomers. The oil-based products exhibit relatively little movement capability, generally 5 % or less, and thus they are traditionally installed in relatively static joints. Acrylic latex polymers can be formulated to possess significant movement, as much as ±25 %, whereas the solvent-release butyl, acrylic, and blocked styrene sealants can move about ±10 %. The elastomerics exhibit significant movement capability, with silicones moving as much as +100 %, –50 %. (+100 % refers to 100 % expansion whereas –50 % refers to 50 % compression based upon the original dimensions of the installed sealant).

Though this chapter provides an overview and general description of sealants, test methods, and specifications, it does not address the suitability of the test methods or specifications discussed nor does it differentiate between cured short-term performance and actual long-term performance and effectiveness of sealant products on buildings and/or other structures [2].

POLYMERS USED IN SEALANTS

Oil-Based Caulks

Oil-based caulks are generally composed of drying oils, mineral fillers, thixotropes, and driers. The oil oxidizes and thereby dries slowly, though the caulk usually sets up to become paintable within a 24 to 48 h period. Oil-based caulking compounds are easy to apply, easy to tool, and are available in a range of qualities. Generally, oil-based caulks exhibit movement of about 5 %. Oil-based caulking compounds are used primarily by do-it-yourselfers [3].

Butyl Sealants

Butyl sealants are based on polyisobutylene or polybutene, fillers such as talc and/or calcium carbonate and additives such as adhesion promoters, antioxidants, and thixotropes. Butyl sealants dry by solvent release.

Butyl sealants can be formulated to move at about $\pm 7\frac{1}{2}$ to $\pm 12\frac{1}{2}$ %. They are widely used in mobile home applications. In addition, another class of butyl sealants that are prepared without volatile solvents are extensively used as the primary seal in dual-sealed insulated glass because of their very low moisture vapor permeation properties [4].

Acrylic Solvent Release Sealants

These sealants are similar to butyl sealants; however, they are based on polymethylacrylate polymers (or polyethylacrylate or polybutylacrylate polymers), resulting in medium-high molecular weight products that, when formulated with colorants, thixotropes, and additives, are used as sealants [5].

Acrylic solvent-release sealants exhibit movement similar to butyl sealants, namely up to $\pm 12\frac{1}{2}$ %. Acrylic solvent-release sealants are versatile in that they adhere to a wide variety of surfaces and, in addition, exhibit excellent resistance to sunlight. Two prime disadvantages of acrylic solvent-release sealants are: (1) they often require heating in the cartridge when applied at lower than room temperatures because their viscosity may become too thick to allow them to be easily applied and (2) they may emit acrylic monomer, which is somewhat odiferous and may be toxic in enclosed areas [6].

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Block Copolymer Sealant

Elastomeric block copolymer sealants, usually based on either styrene, styrene-butadiene, or isoprene, are another class of solvent-release sealants. These polymers exhibit excellent resistance to ultraviolet light, are effective as clear sealants, generally adhere to a wide variety of substrates, and are readily paintable. The sealants can be formulated to move about $\pm 12\frac{1}{2}$ %.

Polyurethane Sealants

Polyurethane sealants are available as either single or multi-component products. The one-component sealant is derived from an in situ reaction of an isocyanate with a hydroxyl component. These components cure by the reaction of the isocyanate (NCO) with atmospheric moisture, forming a polyurea. The sealants contain fillers, thixotropes, additives, and adhesion promoters.

Two-component polyurethane sealants are usually based on an isocyanate-terminated polyether reacted with a hydroxyl-terminated polymer. As with other sealants, two-component polyurethane sealants are combined with fillers, adhesion promoters, and other additives and stabilizers.

Polyurethane sealants exhibit good movement capabilities, easily exhibiting ±25 % movement. They generally adhere well to a variety of surfaces and are widely used in commercial applications, especially where abrasion resistance, i.e., traffic applications, is a prerequisite [7].

Polysulfide Sealants

Polysulfide sealants are sold as both one-component and two-component materials. Two-component sealants are formulated with polysulfide polymers, hiding and color pigments, clays, and mineral thixotropes. The second, or reactive component, consists of a curing agent (e.g., lead peroxide), adhesion promoters, fillers, and stabilizers. Both components are mixed just prior to use [8].

The one-component polysulfide sealants are formulated with ingredients similar to the two-component material except that the cure chemistry is different. One-component polysulfides cure by reaction with atmospheric oxygen and moisture and are generally relatively slow to attain full cure.

Polysulfide sealants can be formulated to move at ±25 % and are used on a wide variety of surfaces. Polysulfides are used widely in insulated glass applications [9].

Silicone Sealants

Silicone sealants are primarily used as one-component products usually referred to as RTV (room temperature vulcanizing) materials. They are polysiloxane prepolymers that react with atmospheric moisture and ultimately cure to form an elastomer. Silicone sealants are cured generally by one of three mechanisms, namely:

1. *Acetoxy cure*—A reaction between methyltriacetoxy silane with polydimethylsiloxane to form an acetoxy-terminated polymer "intermediate." This material is then reacted with atmospheric moisture in order to cure. Acetic acid is liberated during cure, and its odor can readily be noted.
2. *Neutral cure*—These sealants are the result of a reaction between polydimethyl siloxane with methyltrimethoxysilane to form the "intermediate." This "intermediate" then reacts with atmospheric moisture in order to cure. Alcohol is generally liberated during the cure process.
3. *Oxime cure*—In this cure mechanism, methyl triethylmethyl ketoxime silane is reacted with ethyl methyl ketoxime to form an "intermediate" that cures when reacted with atmospheric moisture. Cyclohexylamine, a heavy musty-odor material, is released during cure.

Silicone sealants can be formulated to have a movement capability of as much as 100 % and are used in many applications, especially where long-term durability is required. Silicone sealants are the primary sealants used in structural glazing [10].

Acrylic Latex Sealants

Acrylic latex sealants are essentially formulated from relatively high molecular weight acrylic polymers prepared by emulsion polymerization in an aqueous media and include fillers, surfactants, additives, and thixotropes. Acrylic latex sealants dry by evaporation to form easily applied, highly weatherable products that exhibit good adhesion.

These acrylic sealants can be formulated to move as much as ±25 %; however, they should not be applied at low temperatures and are not recommended for use in continuous damp or wet environments [11].

TEST PROCEDURES

The following is a brief summary of the test methods and procedures used to evaluate sealants. Where appropriate, reference is made to specific specifications and/or procedures where these tests are covered.

Extrusion Rate

This test is performed to measure the discharge rate of single and multi-component sealants (ASTM C603). Single-component sealants are extruded through a cartridge of known volume and predetermined orifice at 50 psi air pressure. The time to empty the cartridge is recorded. Multi-component systems are mixed and allowed to stand for 3 h before being extruded in order to develop information on their application properties after mixing.

Rheological Properties (Flow and Sag)

This test is employed to determine the horizontal or vertical flow properties of the sealant under conditions of extreme variations in temperature (ASTM C661). Stainless steel channels, open ended for testing vertical (non sag) sealants and close ended for testing horizontal (self leveling or pourable) sealants, are filled with the sealant and exposed at an elevated temperature (122°F, 50°C), and at a low temperature (40°F, 4.4°C). Sag (vertical displacement) is measured, and horizontal deformation is noted.

Hardness

This test is used to measure the indentation hardness of a cured sealant using a Shore A Durometer (ASTM C661). If a sealant is too hard, it may be indicative of future problems that can result in a loss of resiliency, thereby resulting in either cohesive breaks or adhesive loss.

Effects of Heat Aging After Cure

Exposure to the atmosphere may cause loss of volatile components after cure, resulting in shrinkage, hardening, or cracking, which may affect the durability of the sealant. This test can be used to predict premature failure (ASTM C792). Sealant specimens are cured for 7 days at standard conditions, then heat aged for 21 days at 158°F (70°C) and evaluated for volatility (weight loss), cracking, and hardness [12].

Tack-Free Time

This is the time required for the surface of a sealant to attain a tack-free state (ASTM C679). This time may be indicative of the time interval required for the sealant to resist damage from light surface contact, job-site or airborne dirt pickup, or impinging rainfall.

Staining of Porous Substrates

This test method is useful to determine possible staining by the sealant on porous substrates (ASTM C1248). The sealant is applied to standard-size joint specimens made of porous materials such as white marble or granite. The specimens are compressed and clamped and then stored for 28 days at various conditions including room temperature, elevated temperature, and ultraviolet-fluorescent weathering. Upon completion of the exposures, the specimens are evaluated for changes in surface appearance and depth of any stain.

Adhesion and Cohesion Under Cyclic Movement (Durability)

The primary intent of an elastomeric sealant is to fill joints in buildings and other structures and thereby render them impervious to the elements. These joints are considered active, meaning that they will expand and contract with temperature change and building movement.

This test method is designed to evaluate the ability of the sealant to withstand expansion and contraction with temperature change and not develop any loss of adhesion to the substrate or any cohesive cracks (ASTM C719). When adhesion loss to the substrate or cohesive cracks within the sealant develop, water can penetrate, thereby resulting in damage to the structure.

Joints are prepared using two similar substrates. The sealant is extruded between the joints (substrates), cured, and then immersed in water for seven days. The specimens are then hand flexed and evaluated for adhesion loss. If no adhesion loss is noted, the specimens are compressed and subjected to elevated temperature (158°F, 70°C) for 7 days to determine whether any heat set or deformation occurs. These test joints are then subjected to 10 cycles of extension at room temperature and examined for loss of adhesion or cohesive breaks in the extended state. If there is no loss of adhesion or cohesive break, the test joints are then cycled for 10 cycles of compression at elevated temperature (158°F, 70°C) and expansion at low temperature (–15°F, –26°C) to simulate joint movement during extreme temperature changes. (Buildings contract when cold, thereby opening up or expanding the joints. On the other hand, buildings expand when hot, thereby closing or compressing the joints.) Upon completion of this cycling, the specimens are examined for the presence of any adhesive bond loss or cohesive breaks.

Adhesion-in-Peel

This test is used to evaluate the adhesive characteristics of a sealant and its ability to maintain a bond to a substrate (ASTM C794). The sealant is applied to the substrate, cured, and immersed in water for 7 days. After the immersion period, the 180° peel strength of the sealant is measured and the amount of adhesive loss to the substrate is determined. An additional set of specimens is prepared on a glass substrate, exposed to UV radiation to simulate sunlight, and then evaluated for the effect of the actinic radiation on the interface of the sealant-to-glass bond by once again measuring peel strength and adhesion properties of the sealant.

Effects of Accelerated Weathering

This procedure is used to evaluate the effects of exposure to ultraviolet radiation and water spray to simulate weathering on the sealant (ASTM C793). After exposure, the sealant is evaluated for surface cracking. After 24 h cold exposure specimens are then bent over a 0.5 in. (1.27 cm) diameter rod under cold (–15°F, –26°C) temperature to evaluate low-temperature flexibility and brittleness.

The following section lists specifications and standards for sealants, as well as their sources.

SEALANT SPECIFICATIONS

Federal Specifications

TT-S-00227E	Sealing Compound Elastomeric Type, Multicomponent (For Caulking, Sealing, and Glazing Building and Other Structures)
TT-S-00230C	Sealing Compound Elastomeric Type, Single Component (For Caulking, Sealing and Glazing Building and Other Structures)
TT-S-01543A	Sealing Compound, Silicone Rubber Base (For Caulking, Sealing, and Glazing in Buildings and Other Structures)
TT-C-598B	Caulking Compound, Oil, and Resin Base Type (For Masonry and Other Structures)
TT-S-001657	Sealing Compound, Single Component-Butyl Rubber Based, Solvent Release Type (For Buildings and Other Types of Construction)

OTHER SEALANT STANDARDS

Insulating Glass

ASTM E774	Standard Specification for the Classification of the Durability Sealed Insulating Glass Units.

Highway/Bridges

SS-S-200E	Sealing Compounds, Two Component, Elastomeric, Polymer Type, Jet Fuel Resistant, Cold Applied.

(American Association of State Highway and Transportation Officials [AASHTO]).

LIST OF ASTM STANDARDS

C509	Standard Specification for Elastomeric Cellular Preformed Gasket and Sealing Material
C510	Standard Test Method for Staining and Color Change of Single- or Multi-Component Joint Sealants
C542	Standard Specification for Lock-Strip Gaskets
C603	Standard Test Method for Extrusion Rate and Application Life of Elastomeric Sealants
C639	Standard Test Method for Rheological (Flow) Properties of Elastomeric Sealants
C661	Standard Test Method for Indentation Hardness of Elastomeric-Type Sealants by Means of a Durometer
C679	Standard Test Method for Tack-Free Time of Elastomeric Sealants
C681	Standard Test Method for Volatility of Oil- and Resin-Based, Knife-Grade, Channel Glazing Compounds
C711	Standard Test Method for Low-Temperature Flexibility and Tenacity of One-Part, Elastomeric, Solvent-Release Type Sealants
C712	Standard Test Method for Bubbling of One-Part, Elastomeric Solvent-Release Type Sealants
C716	Standard Specification for Installing Lock Strip Gaskets and Infill Glazing Materials
C717	Standard Terminology of Building Seals and Sealants
C719	Standard Test Method for Adhesion and Cohesion of Elastomeric Joint Sealants Under Cyclic Movement (Hockman Cycle)
C731	Standard Test Method for Extrudability, After Package Aging, of Latex Sealants
C732	Standard Test Method for Aging Effects of Artificial Weathering on Latex Sealants
C734	Standard Test Method for Low-Temperature Flexibility of Latex Sealants After Artificial Weathering
C736	Standard Test Method for Extension-Recovery and Adhesion of Latex Sealants
C765	Standard Test Method for Low-Temperature Flexibility of Preformed Tape Sealants
C771	Standard Test Method for Weight Loss After Heat Aging of Preformed Sealing Tapes
C772	Standard Test Method for Oil Migration or Plasticizer Bleed-Out of Preformed Tape Sealants
C782	Standard Test Method for Softness of Preformed Tape Sealants
C792	Standard Test Method for Effects of Heat Aging of Weight Loss, Cracking, and Chalking of Elastomeric Sealants
C793	Standard Test Method for Effects of Laboratory Accelerated Weathering on Elastomeric Joint Sealants
C794	Standard Test Method for Adhesion-in-Peel of Elastomeric Joint Sealants
C834	Standard Specification for Latex Sealants
C864	Standard Specification for Dense Elastomeric Compression Seal Gaskets, Setting Blocks and Spacers
C879	Standard Test Methods for Release Papers Used with Preformed Tape Sealants
C907	Standard Test Method for Tensile Adhesive Strength of Preformed Tape Sealants by Disk Method
C908	Standard Test Method for Yield Strength of Performed Tape Sealants
C910	Standard Test Method for Bond and Cohesion of One-Part Elastomeric Solvent Release-Type Sealants
C919	Standard Practice for Use of Sealants in Acoustical Applications
C920	Standard Specification for Elastomeric Joint Sealants
C961	Standard Test Method for Lap Shear Strength of Sealants
C963	Standard Specifications for Packing, Identification, Shipment and Storage of Lock-Strip Gaskets
C964	Standard Guide for Lock-Strip Gasket Glazing
C972	Standard Test Method for Compression-Recovery of Tape Sealant
C1016	Standard Test Method for Determination of Water Absorption by Sealant Backing (Joint Filler) Material
C1021	Standard Practice for Laboratories Engaged in Testing of Building Sealants
C1083	Standard Test Method for Water Absorption of Cellular Elastomeric Gaskets and Sealing Materials
C1087	Standard Test Method for Determining Compatibility of Liquid-Applied Sealants with Accessories Used in Structural Glazing Systems
C1115	Standard Specification for Dense Elastomeric Silicone Rubber Gaskets and Accessories
C1135	Standard Test Method for Determining Tensile Adhesion Properties of Structural Sealants
C1166	Standard Test Method for Flame Propogation of Dense and Cellular Elastomeric Gaskets and Accessories
C1183	Standard Test Method for Extrusion Rate of Elastomeric Sealants
C1184	Standard Specification for Structural Silicone Sealants
C1193	Standard Guide for Use of Joint Sealants
C1216	Standard Test Method for Adhesion and Cohesion of One-Part Elastomeric Solvent Release Sealants
C1241	Standard Test Method for Volume Shrinkage of Latex Sealants During Cure
C1246	Standard Test Method for Effects of Heat Aging on Weight Loss, Cracking, and Chalking of Elastomeric Sealants after Cure
C1247	Standard Test Method for Durability of Sealants Exposed to Continuous Immersion in Liquids
C1248	Standard Test Method for Staining of Porous Substrates by Joint Sealants
C1249	Standard Guide for Secondary Seal for Sealed Insulating Glass Units for Structural Sealant Glazing Applications
C1253	Standard Test Method for Determining the Outgassing Potential of Sealant Backing

C1257	Standard Test Method for Accelerated Weathering of Solvent-Release Type Sealants
C1265	Standard Test Method for Determining Tensile Properties of an Insulating Glass Edge Seal for Structural Glazing Applications
C1266	Standard Test Method for Flow Characteristics of Preformed Tape Sealants
C1281	Standard Test Method for Preformed Tape Sealants for Glazing Applications
C1294	Standard Specification for Compatibility of Insulating Glass Edge Sealants with Liquid-Applied Glazing Materials
C1299	Standard Guide for Use in Selection of Liquid-Applied Sealants
C1311	Standard Specification for Solvent Release Sealants
C1330	Standard Specification for Cylindrical Sealant Backing for Use with Cold Liquid Applied Sealants
C1367	Standard Test Method for Dead Load Resistance of a Sealant in Elevated Temperatures
C1369	Standard Specification for Secondary Edge Sealants for Structurally Glazed Insulating Glass Units
C1375	Standard Guide for Substrates Used in Testing Building Seals and Sealants
C1382	Standard Test Method for Determining Tensile Adhesion Properties of Sealants When Used in Exterior Insulation and Finish Systems (EIFS) Joints
C1392	Standard Guide for Evaluation Failure of Structural Sealant Glazing
C1394	Standard Guide for In-Situ Structural Silicone Glazing Evaluation
C1401	Standard Guide for Structural Sealant Glazing
C1442	Standard Practice for Conducting Tests on Sealants Using Artificial Weathering Apparatus
C1472	Standard Guide for Calculating Movement and Other Effects When Establishing Sealant Joint Width
C1481	Standard Guide for Use of Joint Sealants with Exterior Insulation and Finish Systems (EIFS)
C1487	Standard Guide for Remedying Structural Silicone Glazing
C1501	Standard Test Method for Color Stability of Building Construction Sealants as Determined by Laboratory Accelerated Weathering Procedures
C1518	Standard Specification for Precured Elastomeric Silicone Joint Sealants
C1519	Standard Test Method for Evaluating Durability of Building Construction Sealants by Laboratory Accelerated Weathering Procedures
C1520	Standard Guide for Paintability of Latex Sealants
C1521	Standard Practice for Evaluating Adhesion of Installed Weatherproofing Sealant Joints
C1523	Standard Test Method for Determining Modulus, Tear and Adhesion Properties of Precured Elastomeric Joint Sealants
C1536	Standard Test Method for Measuring the Yield for Aerosol Foam Sealants
C1564	Standard Guide for Use of Silicone Sealants for Protective Glazing Systems
C1589	Standard Practice for Outdoor Weathering of Construction Seals and Sealants
C1620	Standard Specification for Aerosol Polyurethane and Aerosol Latex Foam Sealants
C1635	Standard Test Method to Evaluate Adhesion/Cohesion Properties of a Sealant at Fixed Extension
C1642	Standard Practice for Determining Air Leakage Rates of Aerosol Foam Sealants and Other Construction Joint Fill and Insulation Materials
C1643	Standard Test Method for Measuring the Post Dispensing Volumetric Expansion of Aerosol Foam Sealants
C1681	Standard Test Method for Evaluating the Tear Resistance of a Sealant Under Constant Strain
C1737	Standard Guide for Evaluating Temperature Effects to Aerosol Foam Sealants During and After Dispensing
D2202	Standard Test Method for Slump of Sealants
D2203	Standard Test Method for Staining from Sealants
D2377	Standard Test Method for Tack-Free Time of Caulking Compounds and Sealants
D2452	Standard Test Method for Extrudability of Oil- and Resin-Base Caulking Compounds
D2453	Standard Test Method for Shrinkage and Tenacity of Oil- and Resin-Base Caulking Compounds
E2203	Standard Specification for Dense Thermoplastic Elastomers Used for Compression Seals, Gaskets, Setting Blocks, Spacers and Accessories

CANADIAN STANDARDS

19-GP 5M Sealing Compound, One Component, Acrylic Base, Solvent Curing

CAN/GSB-19.13-M87 Sealing Compound, One-Component, Elastomeric, Chemical Curing

19-GP-14M Sealing Compound, One Component, Butyl-Polyisobutylene Polymer Base, Solvent Curing

CAN/CGSB-19.17-M90 One-Component Acrylic Emulsion Base Sealing Compound

CAN/CGSB-19.24-M90 Multicomponent Chemical-Curing Sealing Compound

AAMA STANDARDS

800-05

Voluntary Specifications and Test Methods for Sealants

–Back Bedding Compounds
–Back Bedding Mastic Tapes
–Glazing Tapes
–Narrow Joint Seam Sealers
–Exterior Perimeter Sealing Compounds
–Non-Drying Sealants
–Expanded Cellular Glazing

INTERNATIONAL STANDARDS ORGANIZATION (ISO) STANDARDS

The following standards are under the jurisdiction of Subcommittee 8 on Jointing Products, Technical Committee 59-Building Construction:

ISO 6927	Building, Construction—Jointing Products—Sealants—Vocabulary
ISO 7389	Building Construction—Jointing Products Determination of Elastic Recovery
ISO 7390	Building Construction—Jointing Products Determination of Resistance to Flow
ISO 8339	Building Construction-Jointing Products—Sealants Determination of Tensile Properties
ISO 8340	Building Construction-Jointing Products—Sealants Determination of Tensile Properties at Maintained Extension
ISO 8394	Building Construction—Jointing Products Determination of Extrudability of One-Component Sealants
ISO 9046	Building Construction—Sealants Determination of Adhesion/Cohesion Properties at Constant Temperatures
ISO 9047	Building Construction—Jointing Products—Sealants Determination of Adhesion/Cohesion Properties at Variable Temperatures
ISO 9048	Building Construction—Jointing Products—Sealants Determination of Extrudability of Sealants Using Standardized Apparatus
ISO 10563	Building Construction—Sealants—Determination of Change in Mass and Volume
ISO 10590	Building Construction—Sealants—Determination of Adhesion/Cohesion Properties at Maintained Extension After Immersion in Water
ISO 10591	Building Construction—Sealants Determination of Adhesion/Cohesion Properties After Immersion in Water
ISO 11431	Building Construction—Sealants—Determination of Adhesion/Cohesion Properties After Exposure To Artificial Light Thru Glass
ISO 11432	Building Construction—Sealants—Determination of Resistance to Compression
ISO 11600	Building Construction—Sealants—Classification and Requirements
ISO 11368	Building Construction—Sealants—Determination of Resistance to Prolonged Exposure to Water
ISO 13640	Building Construction—Jointing Products—Specifications For Test Substrates
ISO 16938-1	Building Construction—Jointing Products—Sealants—Determination of Staining of Porous Substrates—Part 1: Test With Compression
ISO 16938-2	Building Construction—Jointing Products—Sealants Determination of Staining of Porous Substrates—Part 2: Test Without Compression

SOURCES OF SPECIFICATIONS

ASTM Standards

ASTM International
100 Barr-Harbor Drive
PO Box C700
West Conshokocken, PA 19428-2959
(610) 832-9500

AASHTO Specifications

The American Association of State Highway
And Transportation Officials
444 North Capitol Street, NW, Suite 225
Washington, DC 20001
(202) 624-5800

Federal Specifications

Business Service Center
General Services Administration
7th and D Streets, SW
Washington, DC 20407
Contact regional offices

Military Specifications

Commanding Officer
U.S. Naval Supply Depot
5801 Tabor Avenue
Philadelphia, PA 19120
(215) 697-2000

ANSI Specifications

(Also International Standards Documents)
American National Standards Institute, Inc.
1430 Broadway
New York, NY 10018
(212) 354-3300

US Army Corps of Engineers

Chief Specification Section
Box 60
Vicksburg, MS 39180
(601) 633-2531

Canadian Standards

CGSB
Canadian General Standards Board
Gatineau
Canada K1A1G6
(819) 956-0425

American Architectural Manufacturers' Association (AAMA)

1827 Walden Office Square, Ste 550
Chaumberg, IL 60173
(847) 303-5859

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Pavement Marking Materials

James R. Swisher[1]

PAVEMENT MARKINGS GO RELATIVELY UNNOTICED by most people but affect almost everyone every day. They are used not only on city streets, highways, and interstates but also at airports, parking lots, and many commercial and industrial sites. A variety of materials are used for these applications. Some have specific uses, but all must adhere to the surface on which they are applied, show resistance to abrasion and weathering, and perform adequately over their expected life-times [1].

The following discussion will focus on the different types of marking materials being used and the testing of these materials for acceptability.

TYPES OF PAVEMENT MARKING MATERIALS

There are three general materials used for pavement markings. These include liquid coatings, thermoplastics, and tapes. All pavement markings fall into one of these general categories and cover a range of thickness from 8–150 mils. Glass beads or other reflective materials are used with each of these pavement marking materials to provide for night visibility.

Liquid Coatings

SOLVENT-BORNE MARKING

This was the standard material in use for traffic marking for decades. These one-component materials are usually alkyds or chlorinated rubbers that dry by the evaporation of their solvents, followed by oxidation of their binders. They are usually applied hot and under pressure with conventional spray equipment to achieve fast-drying markings. The advantages of using solvent-borne coatings are the vast body of knowledge and experience with these materials—they can be applied over a wide range of environmental conditions and have a low cost. The major disadvantages are the need for frequent applications, especially in high-traffic areas, the release of large quantities of solvent to the atmosphere during drying, and the need for solvent to clean equipment. These solvents contribute to air pollution and become hazardous waste when used to clean equipment.

WATER-BORNE MARKING

Water-borne markings are composed of high molecular weight acrylics and styrene-acrylic latex binders that allow them to be successfully applied on concrete and asphalt surfaces and over several other older markings [2]. Water-borne materials are also one component and must be applied under more stringent environmental conditions than solvent-borne materials. For example, low air and surface temperatures and high relative humidity, lengthen the film formation and dry time of the coating. In addition, due to their corrosive nature, water-borne materials should be handled in stainless steel equipment. However, even with these application requirements, the reduction in solvent emission and associated hazardous waste has enabled these materials to be the choice of many pavement marking entities.

These materials are used in a variety of wet thicknesses from 15 mils for standard lines to 30 mils for "High Build" lines depending on their chemical compositions.

EPOXY

This is a two-component, very durable, high-quality pavement marking material. The two components (pigmented resin and hardener) are stored separately and mixed at the time of application. A variety of cure times can be achieved through formulation adjustments. Close attention must be paid to the mix ratio of the components to obtain optimum performance and durability. Due to their durability, epoxies are used in higher traffic areas where repeated application of coatings would be disruptive to traffic. One disadvantage of epoxies is the loss of color retention due to degradation from ultraviolet (UV) sunlight exposure.

POLYESTER

Polyester is a two-component system used mainly on Portland cement concrete surfaces since proper adhesion is a concern on asphalt concrete surfaces. This coating is a durable, high-quality material that has a useful life of three years or more. Polyester is also very durable and is useful in high traffic areas. Adjusting mix ratios of resin and catalyst gives appropriate cure times. Some disadvantages include monomer emission, hazardous waste generated from solvents used in equipment clean up.

POLYUREA, URETHANES, METHYL METHACRYLATE

These two-component materials are composed of pigmented resins and a hardener. While similar to epoxies, these products are more durable and may contain color or UV stabilizers. These products are relatively new to the pavement marking industry and show good potential.

Thermoplastic

Thermoplastic (also known as hot melt) pavement markings are another durable, high-quality, single-component marking material. They are composed of a mixture of either maleic-modified glycerol resin esters or hydrocarbon resins with plasticizers, pigments, and glass beads. The material is normally melted between 400–425°F and is either sprayed

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or extruded on the road to form a durable material of thickness from 90–125 mils [3]. During the melting process constant stirring of the thermoplastic is very important for the following reasons:

1. To prevent localized burning.
2. To prevent potential color changes in the pigments.
3. To keep the intermixed glass beads suspended.

Thermoplastic may be applied to hydraulic concrete cement or asphalt concrete cement. Thermoplastic performs best when applied on asphalt concrete cement due to thermal bonding. If thermoplastic is being applied to hydraulic concrete cement a primer/sealer is normally required for proper adhesion and durability. Application thicknesses for new stripes are usually 90–125 mils, while re-stripe thicknesses are 30–60 mils.

Traditional yellow, lead chromate pigments are being replaced with organic yellow pigments that require careful formulation to ensure color continuity in both day and night-time environments.

Thermoplastic is also used as a preformed (pre-shaped) material for arrows, stop bars, pavement signs and text markings. The preformed markings are melted to the road surface using heating torches.

Pavement Marking Tapes

Pavement marking tapes can be used as a durable, long-life marking material or as a removable or temporary marking in construction areas. All tapes are composed of three layers: an adhesive layer, a backing material usually made of plastic or aluminum foil, and a pigment and glass bead layer. Application of these tapes will vary between manufacturers with primers being used for some tapes. While most tapes are installed with a weighted roller, some tapes are pressed (inlaid) into the hot asphalt. This inlay method produces a recessed tape that is less susceptible to abrasion from traffic and snowplow blades.

PERMANENT TAPES

These tapes can be divided into plastic-backed and foil-backed tapes. Plastic-backed tapes are 60–90 mils thick and are used as stop bars, crosswalks, arrows, long lines, and skip lines. These tapes may be flat or profiled. Foil-backed tapes are greater than 20 mils in thickness and are used in areas that are free of curves, turns, or stops.

TEMPORARY/REMOVABLE TAPE

This tape is used on construction sites or projects that require the tape to be removed or paved over. To facilitate removal, a plastic mesh or similar material may be added between the adhesive layer and the backing material of the tape. Film thicknesses are from 25–30 mils.

Glass Beads (Retroreflective Optics)

Glass beads are used with pavement markings to increase night visibility. Without the beads, most markings would be invisible at night. Fig. 1 gives an excellent explanation of how glass beads improve visibility. Glass beads must be round to work. Irregular or broken beads will not retroreflect light efficiently back to the driver. Beads vary in refractive index (RI) from 1.50 to 1.90. The 1.50 RI beads are most commonly used for highways, while the 1.90 RI beads are more efficient in light return and found on airport runways or in markings that are visible when wet.

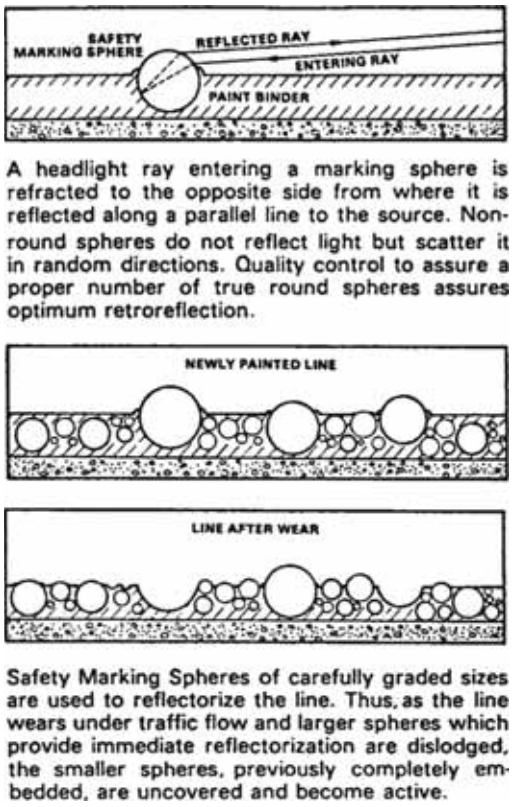

Fig. 1—How do glass spheres work? (from *Potters Safety Marking Spheres,* Potters Industries Inc.)

Glass beads also come in a variety of sizes with a specific size distribution usually being specified. Glass beads are applied to the binder material at the time of application to the road surface. This is usually done by a pressurized spray nozzle so that many of the beads (about 70 %) are initially buried in the marking material. The quantity of beads added to a line will vary with the marking material from 6-25 lb./gal. Some marking materials like thermoplastics have intermixed glass beads in addition to surface-applied beads. Other products—pavement marking tapes—have the glass beads pre-applied at the time of fabrication. Some pavement markings require the application of two separate bead sizes with two separate bead guns. This "double-drop" system is known to improve the visibility of the pavement marking. Other retroreflective optics such as ceramics and bead clusters are also being used to enhance night-time visibility in both dry and wet (rain) environments.

MATERIAL TESTING

Pavement marking materials are tested for conformance to specification in the laboratory and for performance in field evaluations.

Laboratory Testing

LIQUID TRAFFIC MARKINGS

Many of the tests performed on liquid marking materials are standard coating tests and are referenced where applicable.

Liquid Properties

1. **Skinning**—Paints that contain binders that dry by oxidation can form skins in a partially filled container.

These must be removed before use. This test can be performed in accordance with ASTM D154, Guide for Testing Varnishes and ASTM D2805, Standard Test Method for Hiding Power of Paints by Reflectometry, for Water-Bornes.

2. **Fineness of Dispersion**—Commonly called "fineness of grind," this test is not generally specified for traffic marking except in the case of some application equipment [4]. The test is performed in accordance with ASTM D1210, Test Method for Fineness of Dispersion of Pigment-Vehicle Systems by Hegman-Type Gage.
3. **Density or Weight/Gallon**—The density is determined for unbeaded paint by using ASTM D1475, Test Method for Density of Liquid Coatings, Inks, and Related Products.
4. **Consistency**—Determine the consistency using a paddle type viscometer in accordance with ASTM D562, Test Method for Consistency of Paints Measuring Kreb Unit Viscosity Using a Stormer-Type Viscometer.
5. **Stability**—Traffic paints should remain stable in the container for at least six months. Heat-age stability and freeze-thaw stability are often required and can be checked by heating and cooling a specimen through several cycles. Use ASTM D1849, Test Method for Package Stability of Paint, for heat-age stability and ASTM D2243, Test Method for Freeze-Thaw Resistance of Water-Borne Coatings, for freeze thaw stability of water-borne paints. Use ASTM D1309, Test Method for Setting Properties of Traffic Paints During Storage, for the accelerated test and ASTM D869, Test Method for Evaluating Degree of Setting of Paint, for aged paints.
6. **Chemical Analysis**—Identification and quantification of traffic paint components can be made by several means. Infrared spectroscopy can be used for resin identification. Use ASTM D2621, Test Method for Infrared Identification of Vehicle Solids from Solvent-Reducible Paints, to aid identification of solvent reducible resins. Oils and oil acids can be identified by gas chromatography. ASTM D2245, Test Method for Identification of Oils and Oil Acids in Solvent-Reducible Paints. White titanium pigment concentration can be determined using either the Jones Reduction method or the Aluminum Reduction method found in ASTM D1394, Test Methods for Chemical Analysis of White Titanium Pigments. Chrome yellow may be quantified using atomic absorption spectroscopy or by wet chemical methods using ASTM D126, Test Methods for Analysis of Yellow, Orange, and Green Pigments Containing Lead Chromate and Chromium Oxide Green. X-ray fluorescence (XRF) can be readily used to quantify lead chromate and titanium dioxide content. While expensive initially, XRF is generally much quicker than wet methods. Many epoxy traffic markings specify an epoxy content. Use ASTM D1652, Test Methods for Epoxy Content of Epoxy Resins, for this determination. The amine value is also specified on many epoxy traffic markings. Use ASTM D2074, Test Methods for Total, Primary, Secondary, and Tertiary Amine Values of Fatty Amines by Alternative Indicator Method for this determination.
7. **Pigment Content**—ASTM D2371, Test Method for Pigment Content of Solvent-Reducible Paints, is used for solvent reducible coatings and ASTM D3723, Test Method for Pigment Content of Water Emulsion Paints by Low-Temperature Ashing is used for water emulsion paints. ASTM D4451, Test Method for Pigment Content of Paint by Low Temperature Ashing (450°C), is a low-temperature ashing method useful for all coatings that do not contain organic pigments.
8. **Non-Volatile Content**—Sometimes referred to as "total solids," use ASTM D2369, Test Methods for Volatile Content of Coatings to determine the non-volatile content of the paint.
9. **Volatile Organic Content**—can be determined using ASTM D2369, Test Method for Volatile Content of Coatings
10. **Total Volume Solids**—can be determined using ASTM D2697, Test Method for Volume Nonvolatile Matter in Clear or Pigmented Coatings.
11. **Lead Content**—can be determined using ASTM D3335, Test Method for Low Concentrations of Lead, Cadmium, and Cobalt in Paint by Atomic Absorption Spectroscopy.

Appearance and Physical Properties

1. **No-Pick-Up Time**—A quality control test that is useful in the laboratory uses a steel cylinder fitted with two replaceable O-rings that is rolled down a ramp over a test stripe as shown in Fig. 2. This is a control test and shows little correlation with field applications. The no-pick-up time can be determined using ASTM D711, Test Method for No-Pick-Up Time of Traffic Paint.
2. **Dry-Through Dry Time**—This test is conducted at 50 % and 90 % relative humidity.
3. **Scrub Resistance**—This is a wet abrasion test often specified using ASTM D2486, Standard Test Methods for Scrub Resistance of Wall Paints.
4. **Flexibility**—This test evaluates the sample after being bent 180° over a 1/2 in. mandrel per ASTM D522, Standard Test Methods for Mandrel Bend Test of Attached Organic Coatings.
5. **Water Wash-Off**—This is a new test issued in 2008 as ASTM D7377, Standard Practice for Evaluating the Water Wash-Off Resistance of Traffic Paints Using a Water Faucet.
6. **Bleeding**—This test measures the amount of material that passes from an asphalt pavement through the traffic marking material. An arbitrary scale of photographic standards are used, where 10 shows no bleeding and

Fig. 2—ASTM D711 equipment.

2 shows considerable bleeding. Use ASTM D868, Test Method for Determination of Degree of Bleeding of Traffic Paint, contains the photographic standards.

7. **Hiding Power**—Hiding power (or dry opacity) is the measure of the ability of the coating to hide the substrate. Use ASTM D2805, Test Method for Hiding Power of Paints by Reflectometry.
8. **Color**—The color of traffic markings are usually compared to a specified standard. Color differences can be determined visually between the product and a standard. This comparison is fast and acceptable although numerical values are not obtained. The advantage of using color difference instruments are that they provide numerical values that can be compared to future measurements. Visual color comparison can be made in accordance with ASTM D1729, Practice for Visual Appraisal of Colors and Color Differences of Diffusely-Illuminated Opaque Materials.

   To determine the color in terms of tristimulus values or chromaticity coordinates, use ASTM E308, Practice for Computing the Colors of Objects by Using the CIE Systems. Color difference measurements are instrumentally obtained by following ASTM D2244, Practice for Calculation of Color Tolerances and Color Differences from Instrumentally Measured Color Coordinates. To determine the day and nighttime colors of pavement markings use ASTM D6628, Standard Specification for Color of Pavement Marking Materials.
9. **Reflectance and Retroreflectance**—Reflectance is the measure of light reflected from the surface of a material. Many pavement markings are visible during daytime illumination due to their reflectance of light or Luminous Reflectance Factor (Y). This reflectance of light makes the pavement marking material appear lighter than the pavement. To measure the Luminous Reflectance Factor (Y), the beadless sample is generally illuminated at a 45° angle and measured at a 0° angle using the standard CIE illuminant D65. Determine the Luminance Reflectance Factor in accordance with ASTM E1347, Standard Test Method for Color and Color-Difference Measurement by Tristimulus Colorimetry.

   Retroreflectance is a measure of light reflected back close to the light source. In practice, it simulates the car headlights reflecting off of the pavement marking back to the driver. In the laboratory, retroreflectance can be measured on a beaded sample in accordance with ASTM D4061, Test Method for Retroreflectance of Horizontal Coatings. Portable retroreflectometers are used to test pavement markings in field evaluations in accordance with ASTM E1710, Test Method for Measurement of Retroreflective Pavement Marking Materials with CEN-Prescribed Geometry Using a Portable Retroreflectometer. The Delta LTL-2000 portable retroreflectometer (used by several state Departments of Transportation) is shown in Fig. 3. It is designed to simulate the driver geometry and the visual distance of 30 meters. After the instrument is zeroed and calibrated, it is placed over the test line and the reading is obtained. Retroreflectivity can also be measured on the road with a mobile vehicle equipped with measurement instrumentation. Testing has indicated

Fig. 3—Delta, LTL-2000 portable retroreflectometer.

there is similarity between readings obtained with portable retroreflectometers and those obtained in the laboratory using ASTM Test Method D4061.

10. **Resistance to Wear**—This is a measure of a pavement markings' ability to withstand wear from traffic [5]. The test procedure involves dropping an abrasive sand on a dry test specimen until the material is worn away. The test is usually performed on an unbeaded material that is the appropriate thickness. A variation of the test is to drop a specific volume of sand on the specimen and calculate the amount of material lost by weight. The abrasion resistance can be determined by using ASTM D968, Test Method for Abrasion Resistance of Organic Coatings by Falling Abrasive.

THERMOPLASTIC

Thermoplastic material (including hot melt) is supplied in a powdered form or in block form. The material is prepared for testing by melting a sample at its application temperature under constant agitation. A guideline for testing thermoplastics can be found in the American Association of State Highway and Transportation Officials (AASHTO) Standard Test Method T-250. Two methods should be followed when sampling and preparing the thermoplastic: ASTM D7307, Standard Practice for Sampling of Thermoplastic Traffic Marking Materials and ASTM D7308, Standard Practice for Sample Preparation of Thermoplastic Traffic Marking Materials.

Gravimetric and Chemical Analysis—The amount of binder, glass beads, titanium dioxide, or lead chromate or other pigments can be determined in accordance with ASTM D4797, Test Methods for Chemical and Gravimetric Analysis of White and Yellow Thermoplastic Traffic Marking Containing Lead Chromate and Titanium Dioxide.

Appearance and Physical Characteristics

1. **Reflectance**—Measuring reflectance on thermoplastic is the same as for liquid coatings except a patty is used instead of a drawdown coating [6]. Use ASTM D4960, Test Method for Evaluation of Color for Thermoplastic Traffic Marking Materials, to determine reflectance.
2. **Softening Point**—Thermoplastic marking material does not have a distinct melting point but will become gradually softer as the temperature rises. The softening point is useful in predicting the tendency of the

material to flow at elevated temperature. To measure the softening point, melted thermoplastic is cast into brass rings and allowed to cool. The ring of thermoplastic, which is supporting a steel ball, is placed in a liquid bath and heated at a controlled rate. The softening point is reported as the temperature at which the steel ball falls a distance of 1 in. The softening point can be determined in accordance with ASTM D36, Test Method for Softening Point of Bitumen (Ring-and-Ball Apparatus).

3. **Specific Gravity**—The specific gravity of the thermoplastic is determined on the premelted sample. The material is ground so it will pass through a No. 30 sieve. The thermoplastic is tested in accordance with ASTM D153, Test Methods for Specific Gravity of Pigments, Method A.
4. **Bond Strength**—The bond strength of thermoplastic marking material is determined instrumentally using concrete bricks and steel blocks. A melted specimen is applied to a concrete brick with a drawdown blade. Two steel cubes are placed in the hot thermoplastic, and the excess thermoplastic is scraped away from the cubes. After trimming, the steel cubes are removed and the material is allowed to cool. A heated steel cube is bonded to the thermoplastic square with an epoxide adhesive and allowed to cure before the bond strength can be determined on a dynamometer. The bond strength is determined in accordance with ASTM D4796, Test Method for Bond Strength of Thermoplastic Traffic Marking Materials.
5. **Impact Resistance**—Impact resistance is determined on blocks of thermoplastic using an Izod-type impact apparatus. The procedure given in ASTM D256, Test Methods for Determining the IZOD Pendulum Impact Resistance of Plastics, is used except the specimen is not notched.
6. **Flowability**—This test is a measure of the thermoplastic marking materials' ability to flow. It is closely related to the viscosity of the material. The test involves melting a weighed sample in a pint can for 4 h with constant agitation. The can is suspended at a 45° angle, allowing material to flow over the edge until the flow ceases. The residue is weighed and the flowability is calculated. Test the material in accordance with AASHTO Test Method T-250.

PAVEMENT MARKING TAPE

1. **Film Thickness**—The adhesive layer is removed from the tape with a suitable solvent, and the thickness is measured with a micrometer. The glass beads are included in this measurement, which is in contrast to films from liquid coatings where the glass beads are not included.
2. **Reflectance and Retroreflectance**—Reflectance and retroreflectance are measured in the same manner as liquid coatings. For information, see No. 9 under "Appearance and Physical Properties," of Section B, "Material Testing."
3. **Glass Bead Adhesion**—A qualitative test to check glass bead adhesion is to firmly scratch the surface of the tape with a thumbnail. Acceptable adhesion for this test is noted when beads are not easily removed from the surface.
4. **Tensile Strength**—A 1 -in.-wide strip of tape is tested in accordance with ASTM D638, Test Method for Tensile Properties of Plastics, at a test rate of 0.25 in. /min.
5. **Adhesive Shear Strength**—The adhesive shear strength is a measure of the adhesive strength between the tape and the pavement. A 1 × 3 in. piece of carborundum extra coarse emery cloth is applied to the adhesive face of a 1 × 6 in. strip of tape with a 1 in. overlap. A pressure of 50 psi is applied to this overlapped area. The specimen is then tested in accordance with ASTM D638, at a speed of 0.50 in./min.
6. **Skid Resistance**—The skid resistance of tapes are measured on a British Pendulum Tester. This pendulum impact tester measures energy loss as a rubber slider travels over the specimen. The test can be used in the laboratory or in the field. The values are measured in British Pendulum Numbers. The test should be made in accordance with ASTM E303, Test Method for Measuring Surface Frictional Properties Using the British Pendulum Tester.

GLASS BEADS (RETROREFLECTIVE OPTICS)

1. **Gradation**—Gradation of glass beads is a measure of the sphere diameter. AASHTO specification M-247 gives three gradations of glass beads. Type 1, Type 2, and Type IM. Additional types (III, IV, and V) will be added as larger size glass bead sizes are specified. To perform the test, the beads are hand sieved through standard sieves starting with the largest opening and progressing through to the smallest opening sieve. The glass beads are removed from each sieve, weighed and the percent passing each sieve is calculated. The test is performed in accordance with ASTM D1214, Test Method for Sieve Analysis of Glass Spheres.
2. **Roundness**—The roundness of glass beads is another measurable indication of how well a pavement marking will perform as a retroreflective media. As mentioned earlier, only round spheres can reflect light back toward the light source. To test for roundness, the glass beads are mechanically separated by controlled vibration of a glass plate held at a fixed slope as shown in Fig. 4. The glass spheres that are round will roll down the slope while irregular-shaped particles will roll to the side or vibrate to the top. After testing the complete sample, the percent rounds can be calculated by weighing the amount of spheres that have rolled down

Fig. 4—Glass bead roundness apparatus.

Fig. 5—Paint truck.

the slope. The test is performed in accordance with ASTM D1155, Test Method for Roundness of Glass Spheres.

3. **Refractive Index**—To determine the refractive index of glass beads, the beads are treated as a pigment and are tested in that manner. Most pigments are tested using the liquid immersion method (Becke Line method or equivalent) at a temperature of 25°C.

Optical Particle Analyzers are now being used to determine bead size and gradation. While expensive, the optical particle analyzer allows for much quicker testing and a higher degree of precision and quantification of bead samples. ASTM is currently investigating the use of optical particle analyzers.

Note on other retroreflective optics testing: Specific test methods to characterize ceramic materials and bead clusters have not been promulgated (Fig. 5)

FIELD EVALUATION OF MARKING MATERIALS

Field evaluation of traffic marking materials is useful in determining the relative service life of these materials under actual road conditions using transverse lines (Fig. 6). Two evaluation methods are described below:

ASTM D713, Standard Practice for Conducting Road Service Tests on Fluid Traffic Marking Materials

This ASTM method is excellent for performing field evaluations. It is broken up into two parts—Application Process and Performance Criteria.

Fig. 6—Applied test stripes.

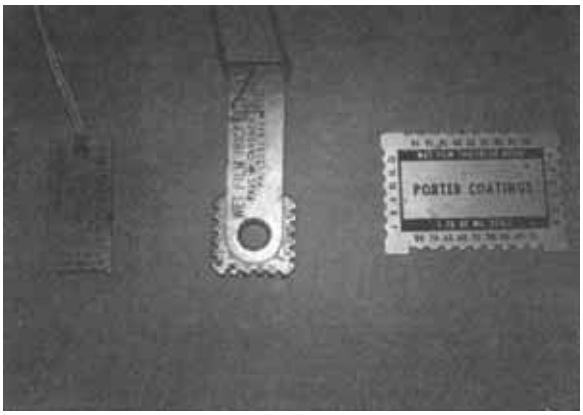

Fig. 7—Wet film thickness gages.

APPLICATION PROCESS

Location for Tests—Pavements should be selected where traffic is free flowing without grades, curves, intersections, or other phenomena that would cause excessive braking or turning. The area should have uniform wear, full exposure to sunlight throughout the day, and have good drainage. Interstate highways are usually excellent choices for testing.

Wet Film Thickness Measurement—Wet film thickness is measured with a wet film thickness gage consisting of a piece of metal with calibrated notches cut at various mil thicknesses as shown in Fig. 7. The gage is placed in a freshly applied line on a test plate and withdrawn. The notch with the highest reading that has paint on it is the wet film thickness. The wet film thickness is measured and adjusted before the test line is applied to the pavement.

Film thickness for thermoplastic is usually measured with calipers on a cooled test panel.

Glass Bead Measurement—There are two methods that can be used to quantify the weight of glass beads applied. The first involves weighing a freshly applied stripe without beads on a test panel and a test stripe with beads. The difference in weight is used to calculate the quantity of glass beads. This procedure is described in ASTM Method D713.

The second procedure involves collecting the beads from the bead gun during a preset time period. The weight of beads collected is determined and used to calculate the application rate for the beads.

Glass bead distribution is checked on a beaded test panel or the road surface. The beads should be evenly distributed across the width of the stripe, approximately 70 % of the beads should be buried in the material, and the remaining beads should be 50 % embedded in the material.

Application Procedures—Before applying any test lines, wet film thickness, line width, glass bead application rate, and glass bead distribution should meet the specification. Several test lines are usually applied. One line is for the Auto-No-Track Time determination (see next section), while the others are for additional evaluations.

PERFORMANCE CRITERIA

Field No-Track Time—The field no-track time is determined by driving a standard passenger car over a freshly applied line. This is usually done at 25–35 mph at the specified no-track time. Any deposit of paint on the roadway or exposure of the pavement under the test line is considered as not meeting the no-track requirement. No track times

range from 90 s to 2 min and are dependent upon air and road temperature, wind speed, sunlight, and humidity. The general correlation between the laboratory no-track time described in ASTM D711 and the field results is that a 7 min dry time by D711 will indicate a 90 second dry time in the field.

Appearance—This is the general condition of the test lines when viewed from a distance of 10 ft. It takes into consideration color, bleeding, darkening, fading, dirt collection, etc. This is done for each wheel track. A numerical value is usually assigned from 0 to 10 with 10 being the highest quality.

Durability—The durability of the material in each wheel track is rated from 1 to 10 (10 indicating no material has worn away). ASTM D913, Practice for Evaluating Degree of Traffic Paint Line Wear, can be used as a guideline.

Retroreflectivity—Retroreflectivity measurements are made in each wheel path using a portable retroreflectometer as previously described. Two ASTM methods should be followed:

ASTM E1710, Test Method for Measurement of Retroreflective Pavement Marking Materials with CEN-Prescribed Geometry Using a Portable Retroreflectometer.

Periodic Field Evaluation

Periodic inspections of the test stripes are made, usually monthly. At each inspection, daytime appearance, durability, color, and retroreflectance values are recorded.

Special Considerations for Pavement Marking Tapes

Application of pavement marking tapes will vary with the type of tape and manufacturer. Many tapes require primers or adhesives to be applied to the pavement before applying the tape. Most are rolled with a weighted roller after application to assure good contact between the adhesive and the pavement. The manufacturer's instructions for application should be followed closely.

In addition to the previously discussed evaluation criteria, removable tapes are also evaluated for their ability to be easily removed. About 90 days after application, a test line is removed by lifting a corner with a putty knife and pulling up the line. An acceptable tape should be removed in large sheets and not small pieces.

AASHTO'S NATIONAL TRANSPORTATION PRODUCT EVALUATION PROGRAM (NTPEP)

In an attempt to improve traffic marking materials throughout the country, the Federal Highway Administration (FHWA) sponsored a research project to evaluate the feasibility of Regional Test Centers for the testing of pavement marking materials in the lab as well as in the field. This study paved the way for the current pavement marking evaluation program, NTPEP. While this program is administered by the NTPEP coordinator, all lab and field testing is conducted by participating State DOT's and other research facilities.

The intent of the program is to provide testing results so users can make the determination of acceptance. Manufacturers submit pavement marking materials to the program for laboratory testing and 2 year field (actual road) testing. The field testing procedures are based on ASTM D713, Standard Practice for Conducting Road Service Tests on Fluid Traffic Marking Materials. As described previously, portable reflectometers are used in lieu of the night-time visibility evaluation. Field testing sites are chosen based upon their environmental conditions. The manufacturers submit their materials for laboratory testing and then apply their materials to concrete and asphalt cement road test sites. Laboratory tests of the materials are conducted in a designated DOT or contracted facility. Field tests of the applied materials are conducted initially and every 30 days thereafter for the first year and every 4 months for the second year. Laboratory and field test results are published periodically in the web-based AASHTO, NTPEP, Data Mine Program.

Laboratory Testing Includes the Following:

Solvent-Borne Paint
- Viscosity
- No Track Dry Time
- Total Solids
- Pigment Content
- Opacity
- Settling Properties
- IR Scan on Vehicle
- Density
- X-ray Diffraction

Water-Borne Paint
- Viscosity
- No Track Dry Time
- Total Solids
- Pigment Content
- Heat Stability
- Freeze-Thaw Stability
- Water Resistance
- Dry Opacity
- Density
- Degree of Settling
- X-ray Diffraction

Thermoplastic
- Specific Gravity
- Bond Strength
- Flowability
- Softening Point
- Low Temperature Stress Resistance
- Bead Content and Grading
- Impact Resistance
- Daylight Reflectance
- Yellowness Index

Preformed Thermoplastic
- Softening Point
- Low Temperature Stress Resistance
- Bead Content and Grading
- Impact Resistance
- Daylight Reflectance
- Yellowness Index
- Color
- Whiteness Index

Epoxy
- Drying Time
- Epoxide Number
- Adhesion to Concrete
- Hardness
- Abrasion Resistance
- Color
- Yellowness Index

Preformed Tapes
Tensile Strength
Ultimate Elongation
Retroreflectivity
Whiteness Index
Adhesion
Skid Resistance
Wear Index

Field Testing—Information and Tests:

Site Location, ADT, Weather Conditions
Pavement Marking Material Description
Application Information
Retroreflectivity
Durability
Appearance/Color
Snow Plow Damage
Removability

More detailed information can be obtained through the AASHTO/NTPEP website at www.aashto.org [7].

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Water-Repellent Coatings

Victoria Scarborough[1], and Thomas J. Sliva[2]

INTRODUCTION

WATER REPELLENTS ARE TRANSPARENT COATINGS formulated for the purpose of protecting porous substrates by preventing the penetration of liquid water. Unlike waterproofing materials and sealers, water repellents allow the passage of water vapor and generally are not designed to prevent the intrusion of liquid water under hydrostatic pressure.

Water is known to penetrate porous materials and contribute to their deterioration [1–3]. Examples include warping and swelling of wood as well as cracking and spalling of concrete and masonry caused by freeze/thaw cycles and dissolved salts. Further, chloride ions in de-icing salts can accelerate the corrosion of reinforcing steel in concrete. Water repellents are used to provide protection against such damage.

Water repellents provide protection by depositing hydrophobic compounds on the substrate, thus modifying the surface tension of the treated area. With some treatments, water may bead on the treated surface.

Compositions

Most water repellents are composed of 1 to 65 % monomeric or polymeric hydrophobic compounds suspended or dissolved in a carrier solvent. The type of compounds used to deliver the water repellency, e.g., acrylic, silconate, silane, siloxane, metallic stearate, etc., generally classifies the products that produce the repellency.

The carrier solvent is selected based on its compatibility with the hydrophobic compounds. Organic solvent carriers can be aliphatic, aromatic, or chlorinated compounds that can be derived from petroleum distillation. These carriers are considered volatile organic compounds (VOC) and, in recent years, have been subject to restricted use by state and federal air emission control regulatory agencies. In reality, solvent borne water repellents are restricted in many parts of the United States. Reformulation efforts have resulted in water borne repellents that are offered by most, if not all, manufacturers.

Classification

Water repellents also are classified as either film formers or penetrants. As film formers, the substrate pores are filled and there is a continuous film on the surface. Examples of film formers include acrylic polymers or silicone elastomers. In most cases, the film-forming portion of the water-repellent is a blend of several different hydrophobic compounds.

Water repellents that are penetrants line the pores of the substrate and generally do not visibly alter the surface of the substrate. Examples of such materials include solutions of metallic stearates or paraffinic waxes. Penetrants also include reactive chemicals such as silanes and siloxanes that covalently bond to the silicate minerals in cementitious substrates. Moisture and/or alkaline material present within the substrate may catalyze this reaction.

SCHEDULE OF TESTING

Most of the laboratory tests used for the evaluation of water repellents are outline in the following sections, Tests on Physical Properties, Tests for Water Repellency of Treated Wood, and Tests for Application on Treated Masonry. All of the listed tests described may not be required for each water repellent examined, and the selection of tests to be conducted may be guided by the type and recommended use of the treatment or as agreed on by buyer and seller. Other tests, as agreed on, may be added.

Tests on Physical Properties

Typical physical properties tested on a liquid water repellent prior to application include weight per gallon, viscosity, drying time, color, flash point, pH, storage stability, total solids, percent nonvolatile content, and VOC content. Many of these tests are outlined in Section 8 of this manual on "Physical Characteristics of Liquid Paints and Coatings" and are summarized in Table 1.

Tests for Water Repellency of Treated Wood

Dimensional Stability

The relative ability of water repellents to retard dimensional changes in wood submerged in water is measured using the "wood swellometer test" and is detailed in Federal Specification TT-W-572, Paragraph 3.7, "Water Repellency" [4]. This test compares the swelling of untreated control specimens with the swelling of treated specimens after each has been submerged in water for 30 min. Similar procedures are described in the National Woodwork Manufacturers Association Test Method NWMA-M-2-81 [5]; in ASTM D4446, "Standard Test Method for Determining the Anti-Swelling Effectiveness of Water-Repellent Formulations and Differential Swelling of Untreated Wood When Exposed to Liquid Water Environments"; in American Wood Preservers Association Standard M-18, "Standard Method of Testing Water Repellency of Pressure-Treated

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TABLE 1—Physical property tests involved in water-repellency testing

Property	ASTM	Title—Standard Test Method(s) for
Weight per gallon	D1475	Density of Liquid Coatings, Inks, and Related Products
Viscosity	D1200	Viscosity by Ford Viscosity Cup
Viscosity	D2196	Rheological Properties of Non-Newtonian Materials by Rotational (Brookfield Type) Viscometer
Drying Time	D1640	Drying, Curing, or Film Formation of Organic Coatings at Room Temperature
Color	D1544	Color of Transparent Liquids (Gardner Color Scale)
Flash Point	D56	Flash Point by Tag Closed Cup Tester
Storage Stability	D2243	Freeze-Thaw Resistance of Water-Borne Coatings
Storage Stability	D1849	Package Stability of Paint (Heat Aging)
% Nonvolatiles	D2369	Volatile Content of Coatings
% Nonvolatiles	D5095	Determination of the Nonvolatile Content in Silanes, Siloxanes, and Silane-Siloxane Blends Used in Masonry Water Repellent Treatments
VOC Content	D3960	Determining Volatile Organic Compound (VOC) Content of Paints and Related Coatings
Total Solids	D2834	Nonvolatile Matter (Total Solids) in Water-Emulsion Floor Polishes, Solvent-Based Floor Polishes, and Polymer- Emulsion Floor Polishes
pH	E70	pH of Aqueous Solutions with the Glass Electrode

Wood;" [6] and in ISO/DIN 4496, "Wood Test Method Determination of the Radial and Tangential Shrinkage" [7].

In Federal Specification TT-W-572b, water repellent effectiveness is measured on treated Ponderosa pine sapwood that is cut into 6 by 38 by 254 mm (0.25 by 1.5 by 10 in.) wafers. The wafers are cut from two adjacent specimens from each of five different boards. Specimen pairs of ten wafers are required to make a set for testing, one for the treated wafers and one for the untreated controls. Five wafers (one from each board) are immersed in the test water repellent for 30 s. The wafers are cured under standard conditions for four days or until constant weight is attained.

The wafers are inserted into a holding device fitted with a micrometer at one end that is known as a swellometer gage. One end of the wafer touches the base of the gauge and the other end just touches the plunger dial of the micrometer. The wafer apparatus is immersed in water for 30 min, and a dial reading is made before and after immersion.

The difference between the dial reading of the treated and the untreated control wafers is divided by the dial reading of the untreated control wafers and multiplied by 100. The average of these five readings represents the water-repellent effectiveness in percent of the product. Federal Specification TT-W-572b requires that a water repellent exhibit a minimum of 60 % water-repellent effectiveness. ASTM D4446 differs from the federal specification in that it requires a 3 min dipping time for water-based water repellents, and it specifies that all control untreated specimens must swell a minimum of 0.8 cm (0.32 in.).

Water Absorption

Water-repellent effectiveness can also be measured gravimetrically using ASTM D5401, "Standard Test Method for Evaluating Clear Water Repellent Coatings on Wood." Water absorption is tested by cutting matched 50 by 100 by 305 mm (2 by 4 by 12 in.) Ponderosa pine sapwood boards. Five boards are treated with the test water repellent by immersing for 30 s. Five boards serve as untreated controls. After curing, the boards to constant weight under standard conditions, they are weighed, immersed in water for 30 min, removed, and reweighed. The difference between the absorption of the treated and the untreated boards is divided by the absorption of the untreated boards and multiplied by 100. The average of the five treated boards represents the water repellent effectiveness in percent of the product.

Unlike with Federal Specification TT-W-572b, the boards used in this test can be exposed to exterior weathering cycles, returned to the conditioning room to attain constant weight, and water repellent efficiency can be determined over periodic exterior exposure intervals to determine long-term effectiveness.

Beading

Water repellents for application on wood substrates can be evaluated for their ability to form and hold a water bead [8]. A suitable test is described in ASTM D2921, "Standard Test Method for Qualitative Tests for the Presence of Water Repellents and Preservatives in Wood Products." After the wood has been treated and allowed to cure, several water droplets are placed on the wood with an eyedropper or other device. The time required for the droplets to lose their spherical shape and flatten out is recorded. The test can be used to compare water-beading ability before and after either artificial or natural weathering. The ability to bead water does not prevent water absorption as described in ASTM D5401 nor does it necessarily correlate with the ability to retard dimensional changes in wood as described in Federal Specification TT-W-572b.

Paintability

If wood is to be painted and a water repellent is used as an undercoat, it may be necessary to evaluate the effects of the

water repellent on the primer or topcoat. Evaluations can include checking the adhesion of the topcoat to the substrate, observing any changes in color to the topcoat, and measuring the drying characteristics of the topcoat. These evaluations may also be made after a periodic weathering of the water repellent-treated surface before the topcoat is applied.

Weathering

Substrates treated with water repellents can be subjected to artificial or outdoor weathering, e.g., using ASTM G151, "Practice for Exposing Nonmetallic in Accelerated Test Devices That Use Laboratory Light Sources;" ASTM G154, "Practice for Operating Fluorescent Light Apparatus for UV Exposure of Nonmetallic Materials;" ASTM G90, "Practice for Performing Accelerated Outdoor Weathering of Nonmetallic Materials Using Concentrated Natural Sunlight;" and ASTM D4141, "Standard Practice for Conducting Accelerated Outdoor Exposure Tests of Coatings." The substrate is evaluated for appearance properties such as cracking (as shown in the pictorial standards of ASTM D661, "Standard Test Method for Evaluating Degree of Cracking of Exterior Paints"), discoloration, mold, and mildew as well as dirt pickup. The substrate may also be evaluated for beading ability or water-repellent effectiveness.

Tests for Application on Treated Masonry

Water Repellency

Water repellency on masonry is determined following procedures described in Federal Specification SS-W-110c, Paragraph 4.3.2 [9], ASTM D6489, "Standard Test Method for Determining the Water Absorption of Hardened Concrete Treated with a Water Repellent Coating," and ASTM D6532, "Standard Test Method for Evaluation of the Effect of Clear Water Repellent Treatments on Water Absorption of Hydraulic Cement Mortar Specimens." Generally, cement or mortar specimens are prepared as described in the method. These are weighed, immersed in water, and the amount of weight gain recorded. The same specimens are dried to constant weight and then immersed in the test water repellent. Three specimens are tested for each of the water repellent under evaluation.

After the water repellent has cured, the specimens are immersed in water for 72 h. The percent water absorbed by the treated specimens is calculated based on the weight of the dry treated specimens.

Other test methods related to the examination of water repellency include ASTM C67, "Standard Test Methods for Sampling and Testing Brick and Structural Clay Tile;" ASTM C97, "Standard Test Methods for Absorption and Bulk Specific Gravity of Dimension Stone;" and ASTM C140, "Standard Test Methods for Sampling and Testing Concrete Masonry Units and Related Units."

Chemical Resistance

The resistance of a water repellent to the intrusion of various chemicals is determined following methods modified from procedures described in ASTM C267, "Standard Test Method for Chemical Resistance of Mortars, Grouts, and Monolithic Surfacings and Polymer Concretes;" ASTM C67, "Standard Methods for Sampling and Testing Brick and Structural Clay Tile;" Report 244 of the National Cooperative Highway Research Program, "Concrete Sealers for Protection of Bridge Structures [10];" and ASTM C672, "Standard Test Method for Scaling Resistance of Concrete Surfaces Exposed to Deicing Chemicals." Cubes of mortar are prepared and then treated, cured, and immersed in a specified chemical solution. Uncoated control cubes are included in the immersion. Typical chemicals used in this test include fuels and oils, various salt solutions, and acid and alkaline solutions.

Differences in weight gain or loss as a function of time are measured and plotted as compared to the untreated control. The rate of weight gain or loss over time during immersion may be more significant than the actual difference. By charting the weight gain or loss over time, the rate of deterioration may be determined.

Chloride ion penetration resistance is of particular interest in testing for the resistance of water repellent-treated masonry, since reinforcing steel in concrete will corrode and deteriorate after prolonged exposure to salt and/or salt solutions. A method for determining the resistance of concrete to chloride ion penetration is described in AASHTO Method T259 [11].

Freeze/Thaw Resistance

Freeze/thaw resistance is determined by means of ASTM D5860, "Standard Test Method for Evaluation of the Effect of Water Repellent Treatments on Freeze–Thaw Resistance of Hydraulic Cement Mortar Specimens." Treated specimens are subjected to cycles of freezing and thawing and then evaluated for weight loss and physical deterioration such as cracking and spalling after each series of cycling.

Moisture Vapor Transmission

Because the passage of moisture vapor through masonry may affect the long-term performance of a structure, water repellents applied to masonry structures may be required to demonstrate their ability to allow the passage of moisture vapor. Several methods are available to measure moisture vapor transmission of the applied film. These methods include ASTM D1653, "Standard Test Methods for Water Vapor Transmission of Organic Coating Films;" ASTM D6490, "Standard Test Method for Water Vapor Transmission of Non-Film Forming Treatments Used on Cementitious Panels;" and ASTM E96, "Standard Test Methods for Water Vapor Transmission of Materials." In a general sense, these methods measure the rate at which water vapor passes through a coating film. The specimen is sealed to the open mount of a cup or dish that contains desiccant. This assembly is then placed in a test chamber with a controlled atmosphere. The cup or dish is exposed to a specified relative humidity and periodic weightings are made to determine the rate of water vapor transmission through the film. With penetrants, the treatment is applied to a masonry substrate and testing is conducted on treated and untreated test specimens. The percent retention of water vapor transmission is reported. Another method is described in NBS Technical Note 883, Paragraph 2.2.2, "Moisture Vapor Transmission on Brick [12]," a method that measures the moisture vapor transmission of the treated brick rather than the film.

Efflorescence

Efflorescence is a usually white, undesirable, powdery deposit that appears on the surface of masonry and concrete products [13]. It is formed by salts dissolved in water

that is passing through the concrete and masonry products by capillary action. When the solution reaches a surface, the water evaporates and leaves the salt on the surface as efflorescence. Although usually white in appearance, it may have other colors that depend on the nature of the salt involved. Although harmless in itself, the deposit often detracts from the appearance of the substrate.

There are two types of efflorescence—the powdery type mentioned above that is easy to remove and a crystalline form that comes about when the deposits are repeatedly dissolved and dried out a number of times. In this cyclic process, the crystalline form of efflorescence is formed, and it is tightly adhered to the surface. It is more difficult to remove than the powdery deposit and removal may require special cleaners or acids. Factors such as low temperatures, ground water, humidity, rain, and other water sources such as sprinklers facilitate efflorescence formation.

Water repellents may be used to prevent the formation of efflorescence. The efficiency at preventing efflorescence can be measured using the method described in NBS Technical Note 883, Paragraph 2.2.2 [12]. ASTM C1400-1, "Standard Guide for Reduction of Efflorescence Potential in New Masonry Walls," ASTM D7072-04, "Standard Practice for Evaluating Accelerated Efflorescence of Latex Coatings," and ASTM C67, "Standard Test Methods for Sampling and Testing Brick and Structural Clay Tile" are useful when investigating this phenomenon.

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Part 14: Analysis of Paint and Paint Defects

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Analysis of Paint

Darlene Brezinski[1]

SAMPLING

THE IMPORTANCE OF APPROPRIATE SAMPLING FOR analytical work cannot be overemphasized. Unfortunately, this topic is often not given sufficient thought, and there is often not enough training on the subject. A clear understanding of the nature of the problem or the reason analysis is needed must be established prior to obtaining a sample. It is extremely important to know the compositional makeup of the bulk material from which the sample is being taken. Without this knowledge, improper sampling can very easily occur. The homogeneity or heterogeneity of the sample along with its stability is very important to consider. The composition of a sample may change once it is removed from its natural matrix or environment due to interactions with a container, ultraviolet light, or air, for example. One should also know in advance what level of precision is required of the analysis and what compositional information is required.

Development of a sampling plan is one of the most important steps in providing reliable samples and consequently accurate and reliable data. The types of samples usually encountered are as follows:

Representative Sample: A sample considered to be typical of the bulk material and whose composition can be used to characterize the bulk with respect to the parameter measured.

Systematic Sample: A sample taken according to a systematic plan with the objective of investigating systematic variability of the bulk. Systematic effects due to time or temperature are typical matters of concern.

Random Sample: A sample selected by a random process to eliminate questions of bias in selection and/or to provide a basis for statistical interpretation of measurement data.

Composite Sample: A sample composed of two or more increments that are combined to reduce the number of individual samples needed to average compositional variability [1].

There are basically three kinds of sampling plans that can be used in a measurement process. Intuitive sampling plans may be defined as those based on the judgment of the sampler. General knowledge of similar materials, past experience, and present information about the bulk material, ranging from knowledge to guesses, are used in devising such sampling plans. Because the samples are based on judgment, only judgmental conclusions can be drawn when considering the data. In the case of controversy, decisions on acceptance of conflicting conclusions may be based on the perceived relative expertise of those responsible for sampling [1].

Statistical sampling plans are those based on statistical sampling of the bulk materials and ordinarily can provide the basis for probable conclusions. Hypothesis testing can be involved, predictions can be made, and inferences can be drawn. Ordinarily, a relatively large number of samples will need to be measured if the significance of small apparent differences is of concern. The conclusions drawn from such samples would appear to be noncontroversial, but the validity of the statistical model used could be a matter of controversy [1].

Protocol sampling plans may be defined as those specified for decision purposes in a given situation. Regulations often specify the type, size, frequency, sampling period, and even location and time of sampling related to regulatory decisions. Not specifically following any part of the protocol could be reason for discrediting a sample. The protocol may be based on statistical or intuitive considerations but is indisputable once established [1].

When decisions are based on identifying relatively large differences, intuitive samples may be fully adequate. When relatively small differences are involved and the statistical significance is an issue, statistical sampling will be required [1].

General Sampling Techniques

It is obvious that the sample submitted for analysis must accurately reflect the bulk material from which the sample was taken. Personnel taking samples should be trained in proper protocol for obtaining samples from bulk material. Equally as important as training is the use of proper containers necessary for storing samples. Many types of containers can alter the integrity of the sample. A paint sample submitted in the original container is not necessarily a representative sample as frequently volatile components may have already been lost or the contents may have been adulterated. Assumptions regarding the integrity of the sample are extremely difficult to make, and good analysts need to constantly bear in mind the history of the sample itself.

Detailed procedures regarding sampling of all sorts of coatings would be impossible to write; however, ASTM Practice for Sampling Liquid Paints and Related Pigmented Coatings (D3925) and ASTM Practice for Sampling Industrial Chemicals (E300) should be examined for detailed recommendations.

All the precision in weighing, measuring, calculating, and so forth has absolutely no meaning if the sample is not

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a valid and representative sample. The sample taken for analysis must totally and accurately reflect the composition of the bulk material from which it was taken. If there is any doubt about the integrity of the sample *as a representative sample,* the analysis should not be conducted as the data has no meaning. This becomes extremely important when dealing with samples where the bulk is large and perhaps not always completely homogenous [1]. In the real world of sampling, it is often very difficult to even know if the sample was obtained properly and if it is representative. The analyst usually has no control over the sampling step itself. In these cases, it becomes important for the analyst to stress that the data are only representative of the sample that has been analyzed and not necessarily representative of the bulk. Rather serious management decisions can be falsely made if the decision is based on data that is not representative data.

Care should be taken to assure that all containers, agitators, and sampling apparatus are clean and that they can in no way contribute to contaminating the sample. Reusable syringes in particular can pose problems, particularly in trace analysis, if they are not cleaned extremely well. Contaminant materials will lead to erroneous test results as the contaminate will be assumed part of the sample. For pigmented coatings that are dispersions, finely divided pigment particles may settle upon standing. Consequently, very thorough agitation is necessary at every stage of the sampling and analysis procedure.

Airtight storage containers are necessary to prevent evaporation of sample material. Volatile solvents may also diffuse through the walls of plastic containers. The loss of volatiles subsequently introduces significant error in such tests as viscosity, weight per gallon, and nonvolatile content. If cap liners are used for samples, they must be made of a nonreactive material. It is also very important in all stages of sampling/analysis that the samples be kept at fairly constant and consistent temperatures. Extremes of temperatures may change the properties of some coatings.

Proper labeling of the sample cannot be stressed enough. Labeling should be done in accordance with prior established standard operating procedures (SOPs) for the laboratory. The more information available on the label, the less likely error will be introduced either in the handling of the sample or in the analysis. Formula composition, if known, can be an asset to the analyst in choosing the best analytical methods and save valuable and costly analytical time.

Laboratory Protocol

The analytical laboratory today must have SOPs. This is standard, acceptable practice today, and laboratories that have not implemented these procedures will find it more difficult to maintain credibility of the data with their clients. SOPs define clearly how each step of the laboratory operates. Clear SOPs are necessary for training, logging samples, calibration, quality assurance, receipt of samples, chain-of-custody, report formats, analytical methods, handling of hazardous materials, etc.

Whatever kind of sampling plan is developed, it should be written as a protocol containing procedures (SOPs) that must be followed. It should address the following:

- when, where, and how to collect samples
- sampling equipment, including its maintenance and calibration
- sample containers, including cleaning, addition of stabilizers, and storage
- criteria for acceptance and/or rejection of samples
- criteria for exclusion of foreign objects
- sample treatment procedures such as drying, mixing, and handling prior to measurements
- sub-sampling procedures
- sample record keeping such as labeling, recording, and auxiliary information
- chain of custody requirements [1]

Appropriate laboratory protocol has established SOPs in place for every facet of the operation. Sample control has to include not only the receipt and handling of the sample but the handling and storage of the data.

Implementation of a chain-of-custody plan for each sample is most critical to good operating practices in the analytical lab today. It provides traceability for the sample upon receipt and distribution of the sample for analysis. The purpose of chain-of-custody is to ensure control of the sample and corresponding data and that the data are verifiable. The flow of samples for analysis and the associated paperwork must be clear to everyone involved in the laboratory.

Analytical Quality Assurance

The validity of analytical data must be clearly established through the documentation of quality assurance practices. This is particularly important because often analytical determinations and the subsequent data may be used as evidence in a court of law. Standard operating procedures should be established and encompass the following: record keeping, sample homogeneity, calibrations, reference standards, calculations, laboratory housekeeping, the statistics of inter-laboratory studies, and practical quality control.

Laboratory accreditation is becoming increasingly important in today's environment to provide a level of confidence in the laboratories' capabilities, personnel, testing procedures, and equipment. It establishes integrity and reliability in the testing and the data. As regulatory requirements become more demanding, the nature of the analytical methodology has been changing to more sophisticated analyses and, along with these changes, there has been an increased emphasis on quality assurance and quality control. Successful laboratories have made major commitments to quality products and quality data. Therefore, the process of verification of laboratory procedures is becoming more important for providing precise and accurate data.

GENERAL TESTING

Before any tests are run on the coating and prior to separation, testing to establish some basic parameters or conformance properties should be run. Among these are flash point, density, water content, nonvolatile content by weight and/or volume, and pigment or ash content. Reference should be made to elsewhere in this manual for more information regarding determination of density, specific gravity, and so forth.

Flash Point

The flash point of a material is defined as the lowest temperature, corrected to a pressure of 760 mm Hg (101.3 kPa, 1013 mbar) at which application of an ignition source

causes the vapor of the specimen to ignite under specified conditions of test. Flash point is one of the properties used to classify liquids according to their flammability by governmental regulatory agencies. Several different flash point methods are available. The analyst must determine which one of these methods is appropriate for the sample to be analyzed and then follow the recommended ASTM procedures. Both Tag open cup and closed cup methods, Pensky-Martens closed cup, and Setaflash tester methods are commonly used in the coatings industry. [ASTM Test Method for Flash Point and Fire Points of Liquids by Tag Open-Cup Apparatus (D1310); ASTM Test Method for Flash Point by Tag Closed Tester (D56); ASTM Test Methods for Flash Point by Pensky-Martens Closed Cup Tester (D93); ASTM Test Methods for Flash Point of Liquids by Small Scale Closed-Cup Apparatus (D3278).] Open cup flash points are only required in the rare customer specification. Department of Transportation regulations specify closed-cup. Laboratories need to be certain of the shipping requirements and the appropriate methods prior to analysis of the sample.

Density

Density is weight per unit volume. It is a key property in the identification, characterization, and quality control of a wide range of paint materials. The density of water at various temperatures is used to calibrate the volume of the container. The weight of the paint liquid contents of the same container at the standard temperature is then determined and density of the contents calculated in terms of grams per milliliter, or pounds per gallon, at the specified temperature.

Density measurements in terms of weight per gallon are commonly used to check paint quality. If the density is not within specification, there is a good chance that there was a mischarge or other serious problem. This could indicate further chemical analysis is required to determine the nature of the problem. ASTM Test Method for Density of Liquid Coatings, Inks and Related Products (D1475) is suitable for the determination of density of paint and related products and components when in liquid form.

ASTM D1475 provides for the maximum accuracy required for hiding power determinations. Automatic equipment for measuring density is available from several manufacturers [see ASTM Test Method for Density, Relative Density and API Gravity of Liquids by Digital Density Meter (D4052)]. For higher precision if working with nonpigmented materials, ASTM Test Method for Specific Gravity of Drying Oils, Varnishes, Resins and Related Materials at 25/25°C (D1963) can be used to determine specific gravity and the corresponding density.

Water (Content) Determination

Control of water content is often important in controlling the performance of paint and paint ingredients and is certainly critical in determining and controlling the volatile organic compound (VOC) content. ASTM Test Method for Water in Paints and Paint Materials by Karl Fischer Method (D4017) is applicable to all paints and paint materials, including resins, monomers, and solvents, with the exception of aldehydes and certain active metals, metal oxides, and metal hydroxides. The Karl Fischer Method has been evaluated for pigmented products containing water in the 30 %–70 % range; however, it is believed that the method is also applicable for higher and lower concentrations. The method consists of dissolving the sample in pyridine, or other appropriate solvent, and titrating directly with standardized Karl Fischer reagent to an electrometric end point.

ASTM Test Method for Water Content of Coatings by Direct Injection into a Gas Chromatograph (D3792) is also used for determining water in many latex systems. That method has not been evaluated for other water reducible paints, but is believed to be applicable. The established working range of the method is from 40 % to 55 % water, but there is no reason to believe that it will not work outside of this range. In this method, a suitable aliquot of whole paint is internally standardized, diluted, and injected into a gas chromatograph. By choosing the correct column and conditions, water can be separated from the other volatile components.

Water content in pigments may be determined in accordance with ASTM Test Methods for Common Properties of Certain Pigments (D1208).

SEPARATION OF SOLIDS AND VOLATILE CONTENT

Separation of solids is routinely performed for determining the percent composition of the coating, i.e., % NVMs (nonvolatile materials), % pigment, and % solvent. In many cases, however, separation of these materials is also necessary for further identification purposes, to check formulation related problems, and for general problem solving.

Nonvolatile Content by Weight

Nonvolatile measurement is one of the most widely used tests for coatings characterization. It determines the quantity of coating remaining after all solvents or water and other volatiles have been removed. When used in conjunction with volume nonvolatile content, the area covered by a gallon of paint or coating can be determined.

It has become customary to determine the amount of NVM, or solids, in a coating and that information is useful to producers, users, and to environmental and health and safety interests in comparing the coverage of competing products and in estimating the volatile organic content. Standard practice has been to accurately weigh by difference from a syringe a small sample of paint into a tared aluminum foil, flat-bottomed dish. The dish is heated for a specified temperature and time (usually to constant weight at 105°C), cooled in a desiccator, and weighed. From this weight and the original weight of the empty dish the weight of NVM may be calculated. The procedure is not as simple as it first appears, and different types of coatings require different methods. ASTM Guide for Determining Volatile and Nonvolatile Content of Paint and Related Coatings (D2832) is intended to aid in the selection of the proper standard for determining the volatile and nonvolatile content of coatings. This guide should be examined carefully and followed prior to determining nonvolatile content.

Perhaps the most commonly used method is ASTM Test Methods for Volatile Content of Coatings (D2369). This method is the procedure of choice for determining the volatiles in coatings for the purpose of calculating the volatile organic content (VOC) in coatings. Correspondingly,

the nonvolatile (NVM, or solids) is used to determine the weight percent solids content.

Another commonly used procedure is ASTM Test Method for Nonvolatile Content of Latexes (D4758). This method should not be used for determining VOC of formulated coatings; however, it is appropriate for obtaining the weight percent of a commercial latex product that, when incorporated into a coating product, constitutes the binder content of the coating.

The nonvolatile content of resin solutions is useful to coatings producers and users for the determination of the total solids available for film formation and for the estimation of VOC. ASTM Test Methods for Nonvolatile Content of Resin Solutions (D1259) provides the detailed procedures.

Nonvolatile Content by Volume

A measure of the volume of dry coating obtainable from a given volume of liquid coating is considered by some to be a better measure of value than percentage of nonvolatile matter by weight. ASTM Test Method for Volume Nonvolatile Matter in Clear or Pigmented Coatings (D2697) is applicable to the determination of the volume of nonvolatile matter (volume solids) of a variety of coatings. This method is intended to provide a measure of the volume of dry coating obtainable from a given volume of liquid coating. This value is useful for comparing the coverage (square feet of surface covered at a specified dry film thickness per unit volume) obtainable with different coating products.

The value obtained may not be equal to that predicted from simple additivity of the weights and volumes of the raw materials in a formulation. One reason is that the volume occupied by a solution of resin in solvent may be the same, greater, or less than the total volume of the separate ingredients: such contraction or expansion in resin solutions is governed by a number of factors, one of which is the extent and direction of spread between solubility parameters of the resin and solvent. The spatial configuration of the pigment particles and the degree to which the spaces between the pigment particles are filled with the binder also affect the volume of a dry coating formulation. Above the critical pigment volume concentration, the apparent volume of the dry film is significantly greater than theoretical due to the increase in unfilled voids between pigment particles. The use of volume nonvolatile matter values in such instances should be carefully considered as the increased volume is largely due to air trapped in these voids.

In methods, the weight and volume of a stainless steel disk are determined. After the disk is coated with the material being tested, the weight and volume of the disk plus dried coating is determined by weighing in air and then by weighing in a liquid of known density, the volume being equal to the quotient of the weight loss of the coated disk (due to the Archimedes buoyancy effect) divided by the density of the liquid displaced. The liquid may be water or an organic liquid, such as low solvency mineral spirits, depending on the nature of the coating being tested. From the measured weights and volumes of the disk before and after coating, the weight and volume of the dried coating film are calculated. Based on the density of the liquid coating and the weight percent nonvolatile matter, the volume of the liquid coating deposited on the coated disk is calculated. The volume of the dried coating divided by the volume of liquid coating, multiplied by 100, provides the volume percent nonvolatile matter in the total liquid coating.

Pigment Content

For most water emulsion paint systems, the pigment content (often called ash) is most often determined following the determination of the weight percent nonvolatiles. ASTM Test Method for Pigment Content of Water-Emulsion Paints by Low Temperature Ashing (D3723) covers a procedure for the pigment content determination. After weighing the dishes for NVM, the dishes are transferred to a muffle furnace and heated at a low ashing temperature of about 450°C for 1 h. Of course the analyst must keep in mind that the method is only applicable to pigments that do not decompose or lose weight at temperatures below 500°C. This would include most metal oxides, silicates, and a majority of anhydrous inorganic salts.

A note of caution is advised, as this may be too low an ashing temperature for some paints. Each system is different, and one cannot assume that this temperature will be sufficient.

To separate pigment from solvent-based paints, ASTM Test Method for Determination of the Pigment Content of Solvent-Reducible Paints by High-Speed Centrifuging (D2698) should be followed. Also ASTM Test Method for Pigment Content of Solvent-Reducible Paints (D2371) provides a centrifugation method for separation of pigment from the vehicle.

Vehicle Separation

Separation of the vehicle from the pigment in solvent-reducible paints is desirable and often required in order to further characterize paint vehicles by chemical or instrumental methods of analysis. ASTM Standard Practice for Separation of Vehicle from Solvent-Reducible Paints (D2372) covers the procedure for separating the vehicle from the pigment by centrifugation.

Solvent Separation

If it is desirable to separate the solvents from the vehicle, ASTM Standard Practice for Vacuum Distillation of Solvents From Solvent-Reducible Paints for Analysis (D3272) details a vacuum distillation procedure. For analysis purposes, however, most people prefer direct injection of paint sample into the gas chromatograph for solvent identification.

Sample Preparation

For many types of analysis, the previously discussed separation techniques are sufficient. Many chemical analyses require further sample treatment in the form of either extractions or digestions. The standard analytical techniques are always applicable in these cases. Extractions are often more attractive techniques for separating inorganic species than precipitation methods, which are more time consuming. Of course the extent to which inorganic and organic species distribute themselves between two immiscible solvents differs greatly depending on the species and the extraction solvents.

Decomposition of the organic material for further analysis requires rather drastic sample treatment and typically involves oxidation techniques. Wet ashing makes use of liquid oxidizing agents such as sulfuric, nitric, and

perchloric acids. Dry ashing usually implies ignition of the organic compound in air or in a stream of oxygen.

Sample dissolution is one of the most common operations in analytical chemistry. Because most quantitative techniques require that samples be introduced in liquid form, thousands of sample dissolutions are performed every working day in analytical laboratories. Despite the importance and widespread applicability of sample dissolution, most conventional digestion procedures are tediously labor-intensive, and a number of them, such as perchloric acid digestion, are potentially hazardous to laboratory personnel [2].

New microwave dissolution techniques make it possible to speed the preparation of solid samples by combining the rapid heating ability of microwave energy with the advantages inherent in the use of sealed digestion vessels. Researchers have found microwave dissolution to be faster, more controlled, more elegant, and more amenable to automation than conventional open-beaker or closed-vessel techniques [2].

The advantages of microwave dissolution include faster reaction rates that result from the high temperatures and pressures attained inside the sealed containers. These containers are made of polymers that will not contaminate or adsorb the sample and do not absorb microwave energy. The caps are designed to safely vent container gas in case of excess internal pressure buildup [2].

The use of closed vessels also makes it possible to eliminate uncontrolled trace element losses of volatile molecular species that are present in a sample or that are formed in the course of dissolution. Such losses can easily destroy the integrity of a measurement. In the field of elemental analysis, significant percentages of elements such as arsenic, boron, chromium, mercury, antimony, selenium, and tin are lost at relatively mild temperatures with some open-vessel acid dissolution procedures. Several of these elements have already been shown to be retained when closed vessels are used [2].

Another advantage of closed vessels is a decrease in blank values as compared to open-beaker work because contamination from the laboratory environment is lower and smaller quantities of reagents are used. The blank value incurred in sample preparation is an important parameter because it frequently determines the limit of detection [2].

Many laboratories, however, have abandoned closed-vessel microwave digestions because of vessel ruptures. Thus safety concerns must be of primary importance and analysts should consult closed vessel suppliers.

CHARACTERIZATION AND CHEMICAL ANALYSIS

Analytical instrumentation has advanced significantly in recent years primarily due to advancements in the field of nanotechnology. Analysts constantly need to be aware of current literature for the most appropriate method of analysis. It is strongly recommended that particular topics be searched on the Internet for relevant literature and state-of-the-art analytical techniques, methodology, and instrumentation.

Analytical Data

The reporting of analytical data is exceedingly important, and every effort must be taken to ensure that the data are sound, defensible, and meaningful. Most basic texts on analytical chemistry discuss the appropriate statistical methods used in dealing with data, standard deviation etc., as well as significant figures. An excellent text by Taylor [1] deals with all aspects of chemical measurements and should be examined thoroughly by all analysts. Also available is ASTM Procedure for Intralaboratory Quality Control Procedures and a Discussion on Reporting Low-level Data (D4210).

In the analytical laboratory, a method of measurement (procedure) is usually followed that specifies the equipment, reagents, sample handling, etc., and the instructions to be followed. The analyst who carries out the method is following what is called a measurement process. The most important attribute of a measurement process is whether it can be made to run in a state of "statistical control." Although repetition of measurement is subject to variability, the achievement of statistical control implies that the statistical properties of this variability are uniform over time, so that it becomes meaningful to use measurements over a limited time span to predict limits of variation for both those and future measurements and to assign the level of confidence to be associated with the limits. To achieve statistical control, all assignable causes of significant variation are removed from the process [3].

Given the existence of statistical control, the two most important other attributes of the process are generally the precision and the accuracy of the results. Precision is universally considered to be the mutual agreement of individual measurements about some mean value (not necessarily the true value), while accuracy refers to the degree of agreement of individual measurements with some true or accepted reference value of the property being measured. When the mean value is not identical with the reference value, the systematic difference is called the bias. We should avoid using the terms accuracy and bias interchangeably; accuracy has to do with the difference between individual measurements and some reference value, while bias represents the systematic difference between the process mean and the reference value [3].

Structural Analysis

All aspects of coatings manufacture, from the screening of raw materials to finished product quality assurance, depend on analysis data. The ultimate goal of analyses is to identify the chemical species contained in a sample and then determine the amount of each species. As such, both qualitative (what) and quantitative (how much) analyses must be performed. It is extremely important to try and obtain all the background information regarding the sample to be analyzed as this information can often save time and expensive analysis costs.

Organic Structural Analysis

A. Instrumental Methods

Spectroscopy is the study of the interaction of electromagnetic radiation with matter, that is, the interaction of wave lengths of visible light, infrared light, ultraviolet light, X-rays, and radio waves and their effect on chemical substances. Spectroscopy allows the study of these effects with instruments that give an enormous amount of information in a short period of time with less stringent sample requirements than is needed with classical chemical techniques. All of the wavelengths in the ultraviolet, visible, and

infrared regions provide valuable information about the structural makeup of molecules.

Infrared Spectroscopy (IR) provides a unique fingerprint useful in the identification of a wide variety of chemical species [4]. Certain infrared wavelengths are absorbed in the sample by the bonds between the atoms, and the absorbance is measured and plotted as a function of wavelength. Since each chemical material has its own particular and unique arrangement of atoms and bonds, its absorbencies are slightly different from those of all other chemicals.

Normally specific functional groups will give characteristic absorbencies, and these groups can be recognized. Thus, there are very specific absorbencies for groups such as carbonyls, amines, alcohols, nitro groups, and isocyanates. Although it may not always be obvious from a spectrum which chemical is being examined, the analyst will recognize these functional groups and know something about the chemical structure.

In addition, IR can be a very valuable tool for reaction kinetic studies, hydrogen bonding, dipolar attractions and solute-solvent interaction studies, examination of the nature of hydration and the nature of inorganic lattices at various temperatures, and for studying the surface of a material by attenuated total reflection (ATR) and variation of composition with depth by variable angle ATR. These are but a few of the numerous applications of IR in the coatings field [4].

If more detailed information is desired and if the sample has some degree of solubility, then *nuclear magnetic resonance* (NMR) analysis can be extremely valuable. NMR spectrometry not only provides information regarding the functional groups that are present but it also provides information about the location of those functional groups relative to each other. In other words, the placement of the functional groups in the molecule can be discerned from NMR data [5].

If the compound is volatile and has some degree of thermal stability, *gas chromatography* (GC) can be very useful for identification purposes as well as for determining purity/ impurities of materials. If a material is identified qualitatively by GC, then that material can be further analyzed quantitatively. If the compound is not very volatile or is unstable under GC conditions it may be possible to analyze it by *high performance liquid chromatography* (HPLC). Here, as in GC, both qualitative and quantitative determinations can be made [5].

For both GC and HPLC, if the peak of interest cannot be readily identified, it can be trapped and further analyzed by either IR or NMR techniques. Current instrumentation allows the analysis of materials like this quite readily by offering instrument capabilities such as the following: HPLC-MS (mass spectrometry), GC-IR, and GC-MS. These instruments allow accurate separation of components followed by subsequent identification.

MS can be applied to the quantitative analysis of organic, organometallic, inorganic and ionic compounds and materials including metals, and alloys. It is used both to confirm the presence of known compounds and to identify compounds of unknown structure. Volatile or gaseous samples, usually organic compounds, can be examined using electron impact (EI) or chemical ionization (CI) to give positive or negative ion mass spectra. Nonvolatile samples can be examined by fast atom bombardment (FAB) or thermospray ionization for inorganic and organic salts, while plasma discharge ionization is used for metals and refractory materials.

The value of MS, of course, is absolute identification of either known or unknown compounds, particularly when combined with information from other spectroscopic techniques. Pyrolysis can also be carried out prior to ionization inside the spectrometer and thus used for characterizing both linear and cross-linked polymers.

Raman spectroscopy [5] is used to determine molecular structures and compositions of organic and inorganic materials. Raman, like infrared, provides characteristic frequencies of various functional groups. However, since the selection rules governing the allowable transitions are different, some frequencies may be observed in the Raman spectrum that do not appear in the infrared and vice versa. Some applications include:

- Examination of aqueous solutions of inorganic compounds. While water gives rise to intense absorptions in the infrared, making unavailable major regions of the spectrum for identification purposes, it is a poor Raman scatterer, thereby allowing the observation of vibrational transitions in the regions obscured in the infrared.
- Structural identifications of water-soluble organic compounds such as amino acids.
- Detection of weak infrared frequencies, such as the stretching vibrations of the following groups: —C=C—, —C=C—, —S—S—, —C— S—, —N=N—, and —O—O—.
- Determination of configurational isomers in both the solid and liquid state [4].

B. Chemical Methods

The techniques used in chemical analysis are of two general types: gravimetric and titrimetric. In a titrimetric analysis, the volume of known solution required to completely react with a functional group is measured. This volume is then related to the concentration of reacting species in the sample. The primary criteria for titrimetric analyses are that the sample is soluble in a suitable solvent and a reagent is found which fully reacts with the species of interest. Determinations of acid, hydroxyl, and oxirane functional groups, as well as elemental analysis for nitrogen content, utilize titrimetric techniques. Titrimetric analyses are quite sensitive, and measurements of concentration at the 0.1 % level are routine. During gravimetric measurement, the weight of material formed during analysis is used to determine the composition of the original sample.

Classical chemical analyses can be further divided into two categories depending upon the type of information desired: functional group determination and the measurement of elemental composition.

The presence of functional groups in polymers and coatings can normally be determined using a combination of chemical and instrumental measurements. Building upon qualitative functional group information obtained from spectroscopic techniques, quantitative analysis can begin. In some cases specific chemical tests are also required to confirm the presence of species indicated by other techniques. The quantitative measurement of the

following chemical species is routinely performed in the laboratory:

Acid (mg KOH/g sample) $COOH + KOH \rightarrow COO^{-}K^{+}$
Amine (meq/g sample) $NH_2 + HCl \rightarrow NH_3 + Cl^{-}$
Hydroxyl (mg KOH/g sample)
Epoxy or oxirane (meq/g or g/eq)
Isocyanate (%)
Acrylate (%)
Olefinic unsaturation
Thiol or mercaptan (meq/g) $SH + Ag^{+} \rightarrow S{-}Ag + H^{+}$

Many of the above are chemical functional groups that may be part of a large molecule or polymer. The level of these species provides information regarding a polymer or coating. For example, many of the polymers used in coatings are formed using multi-step reactions, and the reactions are monitored by functional group analysis. In addition to monitoring polymerization processes, the levels of species in coatings are of importance. When two coatings components are designed to be blended prior to application, functional group determination is needed to insure that the components are mixed in proportions that give optimum physical and durability properties.

Inorganic Structural Analysis

A. Instrumental Methods

Most inorganic compounds are not sufficiently volatile or soluble to allow identification by either gas or liquid chromatographic techniques. *Ion chromatography* can, however, play a major role in inorganic analysis. *Infrared* analysis (IR) is notable for pigment identification as is discussed in a subsequent section.

X-ray fluorescence (XRF) [5] and other emission techniques are used for elemental analysis of inorganic compounds. *X-ray diffraction* (XRD) analysis [5] is an important tool not only in compound identification but also in identifying crystal structures and in crystalline phase analysis.

Thermal analytical techniques such as *differential thermal analysis* (DTA), *differential scanning calorimetry* (DSC), and *thermal gravimetric analysis* (TGA) are all used on a routine basis for identifying and analyzing inorganic compounds, as well as organic compounds. These techniques provide information about the melting points, other phase transition temperatures, and thermal stability of both inorganic and organic compounds. Also, particle size, surface area, and porosity analyses provide useful characterization information about inorganic materials [6].

Inductively coupled argon plasma spectroscopy (ICAP) [5] allows the determination of numerous elements in aqueous and organic solvent solutions. ICAP methods rely on the emission of light by atoms in the sample as opposed to the absorption of light, the principle behind atomic absorption (AA) spectrometry. Liquid and/or solid samples are readily analyzed using inductively coupled plasma (ICP) techniques after appropriate sample preparation steps are taken. ICP analytical procedures employ classical sample preparation methods such as acid digestion, fusion, dry ashing, dilution, and extraction. In practical applications, AA and ICP are quite similar. The major differences are the speed with which ICP handles samples and most importantly its relative freedom from interferences. The technique is desirable for: quantitative determination of trace elements in aqueous and organic solvent solutions, quantitative analysis of pigments in paints and coatings, evaluation of waste materials and total metals content, and detection of trace metallic impurities in polymers.

The surface upon which a coating is deposited plays an important role in the protective properties of a coating system. A single molecular layer of oily contamination can interfere with proper bonding and result in coating adhesion failure. In addition, the oxide layer that forms in a clean metal surface is often mechanically weaker than the bulk of the metal. Under stress, this layer may flake off and carry with it the coating. Techniques for the examination of surfaces may take many forms, but all involve bombarding the sample with atomic or subatomic particles. The bombardment excites the surface of the sample, releasing energy, which can be used to determine elemental or molecular composition. Depending on the technique chosen, the "surface" examined will vary between the first several atomic layers of a sample down to the first several micrometers.

Electron beam X-ray analysis (microprobe) is one of the capabilities generally included with a *scanning electron microscope* (SEM) [5]. High-energy electrons that strike a sample during the image forming process interact with the atoms comprising that surface. Among the species formed during this interaction are X-rays having specific energies depending on the elements present in the sample. Once detected and analyzed, X-ray spectra can yield information on the elemental composition of the sample, as well as indicate the quantity of each element present. Two types of X-ray detectors are in general use. The energy dispersive detector is useful for detecting elements above sodium in the Periodic Table but is not suitable for low-level quantitative analysis. A wavelength dispersive detector observes all elements more massive than carbon and has significantly improved quantitative analysis capabilities. An instrument that contains all the imaging ability of the SEM and has full quantitative analysis capability is called a microprobe. This instrument has sufficient resolution to allow the elemental analysis of a particle less than 1 μm in diameter. The primary disadvantage of the microprobe is that X-rays can emerge from atoms several micrometers below the surface of the sample. Consequently, the signal from a thin layer of surface contamination can be lost in the signal from the substrate.

Ion scattering spectrometry (ISS) and *secondary ion mass spectrometry* (SIMS) techniques involve bombarding the sample with gas ions and analyzing the products removed from the surface [5]. Both methods exhibit very high sensitivity for all elements, including hydrogen, and can analyze a few atomic layers of exposed surface at a time. Resolution is normally on the order of millimeters with the exception of specialized instruments known as microprobes. These techniques are very useful for hazing and chalking problems where very minute amounts of material cause appearance problems at the surface of the coating. ISS and SIMS readily determine the nature and extent of the contaminating material. Cases of substrate contamination leading to adhesion problems are also more easily solved using the data provided by these analytical methods.

Electron spectroscopy for chemical analysis (ESCA) and *scanning auger microscopy* (SAM) are techniques in which

a sample is irradiated with a beam of X-rays (ESCA) or electrons (SAM) to liberate electrons from the top 2 to 5 nm of the surface [5]. The energy of the liberated electrons is then analyzed to provide information regarding the composition of the surface layers in the sample. In addition to elemental composition, information can be obtained on the chemical environment of the elements present on the surface. Through comparison of spectral fingerprints with the spectra of standard materials or a library of reference spectra, compounds present on the surface can be readily identified. ESCA has the capability of observing particles approximately 1 mm in diameter and is well suited to paint films on a variety of substrates. SAM has the ability to study much smaller particles (approximately 0.2 μm in diameter), but the surface must be conductive, limiting its utility to metal surfaces.

B. Chemical Methods

In conjunction with titrimetric and gravimetric measurements, analysis of elemental composition provides important information on coatings systems. Among the many elements determined are: carbon (%), hydrogen (%), nitrogen (%), sulfur (%), chlorine (%), bromine (%), phosphorous (ppm).

The level of nitrogen in an industrial coatings system is an important analytical value because nitrogen is present in melamine, urea, and benzoguanamine oligomers, which are used as cross-linking agents in many coatings. Correct levels of cross-linking agent are essential since physical, chemical, and performance characteristics are directly related to cross-linker levels. Low concentrations of cross-linking agent yield coatings that are soft, water sensitive, and do not resist detergent solutions and the weather. Elevated levels of curing agent have equally undesirable effects since coatings become brittle and lack sufficient adhesion to the substrate. In addition to cross-linking agent, nitrogen content provides information on the presence of polyamide and urethane polymers, which also contain nitrogen.

C. Microscopic Methods

In general, microscopic techniques are overlooked in the coatings industry. This is a significant omission as microscopy can be a wonderful tool for solving problems. The instrumentation is readily available but, unfortunately, trained microscopists are lacking. In many instances of coating failure and/or customer complaint the first step should be a microscopic examination. The following describes the more common and readily available techniques for the coatings laboratory.

Light Microscopes Low-power Magnifiers

Large magnifying glasses, jewelers loupes, linen testers, lenses that can be swung into place over a spectacle lens, and other magnifiers that provide assistance to the naked eye are all occasionally used in coatings analysis. Applications range from inspecting raw materials for inhomogeneities to scrutinizing a defect in a finished, coated surface [7].

The purpose of using a magnifier such as this is to provide an enlarged image so that the viewer can see the problem and/or the surface. For instance, it may become apparent that a fiber is the source of a defect surface problem. Also observable would be a particle at the center of a crater.

Stereomicroscopes

Stereo or stereobinocular microscopes are the next step up from simple magnifiers. They actually consist of two compound microscopes of relatively low magnification that are mounted side-by-side at the correct visual angle, so that the images of objects viewed through them are observed as a true, upright, fused stereo pair. These microscopes are sometimes referred to as dissecting microscopes [7].

Magnification ranges for these microscopes are usually from 2.5× to 200×. Samples can be viewed using various lighting conditions and in most instances sample preparation is minimal.

Polarizing Microscope (PLM)

The polarizing microscope is the chemical microscopist's primary tool. With it, the microscopist can study the morphology of fibers, crystals and particles. Accurate and precise measurements can be made of the optical properties of these substances by which they can be identified and characterized [7].

The majority of the analytical work undertaken with a polarizing microscope is performed by transmitted light. To look at a paint film by transmitted light, the microscopist must prepare a thin section using a device called a microtome. The sections range in thickness from tens of micrometers to a few angstroms and can be cut and mounted for microscopical observation [7].

Other Light Microscopes

Certain problems may require the use of other microscopes such as: interference microscopes, fluorescence microscopes, hot-stage microscopes, or an infrared microspectrophotometer. The latter is a microscope with an infrared spectrophotometer attached and is often used to identify the composition of multilayer paint films.

The use of Fourier transform infrared microspectroscopy (IMS) has increased greatly in the last several years. Utilization of IMS often eliminates or reduces the need for sample preparation techniques since a defect area can be analyzed directly without physical or chemical extraction. Samples can be analyzed by:

- Transmission, where the IR beam passes through the sample
- Reflection, where the IR beam reflects from the sample surface
- Attenuated total reflection (ATR), where the IR beam typically penetrates from 0.5 to 2.0 μm into the sample [8].

These three basic methods for IMS have been utilized for years and recent improvements have focused on the use of automation features such as mapping and autofocus to speed up analysis. Today's instrumentation features simultaneous view and collect features, which provides significant improvements in data collection time and efficiency. There is a continuous, full view of the sample area and a real-time spectrum preview to quickly find the optimum sample point [8].

Electron Microscopes

Scanning Electron Microscope

The SEM is the most useful electron microscope for the coatings lab. It provides a large range of magnifications, great depth of field, and the ability to obtain elemental analysis when it is equipped with an X-ray (EDS) analysis system.

SEMs are used for a variety of analyses, including pigment characterization, surface morphology measurements, and paint-film formation examination. The real strength of SEM is the ability to provide high magnification images of a sample and detailed chemical information on a micrometer-size scale [9].

The only requirement for SEM examinations is that samples are able to withstand the vacuum conditions in the microscope and are thermally stable during electron-beam irradiation. Most components used in coatings, such as resins, pigments, fillers, and other additives, are insulating materials. These materials need to be coated with a thin metallic film to render the sample surface electrically conductive, so that the specimen can be examined in the SEM [9].

X-Ray Microanalysis

Most SEM work is done using electron beam voltages of 10 – 30 keV. At these voltages the electron beam has enough energy to knock out inner-shell electrons, which leads to X-ray emission. X-rays are produced for all chemical elements using an accelerating voltage of at least 10 keV and X-ray spectra can be obtained from any area, line, or point on the sample [9].

It is important to remember that while the instruments are capable of performing quantitative analysis with these techniques, it is generally not advisable for paint samples. This is because the typical paint film is not homogenous and therefore the elemental data may be indicative of only the spot that is being scanned. A better estimate of the elemental composition of any paint sample is obtained by choosing several different areas on the sample for examination and comparison purposes.

Transmission Electron Microscope

This microscope is a transmission scope as opposed to the SEM, which is a reflection microscope. The samples for analysis must be very thin for TEM work, which may be difficult. The TEM is a great tool for examination of pigments and extenders as their size is suited for easy sample preparation.

Scanning Probe Microscopy

Scanning probe microscopes (SPMs) are powerful tools for surface metrology—measuring surface features whose dimensions range from interatomic spacing to 100 μm. The common feature of all SPMs is that the measurements are performed with a sharp probe scanning over the surface while contacting or maintaining a very close spacing to the surface. Like SEMs, SPMs image and measure the sample surface; however, SPMs measure surfaces in all three dimensions—x, y, and z. SPMs, like optical microscopes, are easy to use with little or no sample preparation and no vacuum required. They also provide the highest magnifications and resolution [10].

Atomic Force Microscopy

The first commercial AFM was introduced in 1989 and, therefore, this technique can be considered relatively new. It is ideal for providing high resolution, three-dimensional imaging of the surface structure of a film. For coatings, atomic force microscopy (AFM) can be used to understand the properties of a substrate and the effect of a coating on that substrate.

SEM has limitations, in that three-dimensional information is not available, and SEM resolution and contrast are very poor. Other techniques, such as TEM, also provide only two-dimensional data. AFM can be applied to any material, offers a much higher resolution (i.e., to the atomic level), and causes far less surface damage due to the reduction of size and forces involved. The probe tip, which interacts with the sample, is mounted onto a cantilever that translates the forces acting upon the tip in a measurable quantity. AFM can provide the following four main advantages in visualization.

- Precision. The AFM can see structures at various length scales with ease and minimal sample preparation, from subnanometer to hundreds of microns.
- High resolution. It can see the surface with very high vertical resolution and provide detailed three-dimensional visualization.
- Reduced damage. The AFM can image samples in a relatively nondestructing manner.
- Real-time monitoring. Changes in morphology as conditions are varied can be achieved in real-time [11].

AFM images can reveal critical information about surface features and can examine any rigid surface. Differences between supposedly equivalent and smooth surfaces can be seen rather dramatically using this technique. AFM can resolve very tiny features (even down to the atomic level) that are unseen by other means. The technique also allows the analyst to examine a large field of view (over 100 μm) so that comparisons can be noted with visual or optical microscopic examinations. AFM is also useful for rough surfaces, as its vertical range is more than 5 μm. Large samples can fit directly in the microscope without cutting.

AFM works by means of a tiny stylus (probe or tip) that is in contact with the surface of the sample. The most basic component is the scanner that may move the sample or can move the probe over the sample. As the instrument scans in a raster pattern, the stylus rides up and down the surface hills and valleys. The computer stores information at all points and assembles an image. This technique provides extraordinary topographic contract compared to SEM analysis. Various modes of operation can be conducted depending on the analysis required.

Vehicle Identification

Infrared Spectroscopy

Qualitative infrared spectroscopy is a valuable analytical tool that allows the examination of the multitude of materials utilized in the coatings industry. It is the primary tool for vehicle/resin identification in a coating. An infrared spectrum indicates the overall composition of any unknown material in terms of its functional groups. With a minimum of background knowledge, substantial information can be gained from an infrared spectrum by simple functional group identification. However, beginners should be cautioned against making unfounded conclusions based strictly on this technique. As one becomes more acquainted with infrared spectroscopy, the limitations and real complexity of this analytical technique will become more apparent. All laboratories involved in the infrared analysis of any aspect of coatings should have available a copy of "An Infrared Spectroscopy Atlas for the Coatings Industry" published by the Federation of Societies for Coatings Technology [4]. This atlas (inclusive of a 2500-spectra library) is

an invaluable tool and a true benefit to the spectroscopist in the coatings industry.

Occasionally, it is possible to obtain some qualitative information from the infrared spectrum of a pigmented binder system if the system is relatively simple. However, a binder free from pigment should be obtained for an infrared analysis. This means prior separation of pigment, vehicle, and solvent, and a further breakdown of these fractions, if possible. The elemental composition of the fraction should be obtained because in some cases the presence of certain elements will not be obvious from the infrared spectrum [4].

In most cases, band positions are indicative of the functional groups present. The shape of the bands also gives information concerning the functionality of a molecule. The relative intensity of a band in comparison to the intensity of other bands provides information pertaining to the amount and identity of a specific functional group present in a molecule. Functional groups that give rise to a large change in the dipole moment of a molecule, upon undergoing a vibration will have very intense absorption bands. Excellent examples of this phenomenon are the carbonyl and ether groups [4].

Once it is known which bands are characteristic of certain functional groups, the absence of these bands from a spectrum can be used to establish which functional groups are not present in detectable amounts. This method of analysis is important since the spectroscopist is frequently requested to establish the presence or absence of a particular functionality. If there is absorption present in a particular region, no information can be obtained from that region by negative interpretation. Positive interpretation or other techniques must then be relied upon [4].

The simplest method of interpretation is to consider the entire spectrum as though it were a picture and compare this picture with the spectrum of known materials that have been physically or mentally cataloged. If the spectra are the same, or very similar, it is a reasonable assumption that the materials are nearly identical. As experience is gained and more spectra are committed to memory, many materials can be recognized by inspection. Reference spectra prove invaluable in this type of interpretation, especially when a definite identification must be made [4]. There are also very extensive collections of reference spectra with which one tries to match "fingerprints" of unknown materials in order to make positive identifications.

In most cases, the limit of detectability of one material in another by infrared spectroscopy is 5 %. However, depending on the type of material, it may be less than 1 % or as high as 30 %. The limit of detection will depend on the phase, the absorptivity of the particular absorption being used, and the proximity of this band to other strong absorptions. Therefore, it is important to rely upon previous knowledge of the system and to use other confirmatory methods to verify the infrared analysis [4].

In addition to determining polymer type and concentration, the detection of contaminants in complex matrices and the examination of residual reactive functional groups can be done by infrared. The technique has advantages over other analytical techniques in that literally any type of sample can be examined by IR: solids, liquids, or gases. Special techniques are also available to examine surfaces.

Extension of an ultraviolet and visible spectroscopy (UV-VIS) experiment into the near-infrared region allows examination of materials that absorb in that region. Wavelengths in the near-IR region are those longer than visible wavelengths and occur below the red portion of the visible spectrum. A special source and detector are needed to extend into the near-IR, but instrumentation is available that will automatically switch to these at the proper wavelength. A special technique is utilized in the near-IR called diffuse reflectance and is used to measure the total reflected light off of a painted surface. This is done with a device called an integrating sphere that collects all of the reflected light from a surface and focuses it to the detector. In this way, one not only measures the amount of light a sample will absorb, but how much is reflected as well.

Infrared has great utility for the quantitative analysis of polymers, inorganic pigments, solvents, and additives. Solubility of the sample is not a requirement, and many complex mixtures can be determined in this fashion. With the increased utilization of Fourier transform and computer-assisted dispersive infrared spectroscopic techniques, quantitative applications have been further enhanced. The basis for quantitative analysis is, of course, the Beer-Lambert Law [4].

Nuclear Magnetic Resonance Spectroscopy

NMR spectroscopy permits the qualitative and quantitative analysis of many organic materials. When certain nuclei are placed in a strong magnetic field, their nuclear spin states are split into two or more levels due to the magnetic properties of these species. Transitions between these magnetically induced energy levels can then be brought about by the absorption of radio frequency energy. The specific frequencies of the radiation subsequently re-emitted depend on both the chemical and magnetic environment of each nucleus, such that detailed structural information is possible. NMR, as an analytical technique, provides information about how the atoms in a molecule are arranged. It is possible to determine which carbons are present as methyl groups, methylene groups, and so forth. The number of hydrogen atoms attached to oxygen and nitrogen can also be determined, and with these pieces of information the analyst is able to generate a molecular structure.

Samples that are soluble in a variety of solvents can be examined using NMR spectroscopy. It is ideal for structural identification of organic compounds. Qualitative and quantitative analysis of polymer composition, quantitative measurement of polymer mixtures, analysis of copolymer sequence distribution and tacticity, analysis of type and degree of polymer branching, and polymer end group analysis can all be done with NMR. An NMR spectrum of a typical polyester would show each of the dibasic acids and the polyols used in the synthesis of the polyester. NMR can be a superb asset to the analyst along with other tools such as IR for identification of true unknowns and for assisting polymer synthesis identification work.

Miscellaneous Testing

A host of chemical methods exist for further identification of resin components by chemical treatment of the resin to break it down into its original starting components, which can then be analyzed by conventional methods. For

example, a resin may be subjected to aminolysis to form amides of the carboxylic acids and to release the polyols. Upon further treatment, these materials can be readily identified. Scanning of available ASTM methods and Official Methods of Analysis of the Association of Official Analytical Chemists (AOAC Methods) [12] will provide insight into other useful techniques and procedures.

Thermal analytical data can also aid in the identification and characterization of a polymer. DTA or DSC can be used to obtain a melting point, a T_g, and a measure of the thermal stability of the polymer. XRD analysis of the polymer will determine if the polymer is partially crystalline, help to identify the chemical structure of the polymer, and provide information on the preferred conformation of the polymer chains in the crystalline regions [6].

Electron microscopy and XRD techniques describe the submicron morphological features of polymers such as lamellae and crystallites, while optical microscopy is used to study large morphological features such as the size and nature of spherulites in a polymer [6].

Electron probe microanalysis (EPMA) is an elemental identification technique associated with SEM. When materials are bombarded by a high-energy (10 to 50 keV) electron beam, characteristic X-ray fluorescence radiation is produced. By incorporating either energy dispersive or wavelength dispersive spectrometers directly into the instrument, it is possible to obtain X-ray spectra directly on the area as seen by the electron beam. Thus, it is possible to obtain qualitative and quantitative elemental data from a small volume of material for the elements boron through uranium. EPMA has been used extensively for impurity and inclusion identification in polymers [6].

Some unique vehicles may be particularly difficult to analyze, and the determination of residual monomer by gas chromatography often can shed some light on the resin system.

Pigment Identification

The following sections discuss the qualitative and quantitative identification of pigments.

Infrared Spectroscopy

As noted in the discussion on vehicle identification, IR analysis for the qualitative identification of pigments is most common. Procedures and reference spectra may be found in the Infrared Atlas [4]. Infrared is also used for identification of extender pigments.

Inductively Coupled Argon Plasma Spectroscopy

Inductively coupled argon plasma spectroscopy, often referred to as ICP or ICAP, is a technique used to determine the concentration of various elements present in any sample or material. The instrument can provide qualitative and quantitative information and can complete an analysis on numerous elements simultaneously and in a matter of a few minutes. The major strength of the technique, aside from speed, is the ability to detect trace amounts of elements.

A solution is aspirated into the instrument, where a fine aerosol is formed. This aerosol is then introduced into a high-energy argon plasma, where the elements present in the sample are raised to an excited state. When these elements return to ground state, they emit light at wavelengths characteristic of the elements present. The intensity of the light is proportional to the concentration of the element present in the sample. Generally, sensitivity is in the low parts-per-million range for most elements.

The plasma is a highly ionized, chemically inert, hot gas that achieves a temperature estimated to be 10,000°C. A radio frequency generator provides energy to the plasma torch by creating an oscillating magnetic field. A sample introduction device, known as the nebulizer, converts the sample solution into fine droplets or aerosol mists that are transported to the torch by means of argon carrier gas. The high temperature of the plasma dries the droplets and decomposes the sample into individual atoms that are excited and emit light as they return to the ground state. The wavelength of the light produced differentiates one element from another. The intensity of the light produced is a measure of the concentration of the element present in the sample.

The light emitted from a sample containing many elements passes through an optical path that separates the spectrum of light into discrete wavelengths. A detection system, made from many photomultiplier tubes, each representing a wavelength of an element, measures the intensity of light and converts it to electrical energy. The electrical energy is converted into concentration by means of a dedicated computer. The computer performs all instrumental control functions and prints the data.

Some applications of ICP are the following: pigment composition in coatings, industrial influent and effluent analysis, soluble cations and anions in electrocoat baths, organometallic additives in coatings, driers and catalysts in coatings, competitive product analysis, quality control of raw materials, and industrial hygiene analysis.

Inductively coupled plasma-mass spectrometry (ICP-MS) techniques were commercialized in 1983 and it is a very fast growing trace element technique. This is because of its ability to carry out rapid multielement determinations at the ultra-trace level. As a technique it determines the same elements as other spectroscopic methods such as atomic absorption but its speed of analysis and detection limits are highly desirable.

Atomic Absorption Spectroscopy

Atomic absorption spectroscopy, commonly referred to as AA, is designed for measuring the concentration of metallic elements in solution at the parts-per-million level. Atomic absorption is an efficient and sensitive method for performing routine quantitative analysis with a high degree of precision and accuracy. Unlike ICP spectroscopy, this instrument is only capable of analyzing the concentration of one element at a time. Thus, it is more often recognized for its quantitative power rather than its qualitative capabilities.

Atomic absorption methods rely on the absorption of light by atoms. If a solution containing metal ions is aspirated into a heat energy source, such as a flame, the high temperature and environment of the flame causes the formation of free, ground-state atoms in the flame. These free atoms are capable of absorbing light of a particular frequency. If a beam of light having the appropriate frequency or energy passes through the flame, the free atoms in the flame will absorb some of this energy. The decrease

in the intensity of the light beam can then be taken as a measure of the concentration of that particular element in the sample solution.

Atomic absorption instrumentation requires a light source, an atomizer, a monochromator, and a detector. The normal light source used in AA is a hollow cathode lamp. It consists of a hollow cup made from the element to be analyzed. Application of a high potential causes formation of positively charged ions which bombard the cathode, forming excited metal ions which emit light. AA is important since free, uncombined atoms must be formed before light absorption occurs. A solution containing the metal ions is heated to a temperature sufficient to dissociate the ions into atoms. The heat energy can be provided using an air-acetylene or nitrous oxide-acetylene flame. The primary function of the monochromator is to isolate a single atomic resonance line from the spectrum of lines emitted by the light source and direct it through the flame and onto the detector. Photomultiplier tubes are employed as detectors. They measure the changes in light intensity and convert them to electrical signals.

Sample preparation is an essential part of AA. Solid and pigmented samples are ashed to remove organic species. The inorganic components are dissolved in acid and diluted with deionized water prior to introduction into the flame. Non-aqueous AA is an ideal way of determining organometallic compounds to prevent sample loss or conversion of the metallic species into insoluble components.

Atomic absorption complements ICP techniques for the analysis of paints, resins, UV-curable coatings, and other materials. It is also a very useful tool in analyzing waste materials, pigment composition, pollution studies, raw material evaluation, and analysis of organometallic compounds.

Several pigment analysis procedures using AA are standard ASTM methods. Typical procedural examples of AA analysis for pigments can be found in the following:

Standard Test Method for the Determination by Atomic Absorption Spectroscopy of Titanium Dioxide Content of Pigments Recovered from Whole Paint (D4563).

Test Method for Detection of Lead in Paint by Direct Aspiration Atomic Absorption Spectroscopy(D4834).

X-Ray Fluorescence Spectroscopy

XRF is a relatively simple and, in general, nondestructive method for the analytical determination (qualitative and quantitative) of elements. This method is extremely useful because of the ease of sample preparation and its ability to "scan" the periodic table for all elements down to aluminum and sometimes boron. The technique allows for rapid qualitative determination of the elements present. ASTM Test Method for Determination by X-Ray Fluorescence Spectroscopy of Titanium Dioxide Content in Paint (D4764) is a typical application for the technique.

X-Ray Diffraction

The XRD pattern obtained from a material is characteristic of that material. The intensity of a diffraction peak is entirely due to one component of a mixture and is dependent upon the amount of that substance in the mixture. To a minor extent the peak intensity of the component is also dependent on the mass absorption coefficient of other materials present. Since the method utilizes the ratio of diffraction maxima of two chemically similar materials, it is expected that the effects of other constituents will be the same for both materials.

Diffraction measurements can be made on single pigments, pigment mixtures, on films of pigmented coatings and on films prepared from liquid coatings if interfering materials are not present. ASTM Test Method for Ratio of Anatase to Rutile in Titanium Dioxide Pigments by X-Ray Diffraction (D3720) is an application well suited to this technique.

Chemical Methods

The typical chemical methods using titrimetry and gravimetric procedures are always appropriate for quantitative pigment determinations. Some of these techniques have been replaced in recent years by more efficient (not necessarily more accurate) and time saving instrumental methods; however, there are situations where the traditional testing methods are still most appropriate.

Numerous ASTM methods exist for these types of analysis, and one needs to check the index of available test methods. By way of example, the following are noted:

ASTM Test Methods for Chemical Analysis of White Titanium Pigments (D1394).

ASTM Test Method for Arsenic in Paint (D2348).

Additive Identification

Additives can often be the most difficult components to analyze and identify in a coating. They frequently are present in small quantities (often at a few percent or less), and their presence can be masked by major components. In addition, the number of possible additives is large and includes surfactants, plasticizers, defoamers, thickeners, anti-oxidants, etc. It takes a skilled and experienced coatings analyst plus good deductive problem-solving ability to become adept at additive analysis. The volatile nature of some co-solvents, coalescing agents, and some plasticizers makes their identification by gas chromatography fairly straightforward.

Infrared Spectroscopy

For samples containing mixtures, the IR spectrum generally gives information only about the major component(s). However, computerized infrared instrumentation allows one to subtract spectra of the major constituents from a mixture and get the resultant spectrum of minor materials such as additives and contaminants. Thus, it is possible to do a spectral "separation" in just a few seconds rather than a true chemical separation that may take hours. Water and hexane extractions of dried films followed by IR can point to some of the following, for example:

- Cellulosic thickener (which can be confirmed by spot test).
- Long chain aliphatic hydrocarbon "oil" is indicative of defoamers.
- Carboxylate containing component may indicate a polyacrylate salt.
- Nitrile component may indicate mildewcide.
- Dialkyl sodium sulfosuccinate is indicative of a wetting agent.
- Inorganic sulfate may be a possible persulfate polymerization catalyst.

High Performance Liquid Chromatography

High performance liquid chromatography is frequently referred to as HPLC or just often as LC. This technique is used to separate components from mixtures, especially nonvolatile components that are not amenable to GC analysis. Since these nonvolatile components represent about 90 % of all organic compounds, HPLC separation techniques offer extraordinary versatility and capability. Components may be separated either by size or subtle differences in molecular configuration and solubility. Separations based on size are commonly called gel permeation chromatography (GPC) or size exclusion chromatography (SEC). Separations based on subtle differences in molecular configurations and solubility are called partition chromatography. Both quantitative and qualitative information can be obtained by using HPLC techniques.

Samples to be analyzed by HPLC are dissolved using an appropriate solvent or a combination of solvents before they are introduced into the liquid chromatograph. Samples that are not soluble in HPLC solvent(s) are not suitable for analysis using this technique. The actual separation process takes place on a packed column or a series of packed columns through which solvent is constantly pumped. The separated components elute from the column(s) directly into a detector. The detector is connected to a recording device that produces a trace of the separated components versus time, i.e., a chromatogram.

The three most common detectors in HPLC are the differential refractometer, the UV spectrometer and the evaporative light scattering detector. The refractometer measures the difference in refractive index of the solvent and the component being analyzed. The ultraviolet spectrometer measures a compound's absorbance at various wavelengths in the ultraviolet (or sometimes visible) region of the light spectrum. The refractive index detector is most commonly used with size separations, while the ultraviolet detector is usually used in conjunction with partition chromatography. The ultraviolet detector is capable of detecting components in the part-per-million range. The refractive index detector, on the other hand, can only detect components down to the 2 to 4 % ranges. It is referred to as a universal detector because it is not dependent on the sample components absorbing at a particular wavelength of light.

Typical applications include: surfactant evaluation, polymer characterization, additives in polymers, air and water pollution, raw material evaluation, multi-functional acrylates, plasticizers, coalescents, and cross-linking agents.

Ultraviolet and Visible Spectroscopy

UV-VIS examines the absorption of UV and visible wavelengths of light by a sample. This type of analysis is often used as a quantitative measure of a material. Materials that possess aromatic rings such as polystyrene, alkyd resins, and many paint additives will absorb UV light and can be examined. Materials that absorb in the visible region of the spectrum are those which possess color. Chemicals such as dyes can be examined in that region. UV-VIS is very sensitive for the species that absorb in these regions, and concentrations in the low parts-per-million range can usually be determined.

The visible region of the spectrum consists of wavelengths seen through the eye. In a visible instrument, a tungsten filament light is used as a source of visible wavelengths. Wavelengths are separated by a grating and examined one at a time. A photocell detector is used to measure absorbance at each wavelength and a spectrum is recorded.

Ultraviolet wavelengths are shorter than visible wavelengths and occupy the region above the blue end of the visible spectrum. To observe ultraviolet absorbencies, a mercury lamp is used as a source of UV light. Wavelengths are separated by a grating and detected, again by a photocell. An ultraviolet spectrum looks similar to a visible spectrum. Modern instruments combine UV and visible detection, and as the spectrum is being scanned the instrument will automatically switch from one source to another. Observed absorbencies are directly proportional to concentration of the component of interest.

Materials which do not absorb in the UV or visible region can sometimes be measured by complexing them with an absorbing reagent, usually to develop a colored species. Very sensitive methods of this type are used for the determination of formaldehyde, phosphorous, and sulfate.

Solvent Identification

Gas Chromatography

GC is a technique for the separation of any species exhibiting a measurable vapor pressure at a temperature up to approximately 300°C, as well as any compounds for which a stable, volatile derivative may be formed. Both qualitative and quantitative information can be obtained.

Most GC samples are liquids or solutions at room temperature, although instrumentation may be adapted to analyze solid and gaseous samples. Liquid samples (approximately 0.001 mL) are introduced to the instrument using a syringe into a flash-heating chamber called an injection port. There, the volatile sample components are quickly and evenly vaporized. In some cases, however, decomposition of sensitive components can occur when they come in contact with the hot metal surface. The analytical chemist may be able to minimize or circumvent this problem if proper precautions are taken. The vaporized components are then carried onto the column and through the gas chromatographic system using an inert gas, such as helium or nitrogen, flowing at a constant rate.

The column is the portion of the chromatograph where the actual separation of components is achieved. A packed column consists of narrow tubing made from stainless steel, nickel alloy, glass, or a number of other materials, filled with fine particles of a packing material. This packing material may consist of polymeric beads or an inert solid material supporting a thin film of a non-volatile liquid. It is the varying degree of interaction between each of the sample components with the packing material that causes the components to become separated in the column. A large number of packing materials of varying chemical composition are available. Columns containing other packing materials are easily interchanged so that different separations can be obtained.

Occasionally, samples will contain a number of components of similar volatility and/or chemical composition that are difficult to separate on packed columns. In these instances, capillary columns are used. Capillary columns are extremely long (100 to 300 ft, 30.48 to 91.44 m), narrow bore tubes made from glass, metals, or fused silica. They are internally coated with a thin film of a nonvolatile liquid

to effect separation. A variety of detectors used alone or in combination can be strategically mounted at the end of the column to monitor the separated components as they exit the column. The detectors available in GC have varying sensitivity and specificity. If needed, some may be operated to detect materials in the sub parts-per-million level.

The response of the detector to an eluting component is electronically converted into a visual representation called a chromatogram. A chromatogram is a plot of detector response versus time elapsed since sample injection. Eluting components are represented as peaks in the chromatogram. The time needed for a component (peak) to elute can be used to help identify the component. The area produced under the peak is related to the concentration and is used in the quantitative determination of the component.

Typical applications include: qualitative and quantitative solvent analysis, odor analysis, pollution studies, purity determinations, determinations of residual monomers, and determination of airborne organic contaminants.

Additional information on gas chromatography may be obtained from ASTM Practice for Packed Column Gas Chromatography (E260). ASTM Test Method for Direct Injection of Solvent-Reducible Paints into a Gas Chromatograph for Solvent Analysis (D3271) describes the techniques used in many situations. Note should also be made of ASTM Test Method for Determination of Dichloromethane and 1,1,1-Trichloroethane in Paints and Coatings by Direct Injection into a Gas Chromatograph (D4457) for exempt solvent analysis for VOC calculation purposes. ASTM Committee E19 on Chromatography is focused on chromatographic techniques. There are numerous ASTM GC test methods for the determination of the purity of specific solvents and for the determination of specific impurities such as benzene.

GC—Mass Spectrometry

GC has been well established as an excellent tool for the separation of volatile species in complex mixtures. A significant limitation of GC, however, is the relative inefficiency and lack of certainty in this technique when the identification of unknown components is required. Mass spectrometry is an excellent tool for qualitative analysis. However, if a complex mixture is introduced into the instrument, the resulting mass spectra of all components are superimposed on one another, making analysis difficult, if not impossible. These limitations are overcome by a combination of GC and mass spectrometry. Sample constituents are separated into pure components using the gas chromatograph; these pure components are then introduced into the ion source of the mass spectrometer for identification. Generally, samples are liquids; however, gases and solids can also be examined.

As the sample components enter the mass spectrometer, they are immediately ionized. Electrons are removed from the sample molecules resulting in the formation of positively charged ions. This is normally accomplished through electron impact or chemical ionization. Each of these ionization techniques has unique properties for providing useful analytical information.

Electron impact ionization occurs when electrons emitted from a hot filament collide with sample molecules causing the loss of one or more electrons. This results in the formation of positive ions that contain excess energy. The excess energy causes many of the resulting ions to break apart or fragment, thus providing the fragmentation patterns used to determine chemical structure.

In chemical ionization, the mass spectrometer's ionization source is pressurized with a reagent gas such as methane, ammonia, or butane. Electrons from the filament collide with, and impart energy to, the reagent gas. The energetic reagent gas molecules subsequently collide with the sample molecules causing the sample molecules to become positively charged. Ions formed in this manner do not contain as much excess energy as ions formed via electron impact ionization. Consequently, very little fragmentation occurs and intact ions containing molecular weight information are obtained.

Following ionization, the sample and fragment ions are sorted according to their respective masses. An appropriate detector measures ion intensities at each mass, and the corresponding signals are transmitted to a computer for further processing and data storage. Results can then be displayed in graphical or tabular form. Interpretation of the spectra and comparison with a library containing thousands of reference compounds allows sample composition to be determined by the analyst.

Typical problems examined using GC-MS include: the qualitative identification of volatile organic species and contaminants in coatings and coatings raw materials, quantitative analysis of volatiles at the parts-per-million and parts-per-billion level, evaluation of potential odor causing species, and determination of polymer composition following pyrolysis and chemical degradation. Other uses include: characterization of complex solvent systems; monitoring of waste streams and ground waters; characterization of polymer products, by-products, and intermediates; identification of odor problems; and monitoring of raw materials for potential contamination.

TRACE ANALYSIS

With the development of sophisticated instrumentation over the past two decades, the ability to increase sensitivity in lower detection limits for many materials has increased. This is particularly true in the areas of metals analysis. As a result, many regulatory and compliance agencies have changed their detection limits to reflect this increased capability. For EPA (Environmental Protection Agency), OSHA (Occupational Safety and Health Administration), and FDA, and FDA (Food and Drug Administration) compliance, trace analysis is extremely important. Many manufacturers require trace analysis to identify contamination, to verify product purity, and so forth. Analysts must be prepared to provide data in the parts per billion (ppb) and sub ppb range when necessary, and this frequently involves good concentration techniques as well as good methodology and instrumentation.

Certainly techniques such as GC, MS, and HPLC are capable of measuring components in solution well below the ppm range. The specificity of MS and its sensitivity for organic compounds has made it a common tool used in EPA protocols for pollutant-related analysis. Coupled techniques such as GC-MS, LS-MS, and ICAP-MS are also available today and can provide very low-level analysis. Commonly

used trace element procedures such as AA, ICAP, ion selective electrode analysis, neutron activation analysis, and optical emission spectroscopy all offer low-level analysis. ICP-MS detection capabilities are comparable to those of graphite furnace atomic absorption spectrometry. For many elements ICP-MS provides quantitative analyses down to the parts per trillion level.

In addition, for inorganic compounds, scanning electron, microprobe, and transmission electron microscopy are useful for trace analysis. Surface techniques such as X-ray photoelectron, Auger, and SIMS are also useful as qualitative and quantitative measurement techniques.

At the very small concentrations that characterize trace and ultratrace analysis, and with the minute samples employed in microanalysis, the limit of detection, a new criterion of performance, becomes important. Because noise itself now becomes limiting, many questions arise. For example, how large must the reading from a sample be compared with that from a blank for a person to report that analyte is present?

At the detection limit, statistics and chemistry become intimately mixed and statistical procedures must be used to interpret chemical results. The detection limit is simply the smallest concentration of analyte that can be certified as statistically different from a blank. To determine the limit, two sets of measurements are necessary. In addition to a regular set, many measurements (10 to 20 are recommended) must be made on a blank under the same conditions. It must simulate regular samples but be without analyte.

To calculate the limit of detection, one begins by observing the limiting response. For a given measurement procedure, it is the smallest response that can indicate with reasonable probability that a particular analyte is present. To obtain the limit of detection from the limiting response requires a calibration curve or a standard addition curve. A usable curve will be one based on quite pure standard solutions of extremely low concentration. The alternative, a long extrapolation of a calibration curve beyond the lowest points for standards even in those favorable cases in which the curve is linear, will invite substantial error.

Actually, as quantitative measurements at the trace level have become more important than simple detection, a limit of quantification or *limit of determination* is recommended by IUPAC for comparison of the relative merits of different trace methods rather than the limit of detection.

The future of analysis will become more sophisticated with the development of more sensitive instrumentation and computer technology. Robotics and autosampling will also enhance the development of analysis and reduce the amount of error that is introduced in analysis. These changes tend to impose more sophisticated demands in analysis from customers and regulatory agencies. There is a tremendous burden on the analyst to be conscious of extraordinarily good laboratory techniques, the limitations of the instrumentation, and the reporting of sound data.

FORENSIC PAINT ANALYSIS

Forensic science is the application of the natural sciences, such as chemistry, biology, physics, and biochemistry to criminal and civil laws that are enforced in the criminal justice system. The field of forensics is very broad, encompassing medicine, pathology, dentistry, and even paint.

Coatings are routinely analyzed in local crime laboratories along with hair, fiber, blood, and other evidentiary materials. Paint is often transferred from the surface of one object to another when a crime is committed. Tools that are used for breaking and entering, such as screwdrivers or crowbars, often have tiny particles or smears of paint that have transferred from the point of entry to the tool. A tool can also be the source of paint that is transferred to a victim. Devices containing explosive charges, vehicles used to transport explosives, and objects removed from the scene of an explosion often contain paint. Fragments of wood at a crime scene can also be coated, and the coating can prove to be a valued piece of evidence.

Each year literally thousands of vehicular hit-and-run cases occur, resulting in personal injury and death. Consequently, automotive coatings are frequently and routinely analyzed in most crime labs around the world. The analysis is often very difficult for forensic examiners because the sample size available to the analyst—the paint chip—is extremely small, often less than 1 mm. Many times only a paint smear is transferred to the clothing of a hit-and-run victim. Forensic paint examiners might be called upon to identify the make, model, and color of the automobile involved and/or compare the available paint evidence to another sample to establish a common origin or match to a suspect vehicle.

For the forensic examiner, the analytical examination of paint is quite different than it is for the paint chemist in a manufacturing facility. The forensic paint examiner is often presented with very small paint chips or fragments, or even smears of paint. They are dealing with a dried paint film and consequently have no knowledge of whether the source of the paint was from solvent or waterborne coatings or a powder coating. The job of the forensic examiner is to try to determine from the paint chip an identification of the polymeric resin system or binder, the pigment composition, both organic and inorganic, and the additives if possible. Identification of additives is particularly difficult in most instances because the level of additive used in paint manufacture is very low and is usually on the order of 5 % or less. There are some additives, however, that are very unique in chemical composition and can often be an aid to identify similar paint systems. A concise monograph on coatings additives is recommended as a useful guide for paint analysts [13].

Paint chips or smears may be examined for comparison and/or identification purposes. Comparative analysis subjects two or more samples from different sources to the same rigorous analytical testing to determine if there is a common origin. For example, how does the paint smear that is transferred to a victim's clothing in a hit-and-run compare to paint obtained from a suspect vehicle? By contrast, the purpose of the identification process is to identify the chemical composition of the paint particles with as much certainty as current analytical methods and instrumentation will allow.

The analysis of paint chips by the crime laboratory usually includes microscopy; infrared spectroscopy (FTIR);

some type of elemental analysis, such as energy dispersive X-ray analysis (EDX); and quite often pyrolysis gas chromatography-mass spectrometry (PGC-MS). For the forensic paint examiner, other than visual examination, a microscopic analysis is the first approach to identifying the sample.

Optical and stereo microscopic techniques are extremely important in paint examination because they determine the number of paint layers, the thickness and color sequences of the layers, and pigment features such as texture, particle size, shape, and distribution. IR is also widely used to identify the polymeric resin (binder) and, depending on the instrumentation, provide a great deal of information regarding pigment identification. The greater the analytical capability of the laboratory, the more data is available to determine with a great deal of certainty whether the paint recovered from a crime scene is different from (or similar to) that of suspect samples.

Analyzing automotive paint chips is, in some ways, easier than analyzing other types of paint (such as architectural) that are found at crime scenes because of the multilayer nature of automotive coatings. For automotive systems, it is fairly typical for automotive original equipment manufacturers (OEMs) to use four distinct paint layers particularly for the steel body frame. There is an electrocoat layer, a primer layer, a colored basecoat layer, and a final clear topcoat. Each of these layers is distinct in terms of resin and pigment composition. This layering, along with the thickness and subsequent identification of each layer and the components in each layer, can become very useful in determining a possible make, model, and color of a suspect vehicle or in determining a match to a suspect vehicle. Analysis is conducted on all the layers: clearcoat, colorcoats, primer-surfacer, and electrocoat.

Sometimes unique colors and/or pigments in the primer-surfacer and colored basecoat layers can provide the analyst with distinct and discriminatory information. Color becomes important for the forensic paint examiner if a known and questioned sample is present. There are hundreds of different colors and shades used in the paint industry and a spectrophotometric analysis can often shed a great deal of information about the samples. Microspectrophotometers provide an objective color measurement as opposed to subjective visual comparisons. Spectrophotometers measure the light that is transmitted, reflected, or absorbed by a sample in the visible and ultraviolet ranges.

Consumer demand has driven the pigment industry to develop many unusual and special effect pigments. This is particularly noticeable in the automotive industry. There are the conventional or absorption pigments where light is absorbed and scattered. A completely different optical behavior can be observed with the group of effect pigments including pearl luster and metal effect pigments. Metal effect pigments consist of small metal platelets (for example aluminum, titanium, copper) which operate like little mirrors and almost completely reflect the incident light. The dominant class of pearlescent pigments is based on platelets of natural mica coated with thin films of transparent metal oxides [14].

Interference and angle-dependent color effects can also be achieved by layers or particles based on liquid crystal polymers. Another new technology involves the use of holographic pigments that are prepared from grinding of holographic films to small particles. All of these new technologies place an added level of difficulty on the analyst but they also provide some discriminating characteristics for pigment and layer analysis. This can be a significant advantage for the forensic paint examiner. It is also wise for the paint examiner to study the pigment paint literature for developments in this area.

Pyrolysis gas chromatograph and PGC-MS analysis can be a valuable tool for comparing many paint formulations. Very small paint chips can be used (on the order of a few micrograms). As the chip is heated the polymeric decomposition products are recorded. This pattern of decomposition product (or pyrogram) can often be used to compare paint samples and distinguish one from another. Pyrolysis techniques have been quite successful for acrylics in particular.

As technology has shifted toward lower-molecular-weight materials, waterborne and powder-coating systems, there have been an increasing number of additives used in formulating. Newer pigment technology, particularly in automotive coatings, also places an increasing burden on analysts.

Forensic paint analysts are faced with grave responsibilities in analysis and interpretation of data. Scientists must be extremely well trained and capable in the area of analytical techniques and also must be qualified paint examiners, possessing a fair amount of knowledge regarding paint composition and the raw materials used within the industry. It is a serious responsibility because the analytical results used in a courtroom may significantly affect the outcome of a trial and a person's life.

The most ideal situation occurs when there is a physical match between a paint chip recovered from a crime scene and a suspect vehicle. The majority of paint analysis will not be sufficiently different or unique such that the sample can be matched to a single source.

For more information regarding the forensic analysis of paint, one should refer to the following: ASTM Practice for Receiving, Documenting, Storing and Retrieving Evidence in a Forensic Laboratory (E1492) and ASTM Guide for Forensic Paint Analysis and Comparison (E1610).

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The Analysis of Coatings Failures

George D. Mills[1]

THE TESTING OF COATINGS ALWAYS HAS A RELA-lationship to coating failures, either directly or indirectly. Testing before failure helps to ascertain serviceability, establish the best formulation variables, maintain quality assurance of coating products during manufacture, develop storage and application parameters, ensure specification viability, and, in essence, prevent early failure. Testing after failure assists in determining cause, hopefully prevents future coating failures of a similar nature, and aids in placing liability.

Failure modes run the full gamut. Coating failure can originate from within, as with deficiencies in a coating's formulation or its manufacturer. Anomalies in the coating's film-forming chemistry from competing atmospheric side reactions are very common with some urethanes and epoxies. Failures can originate external to the coating material from improper specification, inappropriate or inadequate surface preparation, and application deficiencies. When a failure occurs and is investigated, the coatings practitioner must maintain an open mind. Often there are multiple causes impacting the failure.

The analysis of coating failures should follow a systematic program based on the "scientific method." Briefly this translates to (1) investigate, (2) hypothesize, (3) test, and (4) conclude or reconsider. Test programs after failure are often a part of the failure analysis process and have the purpose of establishing viability of a proposed failure mechanism. Designing the test and evaluation program requires knowledge of the total process from specification to paint manufacturing to paint application. In part, it requires knowledge of the laws of physics and chemistry that are controlling what is happening at interfaces. The coating system contains many types of interfaces including the substrate/coating interface, emulsion resin particle/carrier surfaces, inter-coat interfaces, and the interfaces between the pigments and binder in the coating formulation. The chemistry and physics of solutions controls apparent viscosity and can impact osmotic failure modes. Polymer curing and weathering reactions, corrosion, and dimensional stability after cure are just a few of the other sources of coating failures often reported. As a preliminary to designing test programs to determine failure modes, the investigator must appreciate not only the processes of surface preparations, cleaning, and pretreatments, but coating application techniques as well. He must be knowledgeable about the different types of coatings and their typical degradation and stabilization mechanisms.

Coating failures may manifest themselves as a change in physical or chemical properties. Changes in gloss, color, extensibility, chemical resistance, and vapor/gas transmission coefficients are common problems. Failures associated with delamination of a coating from its substrate are usually classed as "adhesion" failures, although they are often a delamination through a weak boundary layer (WBL) near the interface. Osmotic activity from solvents or coating constituents within the film or salts beneath the film is a common failure mode in some environments. Under film corrosion is often considered as a coating failure and may result in substrate damage.

Coating failure analysis is extremely important for various reasons. One of the most important is simply to "ensure" that the failure does not happen again. While this sounds noble, the experience of most investigators is to the contrary, for one sees the same problems occur repeatedly. Paints and coatings are very sophisticated chemical systems. Since all of the natural forces impacting the chemistry and physics of the system are operative, the total picture is seldom known. Most often, a very naive conception of the situation is developed and action is taken for one particular reason while failing to consider a multitude of other less familiar causations.

Truly successful investigations of coating failures necessitate knowledge of the coating system's chemistry and the many applicable evaluation and test procedures available. To appreciate which test regime would be appropriate for a specific failure situation, the investigator must understand much about the coating itself. This includes knowledge of the components formulated into the coating, its curing chemistry, the chemistry and physics of interfaces associated with the coating, and any interfering and competing atmospheric side reactions. These side reactions include the impact of ambient application temperature and relative humidity as they impact curing, inter-coat adhesion, and the total coating matrix as applied. One must consider application equipment and procedures, with a host of related potential problems. This might include considerations such as off-ratio mixing (including "zone curing" from insufficient mixing), use of thinners that are non-solvents or that may be contaminated with water from storage outside. There is the possibility that paint formulation and manufacturing problems are potential typical sources of coating failure problems.

Designing the proper test regime before a coating failure occurs is very important. It is difficult, if not impossible, to assess all of the variables that will be seen in the field after the coating is applied. Reconstruction of a failure situation is even more difficult, and it is usually impossible to match the original application situation totally.

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This is particularly true in off-ratio mixing problems or the problem of "zone curing". Zone curing occurs when the two-part coating is not mixed totally. For epoxy systems cured through amino functional curatives, over stirring of the curative where air is allowed to be drawn into the coating material, carbon dioxide (an acid gas) in the air is reacted with the curative. This effectively blocks the curative and does not allow reaction with the epoxy. The final "hardened" epoxy will display various degrees of cure even when the prescribed "mixing ratio" was followed. Advanced instrumental techniques using cryotrapping of pyrolyzed polymer fragments followed by gas chromatography using a mass spectrometer as a detector have proven extremely helpful [1].

The design of a test program to demonstrate feasibility of a particular failure mode is best accomplished by considering five basic questions. These questions guide the investigator through the logic that assists one in understanding the potential failure modes. The basic questions are as follows:

1. What is the actual coating failure?
2. What is the coating system?
3. What was the desired property of the coating that failed?
4. How was the coating applied?
5. What evidence is presented by the samples of failed coating?

There are many chemical instrumental techniques of analysis available to the investigator. The data from some of these laboratory instruments allows one to know the actual coating failure. The task sounds so simple, but it is remarkable that past experience has shown that many of the failure, are not as first thought as will be pointed out in the ensuing material. To aid the reader, a few of the instrumental analysis techniques and their common abbreviations along, with selected web addresses, are given below.

DSC = Differential Scanning Calorimetry; http://www.colby.edu/chemistry/PChem/lab/DiffScanningCal.pdf

DFT = Dry Film Thickness; http://www.icc-astec.com/faq/coverage-solids.php

EDX = Energy Dispersive X-ray; http://www.eusoftcomp.net/FILES/edx_technique.pdf

FTIR = Fourier Transform Infrared Spectroscopy; http://www.siliconfareast.com/FTIR.htm

GC/MS = Gas Chromatography Mass Spectrometry; http://www.scientific.org/tutorials/articles/gcms.html; http://www.shimadzu.com/products/lab/ms/tutorial/oh80jt0000007e8m.html

GPC = Gel Permeation Chromatography; http://biomed.tamu.edu/MTE/files/gpc.pdf

HPLC = High-Performance Liquid Chromatography; also called High Pressure Liquid Chromatography; http://en.wikipedia.org/wiki/High-performance_liquid_chromatography

IC = Ion Chromatography; http://www.ceram.com/testing-analysis/techniques/ion-chromatography-ic/

Methyl Ethyl Ketone (MEK) = rub test; http://www.trl.com/services/materialstesting/paint_solvent.html

ASTM D4752 = Quality Assurance/Quality Control QA/QC; http://www.ct.gov/dep/cwp/view.asp?A=2715Q&=324958

SEM = Scanning Electron Microscopy; http://www.charfac.umn.edu/sem_primer.pdf

TGA = Thermal Gravimetric Analysis; http://www.eaglabs.com/techniques/analytical_techniques/tga_dta.php

UV-Vis = Ultraviolet-Visible: spectroscopy; http://www.standardbase.hu/tech/FinalHUTechUV-Vis.pdf

Weak Boundary Layer (WBL) = http://web.mst.edu/~wlf/Adhesion/Good.html

X-ray diffraction (XRD) = http://web.pdx.edu/~pmoeck/phy381/Topic5a-XRD.pdf

X-ray photoelectron spectroscopy (XPS) = auger; http://en.wikipedia.org/wiki/X-ray_photoelectron_spectroscopy

WHAT IS THE ACTUAL COATING FAILURE?

A coating failure exists when a coating fails to accomplish all of its intended tasks during its engineered design life (EDL). Usually, a failure in a particular primary property prompts the investigation and leads to the declaration that a coating failure exists. The first step in analyzing a failure is to clearly define the problem. While this appears at first glance to be an easy and straightforward task, it is not. A typical example is the mistake of identifying a delaminated coating automatically as lost adhesion. Loss of adhesion, by definition, is a delamination between two dissimilar surfaces, as with a primer and substrate or two coats of paint. In contrast, a cohesion failure is delamination through one material in the coating system. This results in splitting a layer leaving two surfaces that are the same material. One must appreciate that a splitting layer may be only a few molecules thick and appears to be a true adhesive failure.

There can be numerous reasons for a coating to break away from its substrate. While adhesive loss is possible, cohesive delamination within a WBL is very common. A good example is a coating applied over improperly prepared zinc galvanizing where cohesive failure occurs in the zinc oxide-zinc carbonate layer and is automatically written off as a saponification problem, even though the coating may not be susceptible to (or capable of) saponification. Another very common cohesive failure is the apparent delamination of an amine-cured epoxy applied over an amine carbonate that has formed on (or exuded from) an earlier applied epoxy coating. This cannot usually be seen with the unaided eye. Splitting within a "transparent" layer

near the interface will appear as if the problem is adhesive rather than cohesive failure. Interrogation of the coating interfaces by the proper instrumental technique is the only way to determine the locus of failure in delamination failures.

Many tests associated with coatings may be brought to bear in providing answers. While most of these tests are established ASTM procedures, some are related to task-specific, chemical analysis. These include auger spectroscopy, X-ray photoelectron spectroscopy (XPS), and other surface analysis techniques that are limited to "seeing" only the outer few angstroms of the surface. Ion bombardment, which ablates the surface, allows "seeing" an elemental analysis as a function of depth into the outer layer. Techniques such as energy dispersive X-ray (EDX) will evaluate the surface but are much more energetic, thus giving an average elemental analysis much deeper into the sample being evaluated [2].

Osmotic blister formation is another area often misunderstood. The analysis of osmotic paint failures is addressed in depth within this book. Osmosis requires one solvent (by definition, the specie present in the greatest concentration) and one or more solutes. Analysis of the blister fluid is required to determine the source of the driving force. While water is often the source of solvent with inorganic salts or dissolvable organic solutes, other organic solvents are seen in some industrial tank-lining problems. Analysis of the blister fluid is best accomplished by gas chromatography/mass spectrometer (GC/MS) for organic solutes [1] and ion chromatography or EDX (after evaporation) for inorganic solutes [2]. To the contrary, "blister-like" formations in inorganic zinc-rich or flame-sprayed metallic coatings may look like osmotic blisters, but they are usually caused by the production of powdered corrosion products (typically oxides and/or carbonates) under or within the film [3]. It is safe to say that the problem cannot be solved and proper liability placed until the true coating failure problem has been identified.

WHAT IS THE COATING SYSTEM?

Failures are often related to the generic type of coating under investigation. As such, the failed coating should be identified as a preliminary step in understanding the potential failure modes that exist leading to the failure. Alkyds have failure modes different from acrylic latex systems. Epoxies will often fail differently from urethanes. Alkyds over vinyl primers are susceptible to differential water vapor transmission problems causing alkyd delamination from the vinyl in damp climates. Moisture-cured systems such as urethanes, epoxies, and ethyl silicate zinc-rich systems when applied in very dry atmospheres cannot cure properly. Urethanes and some latex systems present problems in wet atmospheres.

Although a coating is any material applied to another surface, each coatings practitioner will have a view of coating systems shaped by his/her experiences. While most coatings are paint-like in nature, many have strikingly different appearances and characteristics with correspondingly different failure modes and different required test regimes. The coatings manager at an automobile factory might work with inorganic metal pretreatments, electrodeposited primers, and robotically applied color coats with wet-on-wet ultraviolet (UV)-resistant clear topcoats followed by water-repellant surface modifications. The pipe corrosion specialists will encounter conventional liquid paints, fused powders, flame/arc-sprayed metallic powders such as zinc, aluminum, or high alloys, and/or plastic tapes wrapped around the pipe with or without primers for external protection. Internal pipe coatings may be the conventional liquid and powdered coatings as well as thin cement linings like those found in many potable water supply lines or fused polyethylene mixtures. Because of this great diversity, the coatings analyst will address coating failures of many generic types of films including organic, inorganic, and metallic.

Paints form the largest subgroup of coatings and, as such, will be the focus of this section. Analyzing coating systems before and after failure requires many different testing procedures. Many of these standardized procedures can be found in Volume 6.01 through 6.04 of the *Annual Book of ASTM Standards* [4]. To be efficient, the investigator must have knowledge of the paint formulations of many generic types. Knowledge of the polymer's typical failure mechanisms, individual polymer chemistries with their respective degradation mechanisms, and typical stabilization methods are also very helpful [5]. An efficient investigation requires an appreciation of the tools and instrumentation that can be brought to bear and is tremendously important in determining the testing regime best suited to a particular type of failure problem. This includes knowledge of the capabilities and, equally important, limitations of the analytical instruments being used. One must be able to interpret and challenge test data when necessary. It is this necessity that requires knowledge of the chemistry and physics operative for the system under investigation.

Typically, paint may be considered as being composed of four "subsystems," any one (or combination of them) may produce a coating failure. These are (1) the resin or binder system, (2) the pigment system, (3) the solvent or carrier system if a liquid, and (4) the additives package.

The resin or binder system holds the pigments together and provides physical characteristics such as electrical resistance, flexibility, water and gas permeability resistance, adhesion, etc. The pigment system serves to provide coating strength, vapor transmission resistance, anticorrosive properties at a metal interface, abrasion resistance, color and restricted light transmission as well as other film property enhancements. For less than 100 % solids systems, the carrier system is usually a solvent or dispersing media. For 100 % solids liquid coatings, the dispersing media may be air or the pressure from an airless application system. For powder coatings, super dry air is the delivery system, transporting the fluidized powder through the delivery lines.

The additive package is meant to produce specific effects to the coating system when included in low concentrations. Additives may address potential problems with the pre-applied paint "in the can" or address potential film problems after application. Coating failures may originate from problems associated with quality control of the paint's manufacture as well as problems associated with long-term storage or application. Each type of coating will have some characteristic failure modes, although certain modes will be common to all.

Failure Modes Associated with a Generic Type of Coating

Failure modes tend to follow generic types of coatings. In a very broad sense, coatings may be grouped into three categories based on the final film. These are coatings with organic binders, those with inorganic binders, and those composed of metallic films. The largest category of coatings is those utilizing an organic binder. Organic binders use polymers based on carbon as the primary atomic makeup of their backbone. The paint film at application includes polymer precursors using functional groups such as epoxies, urethanes, vinyls, acrylics, and alkyds. These must polymerize to reach some high molecular weight at which they are capable of forming protective films. Generally, inorganic coatings are those that utilize elements other than carbon for forming a film. These may be silicates, sulfates, or cementations coatings based on calcium. As a coating, each will have some typical failure modes. Metallics may be very thin films used on plastics for affecting gas molecule transmission, esthetics, and abrasion resistance characteristics. They may be thick as with galvanizing or flame/arc-sprayed metallics used for corrosion protection or thin as the aluminum coatings on a potato chip bag.

ORGANIC RESIN BINDERS: POLYMERS BASED ON CARBON

Paints and coatings using organic binders are by far the largest category and will provide the greatest challenge to the failure analysis investigator. These will include binders derived from vegetable oils, petroleum, and cellulose. They can be separated further into groups based on their curing functionality or their polymer origination such as epoxies, urethanes, alkyds, acrylics, chlorinated rubber, or vinyls. They may also be classed by their dispersion system such as solvent, emulsion, powder, waterborne, or 100 % solids.

Organic resin binders will utilize some mechanism for producing the protective film. This film forming/curing mechanism is a potential source of failures. A failure may manifest itself as a film with poor flexibility, poor weather ability, poor chemical resistance, adhesion deficiency, or a host of other shortcomings.

The formation of a paint film may come about by various mechanisms, each having distinctive failure modes. Some typical examples include (1) lacquers, (2) oxidative binders requiring oxygen from the atmosphere, (3) moisture-cured binders requiring water molecules from the atmosphere, (4) chemically reactive cross-linking binders, (5) heat-activated binders, and (6) non-thermal, high-energy cured binders such as UV initiated curing and electron beam.

Lacquers are coatings containing polymers dissolved in a suitable solvent system that evaporates to yield a film. While these coatings are called "lacquers" in the United States, in Europe and other parts of the world, the word "lacquer" is often used interchangeably with the word "paint." Film testing may address sanding characteristics, abrasion resistance, drying times, gas or water vapor permeability, gloss, and color retention, among other film properties. With essentially no chemical cross-linking occurring after application, the solids deposited on each coat will be determined by the percent of dissolved solids. Unfortunately, the viscosity increases as the dissolved solids increases. As such, the maximum lacquer viscosity that allows application will dictate solids content. Since this is related to the polymer's average molecular weight, which must be high for toughness and strength, films of low dry film thickness (DFT) are often seen, and the applied solids will be low. Lacquer film properties are strongly impacted by the solvent system, humidity and other ambient conditions, the application methodology used, and many other factors. Investigation of these type failures, as with most, requires inquiries as to application conditions.

Common failure modes encountered are often associated with thin films and the water susceptibility of the "tailing solvents" used in the formulation, occluded water caused by the use of fast evaporating active solvents producing fogging and cloudiness at application, and others. In acid-modified solution-vinyl systems, reaction with basic pigments will cause viscosity increases and possibly gelation in the can during storage. Other problem areas leading to failures include the "strength" of the solvent system, temperature of the coating solution at application, interaction of solute binder polymer with certain pigment particles, and interaction of some pigment particles with other pigment particles.

Typical failure modes for lacquers include production of cloudiness during application (blushing), use of improper (non-solvent) thinner, "fisheyes" (a surface tension problem), lifting of solvent-sensitive undercoats, and delamination from overcoating sanding sealers containing excessive sterates, among others. Coating softness is often related to the inclusion of non-solvents entrapped in the film if their evaporation or migration rate is less than the true solvents for the coating system. To address this problem, the coating formulation will often have a small "tailing" of slow-evaporating true solvent to allow the escape of these non-solvent diluents.

Because of the large amounts of solvents required and the typically low solids content, this type of coating system is not considered to be environmentally friendly. As such, lacquers are not as popular as they were in the past. Most states have enacted laws that control the maximum value of the volatile organic content (VOC) of the paints, and this has greatly limited their use.

Oxidative binders are polymers that usually require the pressure of atmospheric oxygen to cross-link sufficiently to form a strong film. Paints based on unsaturated vegetable oils such as linseed, soya, tung, tall oil, and others as well as modified vegetable oils, such as alkyds, fall into this category. These coatings require metal catalysts called "dryers" to be included in the formulation. The most common metallic dryers are lead, cobalt, manganese, iron, barium, calcium, zirconium, zinc, cerium, and vanadium. To allow solubility in the paint binder these metals, typically, are added as the octoate. An excess of cobalt dryer in a batch of alkyd paint may result in a surface wrinkling upon curing such as seen in Figs. 1 and 2. These dryers assist in the curing mechanism by increasing the coating's ability to react with atmospheric oxygen. A common failure mode for some alkyd coatings containing organic pigment would be a slow or nondrying paint after application. This occurs when dryers are either left out at manufacture or prematurely bound to a formulated pigment in the coating during can storage. In-can aging will allow adsorption onto the organic pigment particles, causing a loss of activity before application. Some carbon blacks are particularly susceptible to binding

Fig. 1—Alkyds that contain an excess of the cobalt metallic dryer may develop "wrinkles" on its surface.

some dryers. This leads to slow or retarded drying of some black paints that have aged. The in-can age is often available from the coded paint's batch number stamped on each can. The paint manufacturer, usually, will explain how to read the code.

Increased viscosity within the can is often caused by reaction with the oxygen contained in the air space above the coating. Frequently, with highly reactive oxidative binders, a small amount of inert gas may be placed in the head space of the can prior to shipping. Skinning and gelling are problems frequently encountered with this type of curing system. Retardation is controlled by the use of additives such as volatile ketimines. These volatile inhibitors interfere with the cross-linking mechanism, thus extending the life of the coating material after the can has been opened. Often, upon reopening a can of an oxidative type of coating, one will notice that a vacuum has developed. This is due to the reaction with (and consumption of) the oxygen that was in the air in the head space of the can.

Moisture-cured binders constitute a class of organic polymeric materials that require water vapor from the air to cause polymerization. Curing problems can arise with these when the application is done in closed areas with dehumidification (DH) equipment. While the most common of these are the moisture-cured urethanes, epoxies cross-linked by ketimines form another important class of moisture-cured epoxy coatings. Inorganic silanol binders, found in many zinc-rich systems, must have water to complete the hydrolyzation required in forming the cured inorganic silicate binder. Typical failure modes include application of the coating in conditions providing insufficient moisture to complete the cure. Application to surfaces that are damp or excessively wet can create bubble formation in urethanes. Overcoating inorganic zincs before complete hydrolyzation interferes with curing by stopping the reaction with moisture. This produces a zinc-rich primer layer with low tensile strength. Such films will often fail by cohesive failure (splitting) within the inorganic layer, especially after application of an epoxy that shrinks slightly on curing.

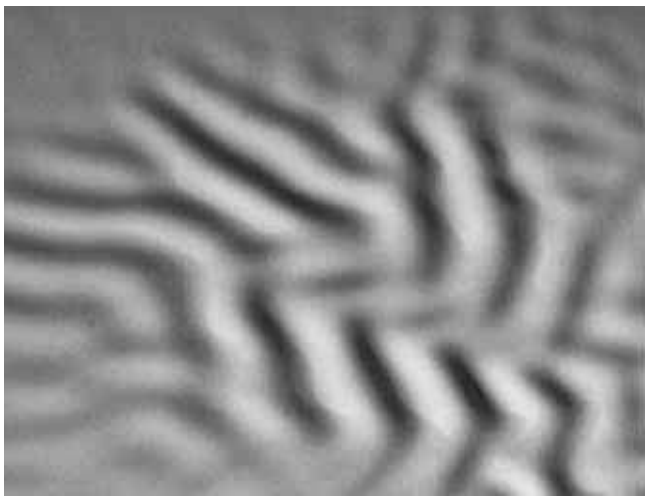

Fig. 2— The microscopic view of an alkyd having an excess of cobalt dryer additive seen in Fig 1.

Failures associated with thinners that contain water as a contaminant present a different kind of problem. For urethane coatings, inclusion of excessive water in the coating matrix will generate gas bubbles of carbon dioxide caused by reaction with the isocyanate groups. In a worst case, the applied coating will be rough with bubbles through the film. In slight contamination cases, this will be evidenced by viewing a chip of the coating from the side through a microscope. Small bubbles will be seen through the coating thickness. When the bubbles are mostly located at or near the interface, there is probable cause to suspect application over a damp surface. Water picked up on the pigmented side of a two-part urethane during the pigment-grinding process during manufacture is a common problem. A Karl Fischer water analysis of the polyol side may reveal the source of the problem.

Water contamination introduced into an ethyl silicate binder can cause premature gelation and shortening of the pot life. Water reaction of zinc and aluminum-metal-containing coatings still in the can often produces gas of sufficient pressure to explode the container.

Chemically reactive cross-linking binders include all two-part systems. This includes epoxies and urethanes that have appreciable reaction rates at room temperature as well as single-package, cross-linking systems that require heating or some other energy source to increase the reaction rate significantly and allow a cure to be attained. Some systems will contain all the reactive polymeric binder precursors

Fig. 3—Large natural gas tanks that were painted during cold weather.

that cross-link with each other to produce the final film. Some systems may generate the required energetic cross-linking specie by a reaction brought about by an outside energy source such as UV radiation, electro-deposition, or high-energy electron beams.

Ambient-cure, two-component, or catalyzed binders such as epoxies and urethanes require a proper mixing ratio to allow the finished film to have its desired properties. Improper ratio mixing can lead to a host of final film problems. These problems include inadequate curing, brittleness, loss of extensibility, loss of chemical resistance, early extensive chalking, and many more. Off-ratio coating systems may be investigated using GC/MS pyrolysis [1].

Epoxies are often cured by amine functional polyamides, amine adducts, or aliphatic amines. Polyamides, being manufactured from long-chain fatty acids, are very aliphatic in nature and, typically, not particularly soluble in the "more aromatic" epoxy side. Because of this poor solubility, it is often necessary to allow extra time after mixing for the reaction products to gain solubility characteristics more closely related to each other. This extra time is called the "induction period" or "sweat-in time" and allows time for the two resins to partially co-react. The partially reacted resin solution eventually changes the solubility characteristics of the binder system sufficiently to completely solubilize all resin components. A failure to reach complete solubility will lead to "zone curing" with macro islands of un-reacted polyamide and potentially un-reacted epoxy resin. Additional failure modes include osmotic blister formation (where the low molecular weight amine is the solute, with condensed water being the solvent), increased amine carbonate formation and exudation to create intercoat delamination problems, film brittleness, poor weatherability, and others.

Application of epoxies cured with amine and polyamide systems in cold weather can present future delamination problems. In cold weather, when the epoxyamine curing reaction slows down, the amine reaction with carbon dioxide and water vapor from air does not slow very much. The formation of an amine carbonate "bloom" develops on the coating surface. See Figs. 3–5.

Additional amine carbonate within the coating matrix formed during spray application exudes to the surface over time. This leaves a weak boundary layer on the surface. When overcoated, the insoluble "greasy" amine carbonate

Fig. 4—Tank after one year showing mildew on areas of constant moisture condensation.

Fig. 5—The urethane top coat over the epoxy primer is peeling as the result of applying coating over the thin layer of amine carbonate formed (and exuded) after primer application.

will not allow adhesion of the next coat and usually results in delamination in less than a year. The interface will be moisture sensitive and potentially provide the solute for osmotic blister formation. The author has found a simple test to evaluate for the presence of the amine carbonates. This is done by applying a drop of 6 *M* hydrochloric acid to a suspected surface while watching the edge of the drop under a microscope. The HCl will liberate the carbon dioxide at the edge of the "wetting front" as the droplet wets the surfaces. The bubbles of gas can be seen in the edge of the drop of liquid. The experiment should be conducted under a microscope since the reaction is rather fast and because often only a small amount of gas is liberated. The gas may present itself as a tiny bubble within the drop of acid solution. To test the amine side of the curing agent for preexisting carbonate salts, add about 1 ml of the resin component to a test tube. Tilt the test tube at about 45°, add a drop of the 6 *N* HCl, allowing it to run down the inside of the tilted tube, and note the production of any bubble formation of carbon dioxide at the acid solution/resin interface. The amount of foam produced is a quantitative indication of the amount of carbonates existing. Grinding pigment into the amine side, in open tanks, often introduces the carbonate and causes variability in the degree of cure of the catalyzed coating.

Heat-activated binders have a cross-linking reaction rate that is too slow at room temperature to allow complete cure. These systems require heating to provide a forced cure. This is true for liquid systems as well as for most thermoset powder coating systems such as fusion bonded epoxy (FBE) coatings. Typical failure modes include abnormal brittleness, discoloration, lack of design physical properties, lower chemical resistance, and other problems. Causes may stem from formulation problems such as batch-to-batch variation in catalyst level or incorporation, as well as problems associated with variable temperatures within the pass-through ovens or heating equipment. Low temperatures caused by variations in metal heat capacity due to variations in metal mass of a coated part are seen often in powder coating systems as producing curing anomalies. Since the cured coatings will typically have elevated glass transition temperatures, T_g, the differential scanning calorimeter (DSC) is the instrument of choice in determining quality of cure [6].

Non-thermal, high-energy-cured binders require an energy source other than heat. These coating systems are typically employed on fast-moving, automated industrial lines. The coatings include both ultraviolet radiation curing systems as well as electron and other high-energy beam curing. Because the energy source must be "felt" through the polymer layer, UV-cured systems must be fairly transparent to the energy source and preferably have little or no pigmentation. However, UV-curable colored inks and coatings are commercially available. This usually necessitates that the films be of low DFT.

INORGANIC BINDERS—THOSE BASED ON NON-CARBON POLYMERS

Inorganic coatings are those that do not rely on carbon as the primary atomic composition of the polymer. These include those systems that ultimately end up with an inorganic binder after application. The most common include zinc-rich systems using alkali silicates as the binder. Generally speaking, inorganic coatings are formed from the oxides of specific elements. The silicates are formed from the oxides of silicon. Cement coatings and linings for water pipes rely on the oxides of calcium or variations thereof. Some high-temperature coatings used in flue gas desulfurization stacks are based on calcium sulfate.

A different class of inorganic coatings is those that are chemically reacted onto a metal surface. These include the colored anodized coatings commonly seen on aluminum window and door frames, precipitated zinc and iron phosphate coatings used as anticorrosives on pretreated steel and acid phosphate treatments to zinc and galvanized surfaces, among others. Typical failure modes with these types of coatings will include under-film corrosion and spalling of the coating, especially with cement that has become carbonized from reaction with carbon dioxide and, therefore, lacks the higher pH required to disallow corrosion of embedded steel. Corrosion testing methods such as given in ASTM B117 "Practive for Operating Salt Spray (Fog) Apparatus" (see Table 1) are used often to determine coating quality.

Precipitation-type coatings are usually done from a water solution. Because of this, the surfaces must be able to be wet-out by the water solutions. A typical problem is "spottiness" caused by incomplete thermodynamic wetting of the substrate. This lack of wetting disallows water-based chemical reactions that must occur at the metal interface. The reason for a lack of wetting is usually from oil or other low-energy contaminants on the surface. Investigation of the pre-cleaning system is indicated in these cases. Surfactants are usually added to overcome this problem, but these may then cause an even worse problem if they are not totally removed. One must remember that surfactants are called "surfactants" because of their ability to displace, usually thermodynamically, most adsorbed species on the surface of the substrate. When overcoating a substrate that has been wet with surfactant, these surfactants must be displaced. This can often be difficult or impossible and often leads

TABLE 1—Frequently Used ASTM Standard Documents for Evaluating Paints For Specific Properties

Designation	Document Title
B117-09	Practice for Operating Salt Spray (Fog) Apparatus
D522-93a(2008)	Test Methods for Mandrel Bend Test of Attached Organic Coatings
D523-08	Test Method for Specular Gloss
D570-98(2010)	Test Method for Water Absorption of Plastics
D610-08	Practice for Evaluating Degree of Rusting on Painted Steel Surfaces
D660-93(2005)	Test Method for Evaluating Degree of Checking of Exterior Paints
D661-93(2005)	Test Method for Evaluating Degree of Cracking of Exterior Paints
D662-93(2005)	Test Method for Evaluating Degree of Erosion of Exterior Paints
D714-02(2009)	Test Method for Evaluating Degree of Blistering of Paints
D772-86(2005)	Test Method for Evaluating Degree of Flaking (Scaling) of Exterior Paints
D869-85(2011)	Test Method for Evaluating Degree of Settling of Paint
D968-05(2010)	Test Methods for Abrasion Resistance of Organic Coatings by Falling Abrasive
D1014-09	Practice for Conducting Exterior Exposure Tests of Paints and Coatings on Metal Substrates
D1186-93	Test Methods for Nondestructive Measurement of Dry Film Thickness of Nonmagnetic Coatings Applied to a Ferrous Base Withdrawn 2006-Replaced D7091
D1200-10	Test Method for Viscosity by Ford Viscosity Cup
D1210-05(2010)	Test Method for Fineness of Dispersion of Pigment-Vehicle Systems by Hegman-Type Gauge
D1400-94	Test Method for Nondestructive Measurement of Dry Film Thickness of Nonconductive Coatings Applied to a Nonferrous Metal Base
D1475-98(2008)	Test Method for Density of Liquid Coatings, Inks, and Related Products
D1653-03(2008)	Test Methods for Water Vapor Transmission of Organic Coating Films
D1654-08	Test Method for Evaluation of Painted or Coated Specimens Subjected to Corrosive Environments
D2196-10	Test Methods for Rheological Properties of Non-Newtonian Materials by Rotational (Brookfield Type) Viscometer
D2243-95(2008)	Test Method for Freeze-Thaw Resistance of Water-Borne Coatings
D2244-09b	Practice for Calculation of Color Tolerances and Color Differences from Instrumentally Measured Color Coordinates
D2621-87(2005)	Test Method for Infrared Identification of Vehicle Solids from Solvent-Reducible Paints
D2697-03(2008)	Test Method for Volume Nonvolatile Matter in Clear or Pigmented Coatings
D2832-92(2005)	Guide for Determining Volatile and Nonvolatile Content of Paint and Related Coatings
D3363-05	Test Method for Film Hardness by Pencil Test
D4060-10	Test Method for Abrasion Resistance of Organic Coatings by the Taber Abraser
D4212-10	Test Method for Viscosity by Dip-Type Viscosity Cups
D4214-07	Test Methods for Evaluating the Degree of Chalking of Exterior Paint Films
D4400-99(2007)	Test Method for Sag Resistance of Paints Using a Multinotch Applicator
D4417-03	Test Methods for Field Measurement of Surface Profile of Blast Cleaned Steel
D4541-09e1	Test Method for Pull-Off Strength of Coatings Using Portable Adhesion Testers
D5179-02(2008)	Test Method for Measuring Adhesion of Organic Coatings to Plastic Substrates by Direct Tensile Testing
D6037-96(2008)	Test Methods for Dry Abrasion Mar Resistance of High Gloss Coatings
D6577-06	Guide for Testing Industrial Protective Coatings
D7091-05	Standard Practice for Nondestructive Measurement of Dry Film Thickness of Nonmagnetic Coatings Applied to Ferrous Metals and Nonmagnetic Nonconductive Coatings Applied to Non-Ferrous Metals
G8-96(2010)	Test Method for Cathodic Disbonding of Pipeline Coatings
G14-04(2010)	Test Methods for Impact Resistance of Pipeline Coatings (Falling Weight Test)
G42-96(2003)	Test Method for Cathodic Disbonding of Pipeline Coatings Subjected to Elevated Temperatures
G95-07	Test Method for Cathodic Disbondment Test of Pipeline Coatings (Attached Cell Method)

to eventual delamination or water sensitivity. A short-term test frequently used is the Hot Water Boil Test. This is also called the "Crock Pot Test" since a standard kitchen electric crock pot has been found to work very well. Samples are cut from coated specimens that have been through the cleaning system. These are placed in the crock pot under deionized water for 24 h (or less, depending on type of coating), and the coating is evaluated against a standard of known cleanliness.

METALLIC COATINGS

Metallic coatings are very thin layers of pure metal, usually applied to a substrate for appearance, modification of wear characteristics, corrosion protection, or to disallow the transport of migrating gas molecules through plastic film. They are important because of their ability to modify physical properties of the substrate such as stopping the migration of oxygen, carbon dioxide, and other small molecules through plastics. An example most are familiar with is the shiny metalized coatings seen on food wrappers containing oxidizable vegetable oils. It is usually assumed that these shiny packages are for "aesthetics only," however, these thin metalized films serve to stop the migration of oxygen into the food package. With the trend to eat more unsaturated oils in our foods, the oxygen would react with the unsaturated bonds in the oils to produce a rancid taste. This is associated with the product being old and stale. The bad taste is due to the formation of aldehydes during the oxidation process. One might note that this chemical reaction is the same as the curing reaction of oil-based paints.

FAILURE MODES ASSOCIATED WITH THE PIGMENT SYSTEM, CARRIER SYSTEM, OR ADDITIVE PACKAGE

Some common failure modes associated with the pigment system include: heavy settling; flocculation; lack of wet-out during manufacture; insufficient grind or dispersion development; adsorption of additives such as driers, UV stabilizers, and surface-active agents during storage; and poor color stability with some pigments. Improper use of the anatase titanium dioxide can lead to chalking. Accelerated ageing tests of the formulated coating usually include storage at elevated temperatures with intermediate observations of settling and grind measurements.

The carrier system assists the binder system in forming a film and in developing adhesion during application. For liquid coatings that are sprayed, rolled, brushed, flow coated, or dipped, the viscosity must be within certain limits dictated by the application equipment, final film build desired, and ambient conditions. Additionally, there must ultimately be intimate contact between the binder polymer and the substrate. While this may appear to occur automatically and instantaneously, it does not. Development of adhesion between binder polymer and the substrate is a time-dependent function. Thermodynamic wetting is controlled by the energetics in existence between the actual surface encountered on the substrate by the coating system and the binder. We typically do not expect that the surface being painted to be coated with a material forming a WBL. Thermodynamic wetting is a necessary, though not sufficient, condition for adhesion. Unfortunately, since adhesion development is a dynamic process requiring time for the many "molecular realignments and adjustments" to occur as well as the displacement of molecular species lightly bound to the substrate, high-solids coatings with little or no solvent have a formidable job before them. Displacement of surfactant-type molecules at the interface will usually present a severe challenge and frequently present delayed adhesion failures.

There are always adsorbed species on the surface. Depending on the "sticking" strength of the adsorbed surface species, the binder may not make intimate (molecular) contact with the substrate as its viscosity is increasing to a gel. Adsorbed species include such molecules as vapor-phase water, oxygen, and other gases from the air, oily contaminants, and surfactants from cutting oils or coolants. In thermodynamics, this sticking is related to the heat of wetting. Failure to displace these compounds often results in eventual adhesion problems. One of the roles of the solvent is to assist in wetting out the substrate by displacing the adsorbed species followed by deposition by the binder. The coatings formulator will design the solvent system to assist the polymeric binder in displacing any interfering adsorbed species. But, since desorption/adsorption is a time-dependent process, extremely fast solvents and viscous, high-solids systems may not be able to respond in the time during which the polymer system cures and approaches a gel state. Increases in viscosity after application also present additional problems. There must be sufficient time for adhesion to develop between the binder polymer and the substrate. In some instances, changes to the polymer backbone have been done to produce a more negative heat of wetting [7]. The use of additional mechanical energy as from brushing is always helpful. It is for this reason that brush striping of welds in tanks and critical areas is often required prior to spray application of the first coat.

Solvents are the most common of the paint system carriers. Typical problems encountered might include use of the wrong solvent, allowing water to contaminate proper thinners that have been stored outside, transfer of solvents to oily or contaminated containers, etc. Water, which has been drawn into a solvent container due to temperature changes, is a common work-site occurrence.

Air suspension of powders is an example of a non-liquid carrier system. Powder coatings are usually applied electrostatically by fluidizing the powder with compressed air in a porous bottom chamber. The air-suspended particles are then drawn into an air stream via a venturi nozzle and transported to the point of application. Surfaces being powder coated may or may not be heated before application. With application to hot substrates, the powder melts and flows to produce a relatively thick coherent film. Depending on melt viscosity, flow characteristics, gel time, and thermal transfer characteristics of the melted polymer, air bubbles may be in evidence throughout the film. Due to the poor thermal transfer of the powder coating, the bubbles will be concentrated closer to the heat source, i.e., the substrate. These bubbles have not been a problem with FBE pipe coatings other than to cause a decrease in lateral cohesive film strength. Failure modes common to powdered pipe coatings stem from the use of wet air, plugged ventures and spray nozzles, and irregular heating of the metal surfaces for various reasons. Long-term adhesion problems may develop when application to the steel surfaces occurs at too low temperatures. High steel temperatures favor enhanced thermodynamic wetting although exceeding the

recommended application temperature of powdered coatings may result in foaming or loss of properties.

Variations in adhesion often follow variations in steel surface temperature. When powder coatings are applied to cold surfaces followed by heating through conveyor ovens, film build is usually limited to no more than 2 to 4 mils. Because of the short time allowed for flow and wet-out to occur, surfaces must be very clean and receptive to the applied coating. Typical failure modes are associated with surface pre-treatments, poor adhesion over unclean surfaces, contamination with other non-compatible or off-color powders from the same application system, compatibility with specific surface pretreatments, "wet" air used as the carrier, as well as curing difficulties resulting from catalyst deactivation or poor incorporation during extrusion. Gel particles may result with some catalyst systems during extrusion of the powder coating when the catalyst is "too reactive." This produces bumps in the otherwise smooth, glossy coating.

It is not practical to assume that the practitioner will have experience in all areas necessary to address the multitude of potential problems. Knowledge of application equipment, an in-depth chemical knowledge of the formulations and specific curing mechanisms and the physics of adhesion including the energetics controlling adsorbed molecular displacement, among other things, are required to thoroughly understand the potential problems one will encounter in the field. This should be developed through continued study, close observation, and by asking questions.

Tapes and extruded polyolefin thermoplastic coatings are popular pipe coatings. Sheeted rubbers find use on the risers of off-shore platforms and as acid tank linings. These will have specific failure modes. Rubber must be vulcanized in ovens after application to the tank wall or pipe. Failure modes usually will be associated with the improper cure of the polymer. This could stem from catalyst inactivation caused by the use of improper curing temperatures. Tapes of PVC with various types of adhesive binders are popular pipe coating materials. These may be applied in the cleanliness of a factory or as a "railhead operation" at the point of pipe construction or over the ditch. Extruded polyethylene and polypropylene pipe coatings are usually applied in a factory setting. Sheeted rubber coatings are frequently applied to the interior of carbon steel tanks that will see acid service. This is done both in the fabrication facility and in the field when it is possible to provide sufficient heat to cure the vulcanizable adhesives and coatings used. A common problem often encountered with these systems is the inadvertent inclusion of air bubbles or air pockets under the coating material. Bubble inclusion followed by eventual under film corrosion and perforation of the steel is a major failure mode for this type of coating.

Was the Specified Coating Material Used?

Often it is necessary to determine that the specified coating was used. Typically, Fourier transform infrared (FTIR) analysis of the binder is the analytical method of choice due to the widespread availability of the instrumentation. There is often considerable difficulty in gaining a positive identification of the coating due to interference from the pigments that produce an instrument response added to that of the polymer. The presence of silicates in paints is very common. A silicate peak often obliterates an informative section of the FTIR scan used to identify the polymer in question. Additional problems can stem from the specific technique used. The use of a "diamond anvil" attachment to a FTIR microscope has proven very beneficial in getting good polymer scans in the presence of interfering pigments but on rare occasions introduces some uncertainty when the binder is not totally homogeneous or well dispersed. An expected peak may appear to be missing. A good example is the presence of a crystalline, non-soluble cross-linker containing the cyano functional group in a fusion-bonded epoxy powder coating that is not seen using the FTIR diamond anvil in microscopic transmission mode but that is seen using the typical FTIR attenuated total reflectance (ATR) mode of surface analysis. GC/MS techniques provide a definitive analytical technique for identifying the coating used years after an application [1].

Was the Coating Material Properly Formulated and Manufactured?

Determining the "as applied" quality of a coating years after application can be a difficult task in some respects. On the other hand, it is usually surprising to most that the solvents used in a coating typically remain in the applied coating material for many years. A good example is the trapping of alcohols in cured epoxy coating systems for years after application. Normal-butanol, a very common solvent used in epoxy-polyamides formulations, can be extracted three to five years after application. High-molecular-weight oxyalcohols and glycols are also present for long times and are often found as the solute in an osmotic coating failure. Gas chromatography using thermal extraction (TE) with liquid nitrogen "cryo-trapping" before starting the GC run and a MS for the detector (GC/MS) allows for a positive identification of trapped solvent molecules. The vapor transmission coefficient within the cured coating system dictates the rate of solvent loss after application. The technique is also very useful for identifying the generic type of coating used years after application by pyrolyzing a very small coating chip at a higher temperature. By doing this in a stream of helium and trapping the fragments with liquid nitrogen, an analysis of the fragments will allow one to identify the original polymer [1].

Quality in the manufacture of the coating products includes both the proper formulation for use in the environment intended as well as the eventual commercial manufacturer. There is usually a lengthy testing program required to evaluate the coating formulation before a product is commercialized. A few typical failures seen in the formulation and manufacture include systems formulated to contain low vapor pressure, water-soluble solvents in coatings to be used under water, formulation without required UV or thermal stabilizers for exterior coatings, gelation of acidic binders by reaction with basic pigments, loss of dryer catalysts from a oxidizable coating system, inclusion of carbon dioxide and water vapor into the amine side during the manufacturer of an adduct for a two-part catalyzed coating, and failure to exclude water contaminants during the manufacture of the non-isocyanate side of a urethane coating system.

WHAT WAS THE DESIRED PURPOSE OF THE COATING?

Before designing the test regime to evaluate a specification or starting the investigation of a failed coating, the analyst should ask why the coating was applied. Often it will be intuitive or would be stated in the specification. The design of the testing and evaluation program should include elements encompassing these objectives. Table 1 lists some of the ASTM standard test methods used to evaluate a coating's specific serviceability relative to a particular property. Table 2 lists some of ASTM's standard practices for accomplishing the objectives.

TABLE 2—Selected, Frequently Used ASTM Standard Documents for Evaluating Coatings for Specific Properties

Designation	Document Title
D609-00(2006)	Practice for Preparation of Cold-Rolled Steel Panels for Testing Paint, Varnish, Conversion Coatings, and Related Coating Products
D772-86(2005)	Test Method for Evaluating Degree of Flaking (Scaling) of Exterior Paints
D870-09	Practice for Testing Water Resistance of Coatings Using Water Immersion
D1006-01(2006)	Practice for Conducting Exterior Exposure Tests of Paints on Wood
D1150-55	Single and Multi Panel Forms for Recording Results of Exposure Tests of Paints (Withdrawn 1991)
D1641-04	Practice for Conducting Outdoor Exposure Tests of Varnishes
D1653-03(2008)	Test Methods for Water Vapor Transmission of Organic Coating Films
D1730-09	Practices for Preparation of Aluminum and Aluminum-Alloy Surfaces for Painting
D1735-08	Practice for Testing Water Resistance of Coatings Using Water Fog Apparatus
D2065-03	Test Method for Determination of Edge Performance of Composite Wood Products Under Surfactant Accelerated Moisture Stress
D3002-07	Guide for Evaluation of Coatings Applied to Plastics
D3322-82(2005)	Practice for Testing Primers and Primer Surfacers Over Preformed Metal
D3456-86(2008)	Practice for Determining by Exterior Exposure Tests the Susceptibility of Paint Films to Microbiological Attack
D3925-02(2010)	Practice for Sampling Liquid Paints and Related Pigmented Coatings
D3960-05	Practice for Determining Volatile Organic Compound (VOC) Content of Paints and Related Coatings
D4082-10	Test Method for Effects of Gamma Radiation on Coatings for Use in Nuclear Power Plants
D4214-07	Test Methods for Evaluating the Degree of Chalking of Exterior Paint Films
D4414-95(2007)	Practice for Measurement of Wet Film Thickness by Notch Gages
D4708-07	Practice for Preparation of Uniform Free Films of Organic Coatings
D4712-87a (2005)	Guide for Testing Industrial Water-Reducible Coatings
D5064-07	Practice for Conducting a Patch Test to Assess Coating Compatibility
D5065-07	Guide for Assessing the Condition of Aged Coatings on Steel Surfaces
D5162-08	Practice for Discontinuity (Holiday) Testing of Nonconductive Protective Coating on Metallic Substrates
D5367-08	Practice for Evaluating Coatings Applied Over Surfaces Treated With Inhibitors Used to Prevent Flash Rusting of Steel When Water or Water/Abrasive Blasted
D6625-01(2007)	Practice for Conducting a Test of Protective Properties of Polish Applied to a Painted Panel Using Fluorescent UV-Condensation Light- and Water-Exposure Apparatus
D6904-03(2007)	Practice for Resistance to Wind-Driven Rain for Exterior Coatings Applied on Masonry
D7087-05a (2010)	Test Method for an Imaging Technique to Measure Rust Creepage at Scribe on Coated Test Panels Subjected to Corrosive Environments
D7376-10a	Practice for Outdoor Evaluation of Wet Stack Storage Conditions on Coil-Coated Metals
F940-99(2009)	Practice for Quality Control Receipt Inspection Procedures for Protective Coatings (Paint), Used in Marine Construction and Shipbuilding
G53-96	Practice for Operating Light and Water Exposure Apparatus (Fluorescent UV Condensation Type) for Exposure of Nonmetallic Materials (Withdrawn 2000-Replaced by G154)
G154-06	Standard Practices for Operating Fluorescent Light Apparatus Exposure of Nonmetallic Materials

Coatings provide a renewable surface and allow the engineer to use materials that are more economical or provide a physical characteristic not attainable from the uncoated surface. While coatings frequently provide a variation in appearance, most coatings serve to protect more than to beautify. When the protection is not provided for the full design life of the coating, including the maintenance of all expected and desired protective properties, a coating failure has occurred. Frequently the coating will be evaluated for a particular service through a series of tests. These evaluation programs are designed to assist in predicting failure modes and to assist in the preparation of specifications. Problems often develop when the service does not match the initial testing program.

A major reason for applying coatings to many different types of substrates is to protect the substrate from deterioration. Coatings on steel, when applied properly, have the ability to stop corrosion in hostile environments for a period of time. Coatings applied to wood have the ability to prevent fungus growth and rotting, even in damp environments. Hard metalized coatings protect softer metals from wear. Highly active metalized coatings such as zinc and aluminum have the ability to prevent corrosion of steel in adverse conditions [3]. When coatings are applied to protect the substrate and the substrate sustains premature damage, a coating failure has occurred. Test regimes usually address the perceived problem. Sophisticated a-c impedance and d-c polarization techniques have the ability to measure actual corrosion currents and represent a very sensitive test method for metal substrates. A-C impedance testing is also used to evaluate and compare coating performance in specific environments.

Coatings are often applied to the inside surfaces of pipes, tanks, plastic and paper food packages, food and beverage cans, and rail cars to protect the contents from contamination and/or spoilage. This contamination may originate from the metal container, which leads to discoloration of the product by allowing metal ions to enter.

Contamination in the form of bacteria or degrading reactive gases is frequently a problem in food packaging. Tank coatings may fail by allowing components of the coating to migrate into the products carried within the tanks. Loss of coating components will then lead to coating shrinkage that will stress relieve in various ways leading to failures by cracking, increased osmotic activity, etc., depending on the products carried and the coating polymer fragments remaining. A coating failure that allows product contamination is usually very costly. See Figs. 6 and 7.

Coatings are frequently applied to enhance a substrate's appearance. Because of this, any undesired change in the coating's visual attributes will constitute a coating failure. This would include not only changes in color, gloss, and texture, but appearance failures due to growth of algae and mildew as well. Failure modes related to a loss in aesthetics are usually adverse reactions to the environment, often due to ultraviolet radiation or delamination of the coating.

Small molecules such as water and the acidic gases carbon dioxide, hydrogen sulfide, and sulfur dioxide have the ability to migrate through a polymer film. When this occurs, the possibility of corrosion of the substrate is great. Frequently, coatings are used to interfere with this process. The rate at which these small molecules can pass through a coating or polymer membrane is called the vapor transmission coefficient for that specie. Metal coatings applied to food wrappers inhibit or stop migration of oxygen, thereby disallowing reaction with oils containing double bonds. This maintains freshness. A failure to prevent these molecular migrations in an amount based on the original design parameters constitutes a coating failure. Often this failure mode is closely related to cross-link density or changes in cross-link density after coating degradation.

Fig. 6—Loss of non-bound components such as benzyl alcohol in an epoxy tank lining in a ship leads to considerable coating shrinkage stress followed by cracking to relieve the stress.

Coatings are applied to stair treads and slick surfaces to provide nonslip characteristics. On the contrary, internal pipe coatings should be very smooth so as to provide decreased resistance to flow. This allows increased volumes of fluids with less pressure drop and lower power requirements for the pipeline. Many coatings provide abrasion resistance to a substrate, thereby increasing the substrate's life indefinitely since coatings are a renewable entity. Failure of the coating to accomplish any of these design goals constitutes a coating failure.

Fig. 7—Poor surface preparation and shrinkage of epoxy tank lining that leads to loss of coating in the corner of the tank.

Coatings are frequently applied to metal substrates to modify electrical flow characteristics. Coatings are naturally dielectric, though conductive pigments and additives may decrease internal electrical resistance for special requirements. The electrical resistance becomes an important attribute in accomplishing a particular circuit requirement. A very good example are those coatings applied to metal surfaces that are placed under cathodic protection such as underground pipelines, metal bulkheads at a shoreline, ship bottoms, offshore underwater structures, as well as internal tank linings. ASTM G8, G42, and G95 (see Table 1 and Ref. 4) are methods for evaluating the cathodic disbondment properties of coatings. Because of the generation of large concentrations of hydroxyl ion at coating defects, if the coating is chemically reactive to hydroxyl ion, delamination may occur. If phosphoric acid had been applied to clean the steel, saponification of the pretreatments can be a dominant failure mode with some coating systems.

Conductive coatings are used to dissipate electrical charge. These are found in laser printers and some copy machines. Conductive coatings are also applied to bags, plastic mats, and other articles used around electrical equipment sensitive to the discharge of static electricity. A failure to provide the desired low electrical resistance or conductivity over its planned lifetime constitutes a coating failure.

For materials that expand and contract extensively with changes in absorbed materials such as water and carbon dioxide, minimizing absorption will allow the substrate to remain dimensionally stable. Wood, when "dry," is about 10 to 15 % water. Depending on the type of wood, absorption of water, especially through open-end grain, causes huge changes in the size of the piece of wood. Other characteristics such as flexibility, warping, and cracking are a common occurrence when wood coatings fail. The peeling of coatings on wood usually starts at some break in the film and slowly radiates from the site of moisture ingress. As moisture enters the wood, it expands greatly and pulls the coating from the surface. As it dries out, the wood shrinks. This continual expansion and contraction is a major source of problems for wood coatings. See Figs. 8 and 9.

Paper products must be protected from moisture pickup to maintain strength and integrity. Paper cartons containing milk and other food products are usually protected by surface coatings of wax, polyethylene, or vinyl thermoplastics. Sizing or starch-type coatings are frequently applied to paper to provide a degree of stiffness if "wet strength" is not required.

While gloss is frequently considered an aesthetic property, coatings that have the ability to reflect or absorb specific wavelengths of light are functional coatings. Pigmented coatings engineered to reflect very little radiation are often applied to thermal adsorption devices such as solar heat exchangers. Coatings with adsorption efficiencies approaching 95 % have been developed. Changes in reflection or adsorption characteristics over the coating's planned lifespan constitute a coating failure.

Coatings containing voids or small bubbles have the ability to adsorb and deflect mechanical wave energy such as sound. Changes with time in these adsorption or dampening abilities usually constitute a coating failure. Some of these unique physical properties are impacted by the adsorption of liquids such as water from condensation and may be the subject of test programs when evaluating this type of failure. Knowledge of the physics of wave energy transmission and point reflection through elastic media is necessary to design test programs evaluating these parameters.

Fig. 8—Expansion and contraction of wood occurs when water is absorbed and lost from the wood. The paint film cannot follow the dimension of the wood. This results in peeling paint that pulls fibers from the wood surface.

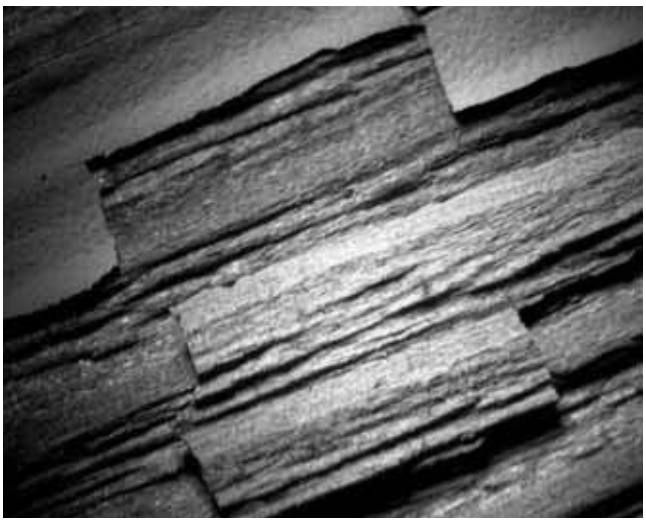

Fig. 9—Microscopic view of wood/paint surface in Fig. 8. Note wood fibers attached to the backside of the delaminated paint chips.

HOW WAS THE COATING APPLIED?

Many coating failures can be traced to problems associated with the procedures surrounding the coating's application. For this reason, each step of the process must be considered. Getting a particular coating applied can be thought of as having been accomplished through a series of steps with multiple responsibilities. These broadly include the following:

1. Preparation and follow through of the specification.
2. Preparation of the surface/substrate.
3. Physical application techniques and equipment.
4. Third-party inspection.

The specification, type of coating being applied and its particular mixing and curing requirements, variations in ambient weather conditions, variations in the condition of the substrate, surface preparation techniques, pretreatments, equipment used during the application, the quality of third-party inspection as well as the applicator's knowledge and ability all play a major role in getting the coating properly applied and minimizing coating failures.

Preparation and Follow Through of the Specification

The specification should serve as the "blue print" for getting the coating properly applied. Its existence implies that someone has surveyed the site to determine any abnormalities that might exist, evaluated the service requirements, reviewed the particular problems unique to the structure and service demands, identified a particular coating with the required service characteristics through prior testing, and provided an adequate application procedure that, theoretically, will meet the use requirements. The specification assists the applicator in knowing what is expected of him and serves as a legal document in times of dispute.

Frequently a coating will be specified by a specific manufacturer's product numbers. Failures in the specification, either in the type of recommended coating or the application procedures, can result in early failure. As such, the specification must be reviewed when investigating a coating failure. Coating materials may have been used that were not on the approved list. Most applicators are not in possession of proper knowledge to make substitutions and usually do not want that responsibility. Coating failures in many forms have resulted from attempts to circumvent the specification. Analysis of very small coating chips by FTIR or GC/MS and compared with known samples can demonstrate compliance or lack thereof [2].

Before specifying a particular coating system, it is usual to evaluate specific candidates in a test program that closely simulates the use environment. This is accomplished either within the owner's organization or by subcontracted third party testing organizations. While most of the required test procedures are found in Volumes 6.01 through 6.04 of the *Annual Book of ASTM Standards,* specific custom-designed procedures may be desired in some unique applications.

Often a particular coating material will require specific mixing and application procedures dictated by its formulation. The coating manufacturer is in the best position to determine this since he is knowledgeable about the components of the coating. Requirements placed on the curing regime, mixing times with requisite induction periods, strainer mesh sizes, and other requirements will be specified by the manufacturer.

Preparation of the Surface/Substrate

The quality of the surface preparation done prior to coating application will strongly influence the life, and quality, of the applied coating. Some contaminants are very harmful and lead to early failure in certain services. Some contaminants can be tolerated, and, while coating life may be somewhat adversely impacted, long-term longevity can be realized. Displacement of some surface contaminants may be addressed by variations in the ability of the solvent system to affect coating wet-out. Contaminates that interfere with adhesion or promote under-film corrosion are particularly troublesome to paints. There are potential problems with all types of surface preparations. The Steel Structures Painting Council (SSPC) has produced specifications addressing some of the most common surface preparations for steel [8]. These specifications will usually dictate the specific surface cleanliness required for service and should reflect that used during the original test sequences. Surface contaminates can impact the surface tension of freshly applied coatings. In one case the concrete floor at a power station was "mopped clean" using a mop that had been used to spread a silicone sealer. The result was a serious surface tension (fisheye) problem in the applied epoxy floor coating. See Fig. 10.

For coatings that have an extended design life, as with automobile bodies, the surface preps are extremely sophisticated. Unique electrodepositing primer coatings require a very clean and totally wet-out surface. Coating failures on this scale have resulted in multimillion-dollar claims. Chemical pretreatments present potential failure problems as well. Cleanliness of the substrate and its impact on adhesion is the topic of many testing programs. But since one must be looking at the surface at a depth of no more than a few angstroms, the analytical techniques required include auger spectroscopy and XPS. The use of EDX to analyze a "surface" is not proper because the area being analyzed will include a depth well below the surface where "adhesion" will occur. While this technique is usually defined as a surface technique, it does penetrate well below the actual surface encountered by the coating as it attempts to "wet-out" the substrate.

Improperly operating equipment is a source of coating failures. A very common problem is the abrasive-blast-

Fig. 10—"Fisheyes" in an epoxy floor coating contaminated with a silicone sealing agent is a surface tension problem. The coating was intended to be smooth and shinny.

cleaning air compressor that passes oil. Oil contamination can be a long-term, serious problem with certain coating systems. While pure aliphatic oil residues, being low-energy compounds, are usually displaced by the active solvents of the coating system such as ketones and esters, oil based systems can present a serious problem. Adhesion between the binder of the coating and the substrate takes time to develop. It is highly probable that adhesion problems will develop with the ingress of water vapor if the interface has been contaminated with strong surfactants and the solvent system does not have time (or ability) to displace them before the coating gels and its glass transition temperature reaches ambient temperature. Analysis of the interface surfaces by XPS can allow a definitive identification of the structure of the molecules forming the interface and is required to identify the locus of failure.

Profile and surface conditions existing at the time of coating application are difficult to evaluate after a coating has been in service for a while. Frequently, though, it is necessary to inspect the substrate under a coating. Paint may be removed by using commercial paint stripper, allowing inspection of substrate profile and the current surface condition. This may include the presence of corrosion products. Mill-scale deposits may be found where the specification calls for complete removal. While the actual profile is not as critical as the original molecular contaminants that could interfere with the thermodynamic wetting process, one can gain insight into the history of the surface being inspected.

For submerged services, a "white metal" abrasive degree of cleanliness is usually specified. If a metal sample may be removed and is bendable, the sample may be subjected to extreme cold, as with liquid nitrogen or carbon dioxide followed by rapid bending. The coating will usually pop from the substrate if chemical bonding has not occurred, allowing a clear measure of the debris that remained at the time of application.

Physical Application Techniques and Equipment

The physical application techniques employed as well as the equipment used can lead to many types of coating failures. Coating defects can range from delamination between coats caused by exceeding the recoat window and pinholes caused by small compressed air bubbles whipped in during highspeed stirring and applied by airless application systems, to curing problems originating from improper ambient field conditions, off-ratio mixing, or inclusion of water contaminants from "bad" solvent. Some defects such as orange peel, sags, and runs will be evident at the time of application, but improper curing of a coating may not become evident until a failure occurs months or years later. The analytical techniques useful in evaluating off-ratio mixing of catalyzed paints depends on the coating matrix, but typically include thermal methods such as DSC, FTIR, gel permeation chromatography (GPC)/high-pressure liquid chromatography (HPLC) of solvent extracts from the failed coating, and GC/MS are typical analytical methods for evaluating cure.

The specific application technique will often present typical failure modes. Test programs that evaluate a particular coating before it is specified will usually utilize the expected application techniques. Application by spray, roller, brush, flow coater, dipping, or trowel requires that the coating material have certain physical properties. Ambient conditions expected at the time of application should be considered. Application may use electrostatics with some powders and liquid paints.

Was the coating properly cured? Was the temperature and relative humidity in the required range? Some moisture-cured ethyl-silicate, zinc-rich systems as well as moisture-cured epoxies and urethanes require that there be sufficient moisture available to allow binder-curing reactions to occur. Overcoating these paint systems before there has been sufficient water pickup can lead to premature coating failure due to insufficient coating strength development. Too much water can cause blushing with high flash lacquers and foaming with urethanes.

The curing of a coating is usually by chemical reaction with the polymer precursors in the paint. All physical laws controlling chemical reactions will be in effect. This means that the reaction rate will be controlled by the substrate temperature since the heat capacity of the coating will usually be considerably less than the substrate. Potential side reactions with atmospheric constituents such as water and carbon dioxide may be a problem with some binders. For moisture-cured systems such as urethanes, epoxies, and ethyl silicate systems, air that is too dry will interfere with polymer curing and the use of DH equipment may present a problem. Excessive humidity may leave surfaces with a microscopic layer of water. With solvent-borne paint systems, this may not be as critical as with the super-high solids or 100 % solids systems. The solvent system is usually engineered to assist in moisture removal by displacement, dissolution, and selective azeotrope formation. Coatings that cannot displace these interfering surface-adsorbed species with properly engineered solvent systems may experience delamination shortly after application. With most coating systems, this may be demonstrated by the addition of thinners of varying "strengths" and noting the delamination sensitivity caused by water vapor. When a coating delamination problem exists with a particular coating system and the "adhesive" qualities may be enhanced by adding active thinner only, one may suspect problems with the thermodynamic wetting of the substrate.

Third Party Inspection

An important part of the professional application program will often include third party inspectors. These are usually required by the owner and serve as monitors and record keepers for the job. Should a failure occur in the future, the records frequently provide the only link to the daily happenings. Data will include paint batch numbers, ambient weather data for each day, humidity and temperatures, wet- and dry-film builds, the thinners used, logging of equipment problems, names of operators, substrate temperature, and a multitude of other data. Very important information useful to the solution of coating failures is often found in the inspection reports. Organizations such as SSPC and National Association of Corrosion Engineers (NACE) can provide lists of certified coating inspectors.

WHAT EVIDENCE IS PRESENTED BY THE FAILURE?

To successfully diagnose the causes of failures in coating systems, the investigator must be fully cognizant of all of the factors affecting the coating's longevity. This includes, but is limited to, (1) a thorough knowledge of the chemistry

of the coating systems being used; (2) factors affecting the cross-linking, cure, or film-forming characteristics of the binder; (3) factors affecting adhesion and potential adverse chemical reactions between the substrate, binder, and environment; (4) corrosion fundamentals and protective techniques; (5) potential formulation problems; (6) potential application problems; (7) the suitability of the specified coating for the service; and (8) the instrumentation that can provide sophisticated answers to the complex questions that exist.

It is rare for all of these disciplines to be found in a single individual and the investigator must be willing to continue their study. New coating polymers are being developed routinely and are being incorporated into coating systems. Their reaction chemistries both with the cross-linkers used to produce the final film and the interfering side reactions with ambient, local, or solvent species may produce unexpected results. Because of this, the successful investigator must be aware of his/her limitations and be willing to seek knowledgeable assistance when necessary.

Those with experience in the formulation of paints and coatings will often have a distinct advantage over others. Understanding the potential shortcomings of the polymers used, the problems forced by the use of environmentally friendly solvent systems, the functions of the additives, the physics of adhesion, and the limitations of the analytical "tools-of-the-trade" will assist in understanding failure mechanisms. Even still, the challenge is tremendous and true solutions may be elusive. It is important to know when to ask for help.

While the investigation of a coating failure requires all of the knowledge discussed, a systematic approach offers the best chance for a successful conclusion. Before beginning the investigation, it is important to follow a preconceived procedure that will ensure that each phase of the investigation is addressed. Since each failure may be somewhat different, there will be opportunities to veer from the path as evidence is produced. The investigation should contain the follow elements as a minimum:

1. Gather background information.
2. Conduct the field investigation.
3. Conduct the laboratory investigation.
4. Consider potential failure modes and test the hypothesis.
5. Report the findings.

Gather Background Information

Inquire as to the nature of the problem. While the first reports coming in from the field will usually lack details necessary for a definitive conclusion, they do provide a picture of the problem as it is perceived. There is little standardization of the descriptions of failures. As an example, coating delamination can occur at the interface or within the coating or substrate. The observer usually will know only that "the coating fell off."

Obtain a copy of the specification. This will provide insight as to potential problems perceived at the initial documentation. The type of coatings and typical failure modes will prompt additional questions.

Obtain relevant daily inspection reports. These will provide data as to the current weather conditions at the time, equipment malfunctions, types of paints used, as well as any problems encountered out of the ordinary. Batch numbers of the coating material will allow queries to the manufacturer as to similar problems that may have been seen with the coating in other situations.

Conduct the Field Investigation

Talk to the applicator if possible, not just the foreman. Inquire as to any recollections about the application. Was the weather at the time of application cold, wet, dry? What was the time of day, direction of surfaces relative to solar heating, surface preparation, blast medium used, and condition of equipment?

Ensure that field test instruments are properly calibrated. The data must be reliable and relatable to other data available from original testing done prior to specification writing and the coating manufacture.

Gather all relevant samples. Representative paint chips from the "bad" area should be matched with representative samples from a "good" area. Fluid from under blisters may be withdrawn with hypodermic syringes and stored in glass bottles. Empty cans, samples of shot/grit from the automatic abrasive cleaning machines, sample debris from the dust collector, liquid samples from degreaser/phosphating baths, etc. will hold clues to potential problems.

Perform adhesion checks if indicated. ASTM D3359 (Test Methods for Measuring Adhesion by Tape Test) describes methods for determining the degree of apparent adhesion of the coating. Frequently, poor or marginal adhesion causes other problems to surface although the coating appears to be intact. Under-film corrosion is a common occurrence when contaminants remain on the steel interface after coating application. Fig. 11 depicts a good use of the tape peeling test. In this case the concrete floors a new auto dealership were painted. The dealer specified their color and the specification was not followed. This required the paint application contractor to then repaint with a different color epoxy. After being occupied the new coating peeled with little difficulty from the original coating due to

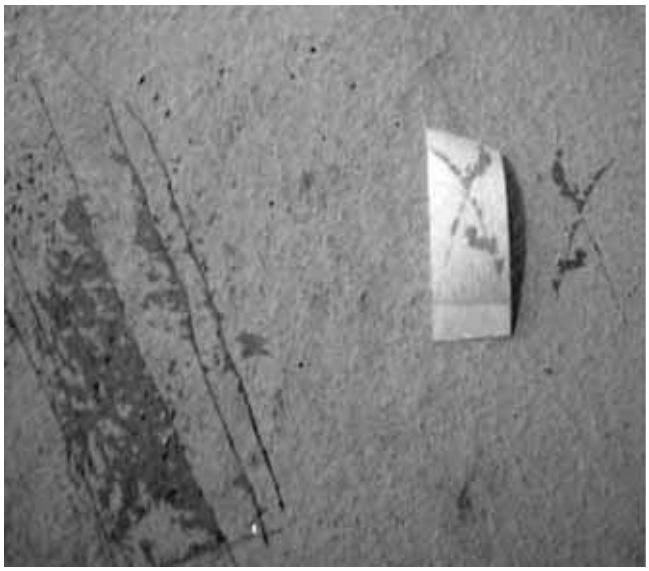

Fig. 11—ASTM D 3359 "Test Methods for Measuring Adhesion by Tape Test" applied to a peeling top coat epoxy soon after applying over the first cured coat epoxy. The first coat was the wrong color. The peeling is occurring in a weak boundary layer (WBL) of carbonated amine that formed on the first coat during application.

the amine carbonate WBL that had formed on the surface of the original coat. While none of the original empty paint buckets were available to test for trapped CO_2, it is probable that a portion of the interfering carbonated amine exuded from the original coating as a result of aggressive stirring of the curative. Discussions with the paint applicator revealed that he was under the misconception that the more he stirred the individual components before mixing the "A" and "B," the better the mixed paint would be.

Inspect surface profile and cleanliness of substrate. The depth and intensity of the abrasive cleaning will determine whether the surface contains "new metal." Profile depth alone is not sufficient to describe the surface. For high-solids coatings with limited active solvents, wet-out of the interface, a requirement for the development of adhesion, may not be possible as the coating increases its viscosity to a gel. As the coating cures to a film and internal stresses began to grow across the outer surface, some coatings can literally pull themselves from the surface. The inability of the coating to encapsulate debris encountered on the surface exacerbates the problem and decreases its total adhesion.

Field test for cure by MEK rubs (ASTM D4752). This test is useful for catalyzed coating systems such as epoxies and urethanes, though not suited for alkyds or latex systems due to active solvent swelling and delamination. If the coating can be resolubilized, there is a high probability that there is a problem with the curing. Off-ratio catalyzation, severe zone curing from inadequate induction time, and deactivation of one reactive component are but a few of the reasons for failure of the MEK rub test. One must remember that the fourth most abundant component in air is carbon dioxide (CO_2) and CO_2 is an "acid gas." As such, carbon dioxide will react with any alkaline epoxy curative such as amines and polyamides while in contact with air. This is the typical amine blush that creates adhesion problems like that seen in Fig. 9. The application of amine/polyamide-cured epoxies will often require mixing. If a vortex is pulled during the stirring of the amine/polyamide curative, carbon dioxide will be stripped from the air and will chemically block that site from reaction with epoxy. For epoxy polyamides with 1:1 mixing ratios, there may be pigments ground into the polyamide side of the paint. Depending on the manufacturing equipment used by the paint producer, there will be some carbon dioxide blocking some of the amine functionality. Most manufacturers do not use a nitrogen blanket during pigment dispersion into the curative side of the epoxy. This amine carbonate will exude from the catalyzed epoxy as it cures and over time to produce delamination problems. This laboratory has developed a test to determine if there is CO_2 blocked amine in the can before mixing at the application site. To test for the presence of carbonated amine a small sample (about one ml) of the curative is placed in a test tube. A drop of six molar hydrochloric acid is carefully deposited below the curative using a pipette or hypodermic syringe. The acid will force the CO_2 from the amine functionality as the hydrogen ion reacts with the amine. This assumes that no calcium carbonate is formulated into the paint.

Photograph document observations. Include relevant data in each photograph. This might include the observation number, test location, film build, highlight of suspect area (both good and bad), and some point of reference. The point of reference might be a pencil, coin, or even the investigator's finger. Cracks in a tank lining may be 1 cm long or 1 m long. A photograph without reference may be impossible to distinguish against a background (wall) of white paint.

Observe all activity in the area that may impact coating application or longevity. When inspecting the coating facility, look about to determine if other activities may present problems. Is the grit blast machine near the degreaser? Is metal shot and grit getting into the phosphating bath, increasing the chance for leaving loose iron particles in the phosphate on the surface to be overcoated? Is automatic welding equipment nearby using silicon sprays as a wire lubricant? Is grit or shot blasting near a powder coating fluid bed or phosphating bath introducing contaminates into the powder or sticking to the steel substrate prior to coating application? These have been the source of coating failures in the past.

Conduct the Laboratory Investigation

After gathering the samples, the analysis may be planned depending on the nature of the problem. In answering those questions posed before, some analytical laboratory work is usually required. Some of the instrumentation and the answers they provide may be summarized in the following discussions about each instrument.

Infrared analysis of coating samples is sometimes useful in determining whether the specified coating was used. Operator technique is very important in obtaining totally definitive information, and results are often marginal. The method is very useful in testing the coatings prior to application when there is a desire to ensure compliance. Microscopic FTIR provides greater sensitivity when analyzing filled polymer solutions, as most paints are [2].

GC is very useful for solvent identification. Solvent retention that leads to osmotic blister formation may be demonstrated by GC analysis of the blister liquid. Because of the migration of the solvent molecules into plastics such as polyethylene, glass collection bottles will provide a more accurate system for sample transportation.

A tremendously useful system of instruments is the "hyphenated" system made up of a pyrolysis/GC/FTIR/MS. In this "instrument" which, in essence, is a laboratory on a bench, paint chips can be analyzed with little or no preparation. Positive identification of generic coating and polymer types, polymer degradation studies, solvent-retention analysis after years in the field, determination of catalysis levels in oil-free polyesters from field sample chips, and numerous other tasks are very easy with the instrument [1].

Ion chromatography is a very useful tool for the analysis of osmotic blister liquid when the problem stems from salts under the film. Analysis of soluble salts taken from a surface is also easy to accomplish by dissolution followed by ion chromatography or after evaporation onto a suitable substrate via energy dispersive X-ray.

Thermal analysis techniques such as differential scanning calorimetry and thermal gravimetric analysis (TGA) are useful in determining some physical properties of coatings. DSC has been used to monitor curing profiles of powder coatings and other thermosets for many years [6]. TGA systems, set up to allow a flowing gas stream to sweep the escaping molecules through a heated gas cell of an infrared spectrophotometer, are now available. This system

of instruments allows studies of the thermal stability of polymers used in coatings.

Surface analysis such as XPS, auger, scanning electron microscopy (SEM), and EDX are analytical techniques that look at the surface of the coating or substrate. Auger and XPS are tremendously important in determining the locus of failure when investigating coating delamination [8]. A major failure mode is the development of, or application over, a WBL. These are not easy to identify with the naked eye. What may appear to be an adhesive failure could be the splitting of an organic layer only a few molecules thick at the interface. This could be due to the loss of reaction caused by a rogue metal specie. Zinc is such a culprit when overcoated with oil-free, polyester-based systems cured by a free radical mechanism. This has been seen when a zinc-rich coating had been applied by mistake and then removed by abrasive blasting. This left trace amounts of metallic zinc alloyed into the steel surface. The zinc interfered with the curing mechanism of the polyester.

Atomic absorption (AA) spectroscopy is useful in determining the concentration of metals in coating systems. While lead, chromium, and other metals are controlled to protect workers and the environment, low concentrations of catalytic levels may be determined as well.

UV weathering characteristics are evaluated in simulated weathering cabinets. When failures are thought to have originated from UV degradation, test regimes may be designed to evaluate the coatings using UV of different wavelengths.

Physical and application characteristics such as percent solids, viscosity, pot life, and others are usually monitored as a quality assurance/quality control (QA/QC) procedure during or prior to application. The requirement to monitor these variables is often included in the specification, and the values can be found on the daily reports of the inspectors.

Liquid chromatography such as GPC and HPLC are useful in evaluating a polymer used as a binder of coatings. Failures associated with the migration of the smaller-molecular-weight fraction to an interface, causing the development of a WBL, is a typical example. QA/QC of incoming resins for use in a coating is another typical use.

X-ray diffraction (XRD) is useful in the analysis of any crystalline material. Since most pigments found in paint are mineral in nature and possess crystalline structure, they may be identified using this technique. Even when a coating system may be lacking an identifying collection of crystalline materials, the "amorphous signature" of the XRD scan has been used to provide information about unknown coating specimens.

Consider Potential Failure Modes and Test the Hypothesis

At some time after starting the investigation, a hypothesis can be drawn. A testing program incorporating this hypothesis may be developed that will assist in proving or disproving the possibility of a failure mode.

REPORT THE FINDINGS

After a conclusion has been reached, a full report should be written. This would include all of the data gathered including pictures. The report should contain sections such as (1) Introduction, (2) Executive Summary, (3) Background Information, (4) Discussion and Laboratory Analysis, and (5) Conclusions. Since a primary reason for failure analysis is to prevent similar problems in the future, the report should be written with that objective in mind. It should also serve as a teaching aid to others.

CONCLUSION

Coating failure analysis will draw from a multitude of disciplines. To increase effectiveness, one must be willing to have an open mind during observation and study the basic chemistry and physics controlling the processes. Do not enter an investigation with preconceived ideas so strongly set so as to be swayed from seeing the small details that will define the actual failure mode. Do not be afraid of the "heavy" chemistry associated with the sophisticated analytical instrumentation that can give one very powerful insight into the systems. This will be a learning experience for all.

While there are some coating mistakes that are commonly made, the reasons for coating failures appear to be limitless. Just as a good mechanic must know how an engine works to diagnose its problems, so too must the coatings failure practitioner know how paints work and the tools available for use in any required investigation. This knowledge of potential failure mechanisms can be extremely helpful to others, as well, including the owner, specifier, paint manufacturer, and applicator. By appreciating potential coating problems, an awareness of many important details is naturally obtained. Learning the complex chemistry of urethanes may be beyond the average applicator, but the knowledge that bubbles in urethanes may be the result of painting over dampness or condensed water on the surface forces an awareness that is very helpful.

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Part 15: Instrumental Analysis

70

Atomic Absorption, Emission, and Inductively Coupled Plasma Spectroscopy

Dwight G. Weldon[1]

A PAINT, EVEN ONE AS SEEMINGLY SIMPLE AS A red-lead alkyd, is actually a very complex system wherein a variety of components such as polymers that may or may not contain reactive functionality, pigments, plasticizers, additives, and solvents must interact in such a way that the dried film offers expected protection. In addition, quite often, the film is expected to provide an aesthetic appeal. Because of this complexity, it is not surprising that the complete chemical analysis of a coating can be a complicated and time-consuming task. Indeed, a complete analysis of all the components may require the use of several analytical techniques, many of which are discussed in this manual.

The intent of this chapter is somewhat more limited, as it pertains only to the analysis of coatings for metallic constituents and more specifically, elements. Such compounds are widely used in the coating industry. Many pigments and extenders are inorganic compounds that may contain metals, and many driers, catalysts, and ultraviolet (UV) light absorbers are metal-containing compounds as, for example, cobalt naphthenate and dibutyltindilaurate. It should be pointed out that in theory inductively coupled plasma spectroscopy can be used to analyze all elements except argon. However, in actual practice, it applies to approximately 70 elements, many of which are not typically considered metallic by most paint chemists.

Classical wet chemical techniques are valuable in determining several of the above-mentioned paint-component compounds. However, a generally simpler, more efficient, and, in some cases, more sensitive way to achieve this involves the use of the related techniques of atomic absorption (AA), atomic emission (AE), and inductively coupled plasma (ICP) spectroscopy. It is the purpose of this chapter to briefly describe the underlying principles of these techniques and to discuss their usefulness within the coating industry.

ELECTROMAGNETIC RADIATION

A useful definition of spectroscopy is the study of the interaction of light, or more generally, electromagnetic radiation, with matter. Therefore, a logical starting place in the discussion of spectroscopic methods is a brief introduction into the nature of electromagnetic radiation.

Simply put, electromagnetic radiation is energy traveling through space at enormous velocities that are effectively the speed of light. The classical interpretation of this radiation ascribes to it a wave-like character with the propagation of the radiation likened to the ripples caused by tossing a pebble into a quiescent pond. However, certain electrical phenomena such as the photoelectric effect are more readily explained by the quantum mechanical interpretation of electromagnetic radiation which describes the radiation as small, discrete wave packets or bundles called "photons." These dual views of radiation as bundles and waves are complimentary and not mutually exclusive.

The classical, wave-like interpretation of electromagnetic radiation characterizes it by either the wavelength (λ) or the frequency (ν). Fig. 1 is a simple representation of electromagnetic wave radiation wherein light is an oscillating vector with a wavelength, λ. From this, wavelength is defined as the length of a cycle, the distance between two successive maxima or minima, and the frequency as the number of cycles that take place per second. The relationship between wavelength and frequency is

$$\lambda = \frac{V}{\nu}$$

where V is the velocity of the wave front. In a vacuum, this velocity is equal to the speed of light, $c = 2.99 \times 10^{10}$ cm/s. Thus, for the radiation traveling in a vacuum, the equation is

$$\lambda = \frac{c}{\nu}$$

The electromagnetic spectrum is described in Fig. 2. The spectrum varies from high-frequency gamma rays, through the visible light region, all the way to low-frequency radio waves. The various regions of the spectrum have different energies, and therefore they interact differently with matter. The relationship between radiation frequency and its energy, E, that arose from quantum mechanics is given by the simple expression

$$E = h\nu$$

where h is Planck's constant, 6.624×10^{-10} ergs-s. Thus, the higher the frequency or conversely the shorter the wavelength, the more energetic the radiation. As described in Fig. 2, the lower energy end of the electromagnetic spectrum involves low-energy processes such as rotation of molecules, whereas the higher-energy ultraviolet and visible light region involves higher-energy processes such as outer electron transitions. It is these transitions that form the basis of AA, AE, and ICP spectroscopy.

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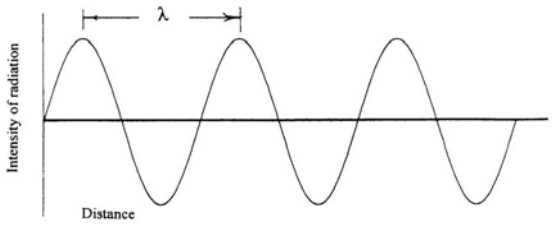

Fig. 1—Illustration of an electromagnetic wave propagating through space.

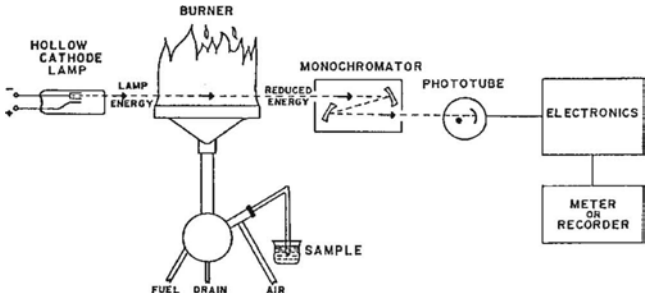

Fig. 3—Diagram of a simple atomic absorption spectrometer.

ATOMIC ABSORPTION SPECTROSCOPY (AA)

Atomic absorption spectroscopy probably is the most widely used of the three methods to be discussed. Basically, samples of coatings are chemically treated and introduced into a spectrometer that has been calibrated with known samples. For example, paint that is analyzed for lead is weighed, ashed at an elevated temperature to remove organic material, and then digested in hot nitric acid. The acid solution is diluted and fed into the spectrometer flame.

A simple, but not entirely accurate, picture of atomic structure involves negatively charged electrons rotating in orbits around a positively charged nucleus. The greatest population of electrons will reside in the lowest energy or ground state. If the atom is exposed to light of an energy exactly matching the difference between a ground-state orbital and an orbital of higher energy, a portion of this light can be absorbed and the electron can be excited such that it moves from the ground-state orbital to the higher-energy orbital. Thus, if a light source of appropriate frequency is available and is coupled with a detector capable of sensing attenuation of this light source, the concentration of a particular atomic species can be determined. This is the basis for AA spectroscopy.

Fig. 3 is a simple block diagram of an AA spectrometer. It consists of an aspirator, which is used to deliver the liquid sample into a flame, and an appropriate light source that is usually a hollow cathode lamp. The cathode is made from the element of interest, encased in a glass sleeve, and maintained at a low pressure with an inert gas such as argon. The light source is positioned so that it can be focused through the flame into a monochromator (prism or grating) and onto a phototube or other suitable detector.

When an electric current is passed through the lamp, it excites the inert gas, which then impinges on the cathode and sputters off atoms of the metallic cathode material. Collisions between these neutral metal atoms and the gas ions result in promotion of the metal atoms to an excited state. When these excited atoms relax back to the ground state, they emit light which is characteristic of the cathode element, and this light is then focused through the flame.

Intuitively, it would seem that there must be a relationship between the amount of light absorbed and the concentration of analyte atoms in the flame. Indeed, it has been found that if I_0 is the intensity of the incident beam originating from the source lamp and I is the intensity of the beam after it has passed through and been attenuated by the atoms in the flame of thickness or path length b, that the following relationship exists:

$$\log(I_0/I) = (k/2.303)b$$

where k is a constant. This relationship is known as Lambert's law. Beer found that increasing the concentration of

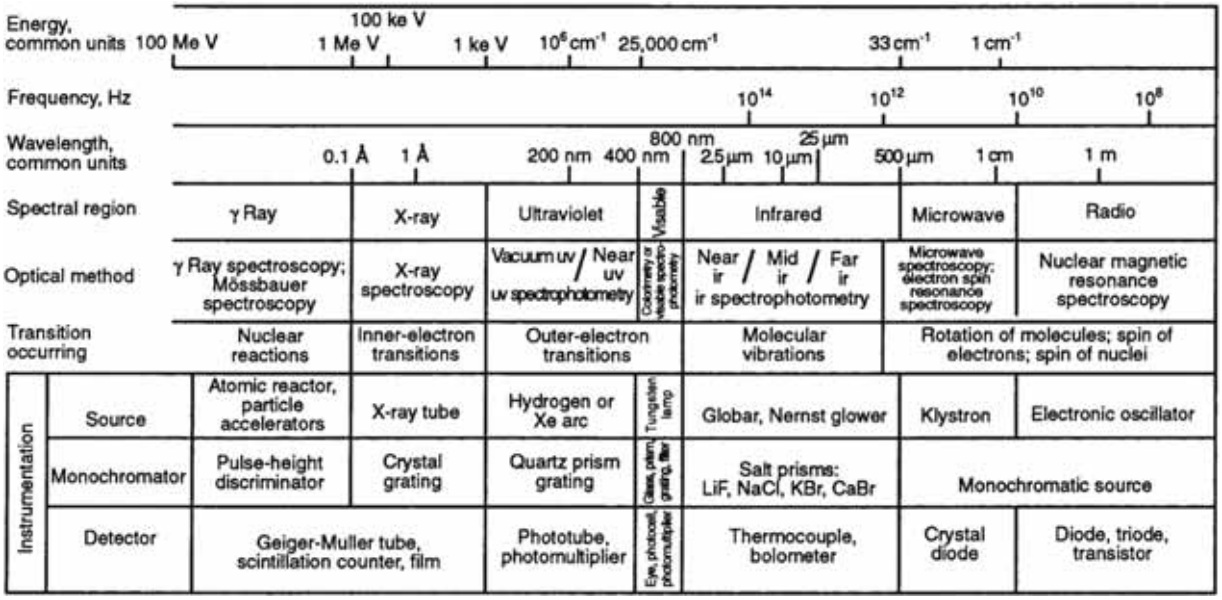

Fig. 2—The electromagnetic spectrum and corresponding spectroscopic methods [1]. (Printed with permission of The McGraw-Hill Companies, Inc., from Olsen, E.D., *Modern Optical Methods of Analysis,* 1975.)

analyte had the same effect as a proportional increase in path length. Therefore, the constant k is proportional to the concentration C of analyte and the relationship may be written as

$$\log(I_0/I) = abC$$

where a is the new proportionality constant. The expression is known as Beer's law.

The ratio I/I_0, which is dimensionless, is called the transmittance, T. In practical work, the terms "percent transmittance" [$\%T = (I/I_0)\ 100$] and "absorbance" [$A = \log(I_0/I) = -\log T$] are the parameters most often used, and Beer's law is often expressed as

$$A = abC$$

Because the relationship between absorbance of an analyte and its concentration depends on the constant, a, and the path length, b, each instrument must be calibrated before a quantitative analysis can be performed. Methods of calibration are discussed in the references to this chapter and in many other analytical texts. Often calibration involves measuring the absorbance of a series of standards of known concentration and constructing a calibration curve, or the use of internal standards [1].

One of the inherent drawbacks to AA is the need to use a different lamp for each element to be detected, although some multi-element lamps that contain as many as five or six metals exist. Since specific cathode tubes are needed, AA is quantitative and not qualitative in nature.

Flame Characteristics

Although the processes taking place within a flame are very complex, the flame serves three basic functions:

- sample volatilization
- decomposition of molecular compounds to the elements of interest
- excitation of the individual atom (AE only)

The flame consists of three regions: an inner core, an interconal zone, and an outer cone. The analytical measurement is generally carried out in the interconal zone, which is the hottest part of the flame. The height of this zone above the burner varies with the type of gases being burned, their flow rate, and the burner type.

A very important property of the flame is its temperature, since thermal energy is responsible for decomposing samples into individual atoms and, in the case of AE, for exciting the atoms thus formed. The most common flame type is the air-acetylene flame, which achieves an interconal-zone temperature of approximately 2200°C. If a nitrous oxide-acetylene flame is used, the temperature is approximately 2900°C.

Hotter flames are usually more advantageous because they reduce the number of chemical interferences. One primary source of chemical interference is compound formation within the flame, resulting in broad-band absorption and emission. As flame temperature is increased, many of these compounds are decomposed into the free atoms and the problem is eliminated. Also, hot flames are desirable in AE since they will provide more energy for the excitation of an increased number of elements. Too high a temperature should be avoided since it is possible that a significant portion of the neutral atoms may become ionized rather than simply excited.

Graphite Furnace

A modification of AA involves the use of a graphite furnace rather than a flame to achieve excitation. Small graphite tubes or boats that have electrical contacts through which an electrical current can be passed are the basis of this technique. A small amount of sample is precisely measured into the graphite furnace, the current flow is begun, and a very high temperature is achieved, resulting in the production of an atomic vapor.

The graphite tubes are usually about 5 cm in length and about 1 cm in diameter. The sample is introduced with a micropipette through a hole in the top of the tube. The radiation from the hollow cathode lamp is focused through the axis of the tube. Heating is usually accomplished in stages. The first stage is a low-temperature step that has the purpose of volatilizing any water or solvent in the sample. The second, somewhat higher temperature step, is used to ash the sample, and this is followed by a rapid increase in current to achieve temperatures of 2000 to 3000°C and atomization of the unknown elements whose absorption is then measured.

The main advantage of the graphite furnace technique is improved detection limits due to greater sampling efficiency. Flames have low efficiency because flow down the drainage tube (see Fig. 3) results in most of the sample never getting to the flame, and also because the residence time of the atoms in the analytical portion of the flame is very brief. In contrast, graphite furnace atomizers utilize almost all of the sample and residence time is greatly increased.

Cold Vapor and Hydride Generation

Some elements, such as mercury, arsenic, tin, and antimony, are best analyzed in the vapor state. In this technique, the elements (except mercury) are converted to their gaseous hydrides with sodium borohydride in a reaction vessel. The gaseous hydrides are swept by an inert gas, such as argon, into a heated quartz cell that is located over the burner assembly area heated by the flame. A cold vapor technique is used for mercury.

An example where this technique might be useful is the case of tin. Organotin compounds are often used at very low levels as catalysts in certain urethane coatings. The typical detection limit for tin by conventional flame AA is 0.1 part per million (ppm), whereas the detection limit for the hydride method is 0.0002 ppm [2].

ATOMIC EMISSION SPECTROSCOPY (AE)

Instrumentation for atomic emission spectroscopy is very similar to that used for AA. In fact, the same instrument can usually be used for both methods. AE relies on detection of energy emitted from excited atoms as they relax to their ground state configuration as opposed to measuring the decrease in signal strength due to absorption of energy by ground state atoms being raised to an excited state. Since in AE the source of the measured light is the analyte itself, there is no need for an external light source such as the hollow cathode lamp used in AA. For this reason, the technique is more readily adaptable to multi-element analysis than AA. However, the number of elements readily analyzed by AE is considerably smaller than that detected by AA.

SOURCES OF INTERFERENCE

Spectral interference can affect AA and AE results. It can be caused by the overlapping of a line or band originating from an impurity element with the line being measured. For example, in emission analysis of sodium, the presence of calcium can give rise to spectral interference since thermally stable calcium hydroxide can form in the flame. This compound emits a band of radiation that overlaps the characteristic 590-nm line of sodium. This can be reduced to a certain degree if a monchromator of high resolution is used in AE.

Such spectral interferences are less common in AA than in AE. In AA the line source is the extremely narrow line produced by the hollow cathode lamp, and, therefore, monochromator resolution is less important in AA. However, there are still a few cases of spectral interference in AA. For example, both iron and platinum have absorption lines very near 272 nm, and manganese and gallium have lines near 403 nm.

Problems can be caused by chemical interference, which can decrease the population of free metal atoms and thereby yield an artificially low result. For example, many elements form stable oxides or hydroxides within a flame. Lithium is known to form a hydroxide in the flame. Such interferences can be minimized by increasing flame temperature.

Other types of interference include broad-band absorbance that is caused by molecules that have either formed or not been completely dissociated in the flame or by particulate matter in the flame.

Background Correction

Instrument manufacturers have devised a variety of instrumental methods for background correction. Background correction with a deuterium lamp relies on the fact that this lamp provides broadband continuous radiation in the ultraviolet region. By having a relatively wide slit width, the fraction of this radiation absorbed by the analyte is very small compared to the broadband absorbance due to molecular species in the flame or by scattering. Therefore, this type of interference can be corrected by simply subtracting the absorbance of the deuterium lamp from the absorbance of the hollow cathode lamp.

Another type of background correction utilizes the Zeeman effect. When vapor phase atoms are subjected to a strong magnetic field, a splitting of the electronic energy levels occurs. This produces, in the simplest case, three lines separated by a fraction of a nanometer and is termed the "Zeeman effect." The central, strongest line only absorbs radiation that is plane-polarized with the magnetic field, while the two weaker lines do not absorb radiation of this polarity. By mounting a rotating polarizer after the hollow cathode lamp, absorption by the analyte occurs only during the proper orientation of the polarizer. When the polarizer is in the opposite orientation, no analyte absorption occurs. Since background absorption and scattering occur during both cycles, it can now be subtracted to give only the absorbance due to the analyte.

The Smith-Hieftje technique relies on the observation that when hollow cathode lamps are briefly and cyclically pulsed at high currents, the emission band of the excited species is significantly broadened. The total absorbance from analyte plus background is obtained during the low current cycle, whereas the total absorbance during the high current pulse is primarily due to background. The signals can be subtracted from one another to obtain the corrected, analyte signal.

INDUCTIVELY COUPLED PLASMA SPECTROSCOPY (ICP)

Inductively coupled plasma spectroscopy is another technique for elemental analysis. As with conventional AE, the technique relies on measurement of light emitted when excited state atoms relax to their ground state. The major difference is that ICP accomplishes this through the use of a plasma rather than a flame. The plasma is formed as a result of argon gas being excited by an inductively coupled radio-frequency generator. One of the key elements in the instrument is the plasma torch into which the sample is carried by a rapid flow (~1 L/min) of argon.

The plasma is roughly 2 cm in diameter and is maintained within a water-cooled induction coil at the top of the torch. The torch consists of concentric quartz tubes through which argon flows. The plasma has a very intense, brilliant core. The temperatures in the plasma reach anywhere from 5000 to 7000°C, which is over twice that of most conventional flames used in AE. This higher temperature allows excitation of a greater number of elements than would be possible in a conventional flame, thereby extending the scope of the technique. Furthermore, it shares the advantage of AE over AA in that individual hollow cathode lamps are not required. Therefore, when coupled with either a rapid scanning or a multi-channel monochromator, ICP is a very efficient technique for conducting simultaneous multi-element analyses.

The higher temperature of the plasma in comparison to the flames results in more complete atomization and reduction in chemical interference. Although it would seem that the higher temperature of the plasma would result in increased sample ionization and therefore poorer determination limits, this is not the case because of the suppression effect caused by the large amount of argon ions [3]. Detection limits are typically an order of magnitude better than AA, and the calibration curves are also linear over a much wider range.

Although the various instrument manufacturers have their own designs, there are basically two types of ICP spectrometers: sequential and simultaneous.

In most sequential spectrometers, the light dispersed by a movable diffraction grating is focused on a fixed detector, allowing emission intensities to be measured over a wide range of frequencies. Alternatively, the grating can be kept at a fixed position and the detector moved [4]. Since the scan speed is relatively fast and since there is no need to install and change hollow cathode lamps, the technique is much faster than AA when more than five or six elements per sample are being determined. Indeed, current instruments have throughputs ranging from 20 to 50 elemental determinations per minute [5].

In simultaneous spectrometers, a series or bank of detectors, such as photomultiplier types or diode arrays, are positioned at fixed points about the grating so that light at several, preselected frequencies is measured simultaneously. This is a much faster technique than the sequential method, especially if ten or more elements are being determined per sample. A disadvantage with the simultaneous instruments

is their lack of flexibility. Since only a limited number of detectors can be used, only a limited number of preselected analytical lines can be measured. Typically, instruments can be set up to determine approximately 30 to 40 elements, although some can accommodate more than this.

Therefore, although able to detect more elements at somewhat better detection limits with an extended linear calibration curve compared to AA and AE, the biggest advantage of ICP spectroscopy is speed and especially so when multi-element analyses are performed. However, speed comes at a price. Conventional AA/AE spectrometers can be purchased for $15,000 to $30,000, whereas sequential ICP instruments are typically $50,000 to $75,000, and simultaneous instruments are well over $100,000. Therefore, if only a few samples are being analyzed per day for two or three elements, which is often the case in most coating laboratories, AA or AE is probably the most cost-effective choice.

APPLICATIONS

Approximately 70 elements can be detected in a practical sense with either AA or AE. Detection limits are typically subpart per million. Thus, the techniques are both versatile and sensitive. Although several hours may be required for sample preparation, the actual analysis step is usually extremely rapid. Samples must be introduced into the instruments as liquids of low viscosity with the material to be analyzed in a dissolved state. Some limited work has been done on fine suspension samples.

One of the most common uses of AA spectroscopy in the coating industry is determination of lead. Lead had become a major health concern, and its presence can greatly impact the cost of removal and disposal of old paint from various structures. The commonly accepted method for lead determination is ASTM Test Method for Low Concentrations of Lead, Cadmium, and Cobalt in Paint by Atomic Absorption Spectroscopy (D3335). In this method, the dried paint is ashed to burn off the organic materials and then digested in hot nitric acid. The method is also used to determine cadmium pigments and cobalt contained in some driers.

ASTM Test Method for Low Concentration of Mercury in Paint by Atomic Absorption Spectroscopy (D3624) is used for the determination of mercury that is contained in many common fungicides used in paint. The sample is decomposed at elevated temperature, dissolved in sulfuric and nitric acids, diluted, and analyzed using a cold-vapor AA technique.

ASTM Test Method for Low Concentrations of Chromium in Paint by Atomic Absorption Spectroscopy (D3718) involves ashing dried paint followed by digestion with potassium permanganate and sulfuric acid, dilution, and analysis.

ASTM Test Method for Low Concentrations of Antimony in Paint by Atomic Absorption Spectroscopy (D3717) involves ashing dried paint followed by refluxing with hydrochloric acid and stannous chloride.

Other ASTM atomic absorption and emission tests include:

- ASTM Test Method for Analysis of Aqueous Leachates from Nuclear Waste Materials Using Inductively Coupled Plasma-Atomic Emission Spectrometry (C1109)
- ASTM Test Method of Determining Elements in Waste Streams by Inductively Coupled Plasma-Atomic Emission Spectrometry (C1111)
- ASTM Test Method for Major and Minor Elements in Combustion Residues from Coal Utilization Processes (D3682)
- ASTM Practice for Flame Atomic Absorption Analysis (E663)
- ASTM Determination of Additive Elements in Lubricating Oils by Inductively Coupled Plasma Atomic Emission Spectrometry (D4951)
- A method for determination of zinc in cured films of inorganic zinc-rich primes that has been used in the author's laboratory involves digestion of the sample in 1:1 hydrochloric acid: water for 20 to 30 min followed by filtration and dilution. Results in good agreement with the manufacturer's published values have been obtained for a variety of coatings.

It should be pointed out that the usefulness of AA and AE spectroscopy is not limited to published ASTM test methods. The techniques are versatile, and in-house methods can often be devised to perform a variety of analyses. An excellent source of published test methods can be found in the journal *Analytical Chemistry*, "Application Reviews," usually published in the June 15 edition of every odd-numbered year since 1987 and in the April editions prior to 1987. For instance, the 1989 review [6] listed ten AA and AE methods for coatings and related products. These included determination of lead content in household paints, of nickel and cobalt in coatings for brass, of sodium and silicon in surfactants, and of metallic elements in poly(vinyl chloride). The 1993 review [7] lists 13 AA/ICP methods.

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Chromatography

Rolando C. Domingo[1] and updated by Rey G. Montemayor[2]

CHROMATOGRAPHY IS A TERM THAT DENOTES A myriad of laboratory separation processes based on a differential migration phenomenon. It is particularly effective for the resolution and separation of complex mixtures; hence, it can be used as a chemical preparatory method or, more importantly, as an analytical tool. This potent analytical technique has been widely used in the paint industry for a broad range of coating applications from everyday routine analysis to fundamental research into the nature of organic coating systems. Its use has been so extensive that virtually every type of material used in paint has been affected by chromatography.

Chromatography possesses certain inherent features that offer distinct advantages over conventional analytical techniques: complex mixtures, including isomers and homologs, can be separated; most of the equipment is relatively simple and inexpensive; chromatographic procedures are applicable to a broad spectrum of chemical types and are adaptable to both micro- and macro-size samples; and chromatography is capable of both qualitative and quantitative functions even when applied to multicomponent systems.

The term chromatography was coined by Tswett [1] who, in 1906, used powdered chalk and petroleum ether to separate plant pigments into colored zones of isolated pigment. The technique, as described by Tswett was largely ignored for a long time, and it was not until the late 1930s and early 1940s that Martin and Synge [2] applied the technique successfully to colorless materials, but the name has persisted. The term is currently used to signify a broad group of separation techniques, most of which are independent of color.

GENERAL PRINCIPLES

Chromatography is a separation process that is achieved by distributing the components of a mixture between two phases: a stationary phase and a mobile phase. Those components held preferentially in the stationary phase are retained longer in the system than those that are distributed selectively in the mobile phase. As a consequence, solutes are eluted from the system as localized concentration in the mobile phase in the order of their increasing distribution coefficients relative to the stationary phase. Considered simply, the chromatographic process involves the differential migration of sample components as they are moved through a chromatographic system. The rates of migration for the various components are related to their unequal distribution between two phases, a moving phase and a stationary phase. Distributions are determined by driving and resisting forces that are exerted between the two phases and the components in the sample. These forces are influenced by the chemical structure and the size and shape of molecules present in the chromatographic system and in the sample. Generally, the stationary phase is a finely divided solid serving as an adsorbing surface or a liquid supported by some inactive porous media; the mobile phase is usually liquid or gas. The effectiveness of a chromatographic separation depends upon proper selection of phases, and, although the choice is often made on an empirical basis with heavy reliance on experience, the best results are obtained by the application of established theoretical principles. Phases are selected so as to take advantage of some functional incremental differences in the properties of the compounds to be separated; for the most part, these are differences in molecular size, solubility in the liquid phase, and adsorption to the solid phase. In today's capillary gas chromatographic columns, solid supports are no longer used. Instead, the liquid or stationary phase is coated on to the wall of the capillary tubing. To improve thermal stability, the stationary phases are oftentimes chemically bonded to the tubing wall.

In practice, there are certain basic fundamentals that apply to all differential migration techniques, regardless of the separation media used: flow rates must be slow enough to allow equilibrium to occur between phases; solute concentration must not exceed the adsorption capacity of the stationary phase; and the greater the difference in partition ratio between phases, the shorter the migration path required for resolution. Since the efficiency of all chromatographic processes is governed by the above factors, these concepts should be kept in mind when a system to be used for a given separation is being considered.

Chromatographic separations are conducted usually in columns of carefully graded sorptive powders, in sheets, or strips of porous media such as paper, or in thin layers of powdered adsorbents spread on rigid surfaces. After a suitable system has been selected, a small quantity of the mixture is placed at one end of the chromatographic column and transported through the stationary phase with solvent or gas. Isolated compounds are detected "on column" if they are visible or "off column" by chemical or electronic means after leaving the column. A permanent record of the

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[2] *Imperial Oil Ltd, 453 Christina St. S, Sarnia, Ontario N7T 8C8, Canada.*

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Table 1—Classification of chromatography

MOBILE PHASE	STATIONARY PHASE
GAS	LIQUID
Gas Chromatography (GC)	Gas–Liquid Chromatography (GLC)
	SOLID
	Gas–Solid Chromatography (GSC)
LIQUID	LIQUID
Liquid Chromatography (LC)	Liquid–Liquid Chromatography (LLC)
	SOLID
	Liquid–Solid Chromatography (LSC)

separation may be obtained by photographing the column, by plotting some property of the separated components against elution volume on graph paper, or by electronic recording. Such records are referred to as chromatograms.

GENERAL CLASSIFICATION OF CHROMATOGRAPHY

As all chromatographic separations are carried out using a mobile and stationary phase, the primary classification of chromatography is based on the physical nature of the mobile phase. The mobile phase can be a gas or a liquid giving rise to the two basic forms of chromatography, namely gas chromatography (GC) and liquid chromatography (LC). The stationary phase can also take two forms: solid and liquid, thus providing two subgroups of GC and LC, namely; gas–solid chromatography (GSC) and gas–liquid chromatography (GLC), together with liquid–solid chromatography (LSC) and liquid–liquid chromatography. The different forms of chromatography are summarized in Table 1.

GENERAL METHODS

Frontal, displacement, and elution analysis are the three basic methods for conducting chromatographic separations, and each has its own unique function. Separations are determined by adsorption or partition interplay between sample, stationary phase, and moving phase.

Frontal Analysis

Frontal analysis separations are made by the continuous addition of the sample onto a column containing an adsorbent. As the sample passes through the column, the component having the lowest adsorption affinity for the adsorbent emerges first. After the most strongly adsorbed component has saturated the column, the sample flows through the column unchanged. Only a limited portion of the least adsorbed component can be obtained in pure form. Frontal analysis is not an effective method for resolving mixtures, but it does provide a means of treating solutes having strong adsorption characteristics. This means of separation is seldom used in the coatings industry because of the advances in column technology for both liquid and gas chromatography.

Displacement Analysis

In this method, a concentrated portion of a sample is adsorbed onto a column, followed by the addition of a solvent (developer) that is adsorbed more strongly than any of the components in the sample. As the developer passes through the column, the components are displaced and forced ahead of it. Components will also displace one another so that the one least strongly adsorbed emerges from the column first, followed by the others in the order of increasing adsorption affinity. The component with the greatest adsorption affinity elutes last, immediately ahead of the displacing solvent. Under optimum conditions, each component will move through the column as a "belt" of pure material. A graph, obtained by plotting volume against some physical property of the effluent, will contain a series of steps. Under optimum conditions, each component will move through the column as a "belt" of pure material. A graph, obtained by plotting volume against some physical property of the effluent, will contain a series of steps. Under standardized conditions, the height of each step is used for identification, and the length of each plateau is used to determine relative amounts. When put to practice, all reversibly adsorbed components are moved through the column, but they are not resolved completely. The trailing edge of one component will overlap the leading edge of the following component, and, although it is not possible to completely separate each component in its pure form, normally a relatively pure fraction of each is attainable.

Elution Analysis

Elution processes are conducted by introducing a concentrate of the sample onto a column followed by the addition of an unadsorbed moving phase. As the sample mixture is washed through the column, components are selectively retarded and separated into discrete zones that are isolated by the presence of the moving phase between zones. This procedure contrasts with displacement and frontal methods by having the eluting solvent pass through the sample. Theoretically, complex mixtures can be completely resolved; hence, elution chromatography has the potential of being a good procedure for qualitative and quantitative analysis.

Of the three processes discussed, elution chromatography is the most efficient method for resolving mixtures, which accounts for its being the most widely used form of chromatography.

Adsorption Chromatography

Chromatography can be further classified as adsorption and partition chromatography. In adsorption chromatography, the stationary phase is a solid, most often a powder or granular adsorbent, and the mobile phase is either a liquid or gas. Sample components are separated according to their relative adsorption on active surfaces as they are percolated through an adsorbent bed. For any particular component, the degree of adsorption is related to the competitive attraction exhibited by the adsorbent and developing phase. Thus, if a component is attracted strongly by an adsorbent and attracted weakly by the moving phase, it shows little or no movement through the column. Conversely, if it shows a greater affinity for the moving phase than for the adsorbent, it will tend to move along with the moving phase. Hydrogen bonding, dielectric constants, and dipole moment of the sample and the two phases are factors that greatly influence adsorption separations. In general, strong adsorption is favored by the presence of highly polar compounds in weakly polar moving phases.

LSC denotes the use of a liquid moving phase, whereas GSC indicates a gaseous moving phase. Prior to the introduction of partition chromatography by Martin and Synge in 1941 [2], adsorption chromatography was used exclusively. A vast selection of adsorbents and mobile phases are available, providing a great deal of flexibility for separating mixtures. Various aspects of adsorption chromatography, including technique and equipment, will be discussed in greater detail during the treatment of specific methods such as "classical column chromatography," thin layer chromatography, etc.

Partition Chromatography

Partition chromatography is distinguished from adsorption chromatography by the presence of a liquid that is positioned in the system by sorption to an inactive solid support. The liquid layer is the stationary phase, and the solid merely serves as a support. Separation of compounds is related to their differential solubility in two immiscible phases. Hence, a compound demonstrating a solubility preference for the stationary liquid phase will have its passage through the column retarded. Those that are less soluble in the stationary liquid phase, but readily soluble in the mobile phase, tend to move unimpeded through the column. In a static experiment with a given set of phases, a compound will be distributed between phases in a characteristic manner. This property is referred to as its partition coefficient, *k,* and may be defined as follows:

$$k = \frac{[\text{concentration of compound in stationary liquid phase (g/ml)}]}{[\text{concentration of compound in moving phase (g/ml)}]} \quad (1)$$

Since components are separated by virtue of differences in their partition coefficients, conditions of a test are adjusted so as to take advantage of some factor peculiar to each component that magnifies quality differences in k values. Fortunately, only slight differences are required for separation, and such differences can be achieved by proper selection of stationary liquid phase.

Although partition chromatography is historically more recent, it has surpassed adsorption chromatography as a method for separating complex mixtures. In partition chromatography there is a more rational relationship between the chemical character of materials and their chromatographic behavior, which accounts for its effectiveness when applied to the separation of closely related compounds such as isomers and members of a homologous series. Adsorption chromatography, however, is more limited in its applications; it will distinguish between classes of compounds, but there is little sub fractionation within classes.

LIQUID CHROMATOGRAPHY

Of the various forms of chromatography, the form using a liquid eluent came first. LC is characterized by the employment of a liquid moving phase; the stationary phase may be either liquid or solid. The separation of molecules is based on their preference for a liquid or solid stationary phase relative to a liquid moving phase. LC encompasses established techniques such as paper, thin layer, "classical column," and gel permeation chromatography, all of which have been used extensively for routine and research purposes. For the purpose of clarity and continuity, the different chromatographic techniques will be discussed as separate entities, but, in some cases, there has been a fusion of techniques. For instance, papers have been impregnated with ion exchange materials; gels, the material commonly associated with gel permeation chromatography, have been spread on thin plates for thin-layer separations.

"Classical Column" Chromatography

The term "classical column" chromatography is used here to define procedures usually associated with older forms of chromatography. The method involves the introduction of a sample onto a column packed with adsorbent; separations are facilitated by the addition of a displacing or eluting solvent.

Apparatus and technique—The essential equipment consists of container, adsorbent, and developing solvent. The container for the column of adsorbent is usually a glass tube, from about 5 to 50 mm in internal diameter, with a working height of from 5 to 25 times the diameter. Columns prepared from plastic and metal tubes have also been used. Fritted glass disk, perforated plastic, cotton, or glass wool may be used at the base of the column to support adsorbents such as silica, magnesium and aluminum oxides, calcium phosphate, charcoal, and cellulose. Adsorbents vary in their capacity and activity, with activity increasing with decreasing particle size and water content. If practical flow rates are to be realized, it is necessary to use relatively large particles, but not so large as to reduce the capacity below reasonable limits. In addition, narrow mesh ranges provide more uniformly packed columns and columns of higher efficiency. Adsorbents may be packed in two ways, as a dry powder or as a slurry. To ensure uniformity, the tube should be vibrated frequently and a vacuum or pressure applied during addition of packing material.

Although the activity and capacity of different adsorbents are not the same, the sequence of eluting power for different solvents is the same for any given adsorbent. In order for separation to occur, the eluting solvent must be appropriate to the packing material and sample. For example, a very polar solvent will displace the sample completely with little or no separation of components; on the other hand, a very nonpolar solvent may cause all of the components to adsorb on one section of the column with little migration or separation of components. A general practice is to start the analysis with the most nonpolar solvent and gradually change to solvents of increasing polarity. The process of systematically changing the composition of eluting media during a chromatographic analysis is referred to as gradient elution [2]. Strain [3,4] lists absorbents according to their absorptive strength and solvents in the order of their eluting power.

An analysis is conducted by introducing a sample in a few milliliters of nonpolar solvent and allowing it to flow onto the column. The eluting solvent is added, in small increments at first, and then in large quantities. At no time during the analysis is air drawn through the column. If colored compounds are chromatographed, they are detected visually on the column or in the effluent. Certain

colorless compounds may be examined by fluorescence when exposed to ultraviolet radiation, or the packing may be extruded and the components detected after treatment with reagents. Eluted components are identified by dividing the effluent into aliquots and determining such properties as refractive index, nonvolatile content, *p*H, optical density, etc: Automatic fraction collectors, actuated by weight of fraction or a timing device, can be used to avoid manual collection of effluent.

Classical chromatography, as it is commonly used, is relatively simple but lacks detector sensitivity and is time consuming. The latter is particularly true when a fresh column is required for each analysis. Nevertheless, this type of chromatography has contributed to the general knowledge of organic coatings and to paint analysis.

Applications—ASTM Test Method for Hydrocarbon Types in Liquid Petroleum Products by Fluorescent Indicator Adsorption (D1319) describes the determination of hydrocarbon types in petroleum products. A column is packed with activated silica gel containing a mixture of fluorescent dyes. A hydrocarbon mixture is introduced onto the gel, and isopropyl alcohol is added to desorb the sample down the column. The hydrocarbons are separated according to their adsorption affinities; aromatics are retained the most tenaciously, immediately followed by olefins, and finally by saturated hydrocarbons. The fluorescent dyes are also separated selectively with the hydrocarbon types and make the boundaries of the aromatic olefin and saturate zones visible under ultraviolet radiation. The volume percent of each type of hydrocarbon is calculated from the length of each zone. A separation of this type is an example of adsorption chromatography by displacement; the developing solvent in this case is isopropyl alcohol. Hydrocarbon types in mineral spirits and VM&P naphtha have been determined using this method.

Loeblich and Lawrence [5] used partition chromatography for the qualitative and quantitative analysis of rosin and modified rosin products. The column is packed with 2-aminopyridine-furfuryl alcohol on silicic acid. The alcohol serves as the stationary liquid phase; isooctane is the eluting solvent. Fractions are collected and titrated with 0.01 N sodium hydroxide solution.

Swann et al. [6] used carbon black and asbestos to separate phthalate plasticizers from phthalate resins. Phthalate resins were retained selectively on the column, and phthalate plasticizers were detected and measured by saponification of the effluent.

HIGH PERFORMANCE (OR HIGH PRESSURE) LIQUID CHROMATOGRAPHY

In recent years the term liquid chromatography has acquired new significance by being used to denote a completely integrated column-detector-recorder system. New developments in instrumentation make use of the principles and practices commonly associated with gas chromatography, the object being the attainment of rapid and high-efficiency separations. Traditional methods, out of necessity, employ large samples, slow flow rates, and short columns, conditions that are not conducive to rapid, efficient analysis. With the advent of high-pressure flow systems and highly sensitive continuous flow detectors, operating conditions closely approaching those used in gas chromatography may now be used. The total unit consists of thermostated columns, solvent reservoir, degasser, metering pump, detector, and strip chart recorder/electronic integrator.

The resurgent interest in liquid chromatography has prompted an ever-increasing number of instrument manufacturers to produce highly sophisticated instruments that are capable of multiple modes of operation including adsorption, partition, and gel permeation separations. The term high performance (or high pressure) liquid chromatography (HPLC) will be used in this section to designate adsorption and partition separations based on advanced liquid chromatography technology. Descriptions of liquid chromatographs have been presented by Lambert [7], Stouffer et al. [8], and Jentoft and Gouw [9], the principal differences being in the techniques used to monitor the sample stream.

HPLC has already reached the level of acceptance enjoyed by many other chromatographic techniques. Its potential as an analytical tool is still creating an enormous amount of interest. In the past, most publications were concerned with the refinement of instruments with less emphasis on applications. Presently, publications are now focusing on the applications of HPLC in the paint and coatings industry. HPLC complements other forms of chromatography. For example, HPLC can be used for the analysis of compounds having a broad range of molecular weight, whereas thin-layer and paper chromatography are limited to nonvolatile compounds and GC is limited to those that can be vaporized. HPLC is usually regarded as a relatively slow method when compared to other chromatographic techniques. However, the time necessary to produce a separation is related directly to the resolution required. HPLC can make separations of simple mixtures at speeds comparable with GC; complex samples may still require several hours. Readers are encouraged to read ASTM Practice for Liquid Chromatography Terms and Relationships (E682).

Apparatus and technique—Fig. 1 shows the pertinent components of a liquid chromatograph. Solvent from one of the reservoirs is moved through a degasser by a pulse-free pump that is capable of delivering flow over a wide range of pressures. The flow is split into two streams; one is directed to the reference side of a differential detector, the other is allowed to pass through a sample injector, fractionating column, and finally to the sample side of the same detector. The sample is introduced with a syringe, or sample loop, located at the entrance to the column, and the effluent from the column is generally monitored by a continuous flow differential detector.

Most column packings used in traditional methods for both adsorption and partition separations may be used for HPLC, for example, silica gel, alumina, diatomaceous earth, etc. There have been, however, newly developed packings that greatly extend and enhance the use of HPLC. In the past, the development of LC was impeded by hydraulic difficulties and detector problems, but with the advent of improved solvent transport equipment and high-performance continuous flow detectors, HPLC has been elevated to a position of new prominence. At this point, it is needless to belabor the importance of each of these two factors. However, the performance characteristics of the various detectors should be carefully considered since the type used directly influences the effectiveness of the total system. Some detectors are selective, responding to only certain classes of compounds,

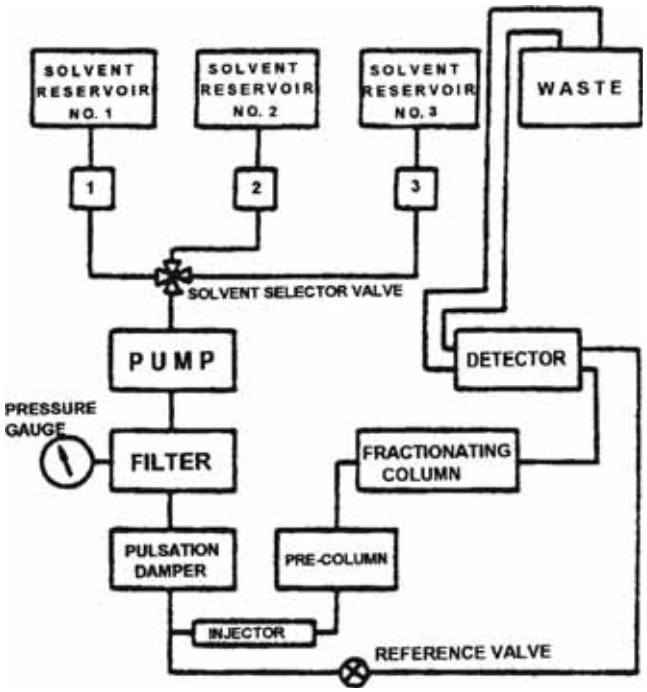

Fig. 1—Schematic diagram of high-pressure liquid chromatograph.

while others are applicable to a wide range of classes and have broader application. For this reason the best use is made of detectors in the context of the complete system and sample to be analyzed. Photometric, refractometric, calori-metric, radiometric, polarographic, and ionization detectors have been evaluated by Huber [10]. He concluded that all of them can be used for HPLC, but that a universal, all-purpose detector is not yet available. Some of the more conspicuous detectors will be discussed briefly so as to provide background regarding principle of operation and area of usefulness.

At the present time, refractive index comes closest to being the universal detector for liquid chromatography. Detection depends on the difference in the refractive indexes of pure solvent flowing through the reference side of the detector and of the effluent from the analytical column; measurement is nondestructive to the sample, the level of sensitivity is good, and operation is simple. Use of the refractive index detector in liquid chromatography is discussed in ASTM Practice for Refractive Index Detectors Used in Liquid Chromatography (El303-95 (2009)). As with other nondestructive detectors, when used in conjunction with an automated fraction collector, the sample can be isolated and subjected to further treatment.

The heat of adsorption detector is also applicable to a wide range of materials since it responds to an almost universal property of materials, heat of adsorption. Thermal changes, induced by the desorption and adsorption of the sample, are sensed, amplified, and recorded as positive and negative peaks on a chromatogram.

The flame ionization detector, also called chain, cord, and belt detectors, combines high sensitivity and quantitative analysis with wide dynamic range. In flame ionization detection, all of the carrier leaving the column can not be directed through the detector; instead, a small wire or belt is passed continuously through the eluting stream collecting a portion of the sample. The carrier solvent is flash evaporated in one chamber, and the sample residue is then moved into a pyrolysis zone where the sample is decomposed thermally and detected with a flame ionization detector. Since the carrier solvent is removed completely, this type of detector is not affected by gradient analysis, but at the same time, its use is restricted to nonvolatile compounds. Obviously, this type of detector is well suited for the analysis of resins, polymers, and oils.

Photometric detectors measure the difference in ultraviolet light adsorption between a sample and reference stream. Since ultraviolet adsorption is parameter-specific, this type of detector is limited to chromophores. This property, of course, can be advantageous when non-ultraviolet and ultraviolet adsorbing compounds emerge from a fractionating column together.

Applications—Bombaugh et al. [11] were able to separate ethylene glycol, cdiethylene glycol, and triethylene glycol using a column packed with porous silica beads; the eluting solvent was water in methyl ethyl ketone, and the eluted compounds were detected using a differential refractive index detector. Poulson and Jensen [12] used an adsorption column composed of 100 to 200-mesh silica gel for the separation of alkene-alkane hydrocarbons. Diatomaceous earth coated with various liquids was used to separate and determine aromatic hydrocarbons [13]. The compounds were sensed with a differential photometric detector. ASTM Practice for Testing Fixed-Wavelength Photometric Detectors Used in Liquid Chromatography (E685-93 (2005)) discussed the use of the fixed wavelength photometric detectors in liquid chromatography.

SUPERCRITICAL FLUID CHROMATOGRAPHY

Supercritical fluid chromatography (SFC) is a relatively recent chromatographic technique, having been commercially available since only about 1982. What differentiates SFC from other chromatographic techniques (GC and HPLC) is the use of a supercritical fluid such as liquefied CO_2 as the mobile phase. As such, the entire chromatographic flow path must be pressurized. Compared with HPLC, SFC provides rapid separations without the use of organic solvents. With the desire for environmentally conscious technology, the use of CO_2 as the mobile phase contributes to efforts to reduce the introduction of environmentally harmful organic chemicals. In addition, SFC separations can be done faster than HPLC separations because the diffusion of solutes in supercritical fluids is about ten times greater than that in liquids. Although solute diffusion in supercritical fluids is about three times less than in gases, SFC allows high resolution at a much lower temperature thus allowing fast analysis of thermolabile compounds. SFC is compatible with both HPLC and GC detectors. As a result, optical detectors, flame detectors, and spectroscopic detectors can be used. Because of the high pressures of SFC, care has to be taken such that detector components are capable of withstanding the usual range of pressures used in SFC systems. This chromatographic technique is not used in the paints and coatings industry.

PAPER CHROMATOGRAPHY

Paper chromatography, as the name implies, uses paper as the separation media. A strip of filter paper is spotted

with the sample near one edge and is arranged so that developing solvent can move by capillary action through the sample. The differential distribution of components between phases (paper and developing solvent) causes them to migrate at characteristic rates. If compounds are colorless, reagents may be applied to reveal them as circular or elliptical spots.

The popularity of paper chromatography can be attributed to several desirable qualities. The method is extremely versatile and simple, it allows for simultaneous analysis of several samples on one paper, and optimization of the developing solvent is easily controlled. On the other hand, one should be cognizant of certain disadvantages. The sample must be non-volatile or be capable of conversion to a nonvolatile derivative before analysis, the length of the migration path is limited, and quantitative analysis is moderate. Most important, extraordinary precautions must be taken to reproduce conditions of test in order for retention data to be reproducible and significant.

Apparatus and technique—The equipment necessary to conduct paper chromatography involves materials common to most laboratories. Whatman No. I filter paper has been the type most widely used, but for many analyses, other types of filter papers are adequate and sometimes preferred. A large assortment of containers has been employed as developing chambers: glass jars, test tubes, graduated cylinders, specimen tanks, and pipes can all be used if thev are provided with tight-fitting lids. An unlimited number of liquid mobile phases are available; the type used is dictated normally by the polarity of the sample.

Capillary action is the principal dynamic force involved in ascending, lateral, or radial paper chromatography. However, in the case of descending chromatography, the movement of solvent is initiated by capillary action and finished by gravity. Occasionally, particularly when complex mixtures are encountered, it may be necessary to employ, a two-dimensional technique. In this type of analysis the separation is carried out using one solvent in one direction. drying the sheets, and finishing the separation at right angles with another solvent. In all paper chromatographic separations, it is essential that the internal volume of the developing chamber be saturated with vapors from the eluting solvent.

If cellulose papers are exposed to water vapor, they will adsorb about 22 % of water that may serve as the immobile liquid phase for reverse phase chromatography. Where water is impractical as an immobile phase because of sample insolubility, papers can be impregnated with other liquids such as kerosene, silicone oil, and olive oil. It is sometimes necessary, for the solution of special problems, to alter the composition of the paper. This can be done by direct chemical treatment or by the addition of a material having special properties, such as an ion exchanger. Paper of this type represents a departure from conventional paper chromatography since principles based on other techniques are involved.

Under stringently controlled conditions, compounds may be identified by their R_f values. The R_f value is the ratio of distances traveled by a compound and the solvent front, expressed as follows:

$$R_f = \frac{\text{distance traveled by compound}}{\text{distance traveled bt solvent front}} \qquad (2)$$

Although the use of R_f values is well documented in the literature, they are often difficult to reproduce and should be used with caution. When R_f values are reported, detailed information concerning all of the operating parameters must be stated.

Since it is possible to conduct multiple analyses on one sheet, an unknown mixture can be identified by analyzing it in parallel with standard compounds; direct comparison can be made with respect to the retention characteristic of both the sample and standard. If standards of known concentration are run simultaneously with the unknown, the amounts of each isolated component can be estimated from their relative intensities.

For additional information regarding the theory and practice of paper chromatography, the reader is referred to books by Hais and Macek [14] and Block et al. [15].

Applications—Dicarboxylic acids and polyols have been identified in polyesters [16] by paper chromatography. Following dissolution of the resin with alcoholic potassium hydroxide, isolated dipotassium salts were converted to their corresponding acids and separation was accomplished by ascending technique. Polyols recovered from the saponification filtrate were separated by a two-dimensional technique; chloroform-ethanol mixture, used first in one direction, was followed by elution at right angle with ether saturated with water. Dicarboxylic acids were visualized with bromcresol purple, and polyols were detected by spraying with ammoniacal silver nitrate. Tawn and May [17] identified dicarboxylic acids and polyols in alkyd resins using a similar procedure.

Mills and Werner [18] identified various types of natural resins using reverse phase chromatography. Papers were wet with kerosene and were blotted to remove excess kerosene. Samples were chromatographed with a liquid moving phase consisting of isopropanol-water-kerosene. The papers were dried, sprayed with a carbon tetrachloride solution of phenol, and exposed to bromine vapor. Colors varied according to the type and amount of resin.

THIN-LAYER CHROMATOGRAPHY

In thin-layer chromatography (TLC) an aqueous slurry of a finely divided adsorbent mixed with a binder is spread on a glass plate so that a uniform, coherent film adheres to the glass. Coated plates are dried and activated by baking in an oven for a prescribed length of time. An analysis is conducted in much the same manner as in paper chromatography. A plate is spotted with a sample and placed in a chamber containing solvent. After the developing solvent has irrigated the TLC plate, the plate is removed from the tank, dried, and compounds are detected with appropriate reagents. As in paper chromatography, the vital driving force exhibited by the mobile phase is that supplied by capillary action; separation is due to adsorption or partition processes.

Paper chromatography and TLC are similar, and both share some of the same advantages such as high sensitivity, selectivity, and low cost. TLC, however, provides sharper zone separation and increased speed, 20 or 30 min for most TLC analyses as opposed to several hours for paper chromatography. TLC is subject to most of the disadvantages described for paper chromatography, for example, compounds must be nonvolatile, have a limited elution path, etc.

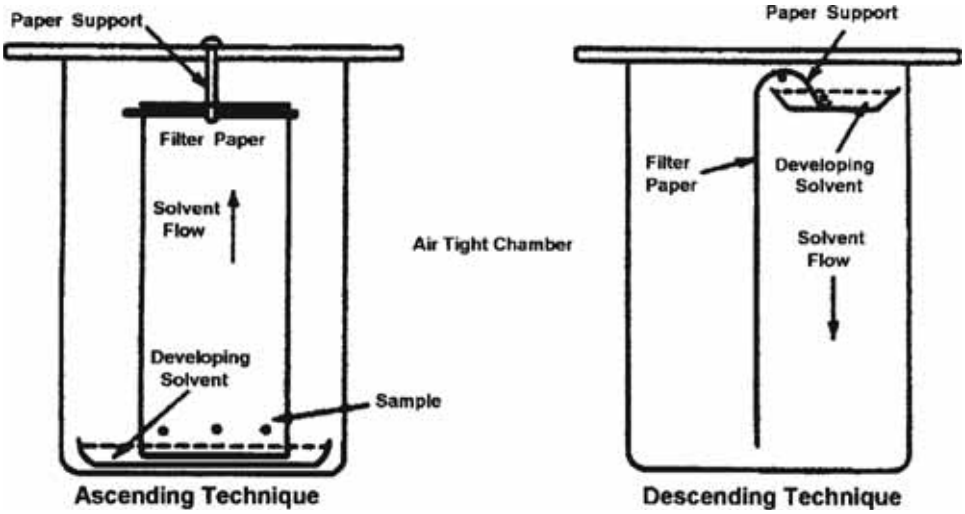

Fig. 2—Apparatus for paper chromatography.

Apparatus and technique—Equipment requirements for TLC are minimal. The basic materials, as shown in Fig. 2, consist of a tank, plate, adsorbent, visualization reagent, rack, and adsorbent applicator. Relatively inexpensive equipment can be purchased from distributors of chromatographic supplies; if necessary, however, apparatus can be usually improvised from material found in most laboratories. A developing tank must have a tight-fitting lid, and it should be large enough to receive 2 × 8 in. (5.08 × 20.32 cm) or 8 × 8 in. (20.32 × 20.32 cm) plates, but not so large as to require a large solvent reservoir. A "tankless" system can be arranged by sandwiching the thin layer between two plates and placing the sandwiched layer in a shallow trough containing solvent. The nature of the adsorbent plays a major role in determining the type of separation that will be obtained. In a broad sense, any of the adsorbents used in column chromatography can be used to prepare thin films provided they are available as powders of uniform particle size. Silica gel and aluminum oxide are used most frequently. The homogeneity and quality of adsorbent powders are important factors to be considered if well-defined results are to be obtained. For a given adsorbent, the migration of components in a mixture is determined by the choice of mobile liquid phase; its polarity can be altered to enhance or suppress the movement of the components. For example, if a sample moves with the solvent front, the polarity of the mobile phase should be reduced by choosing a solvent of lower polarity or by mixing solvents of different polarity. Conversely, if a sample shows little tendency to move, the polarity of the eluting solvent is increased by selecting a solvent occurring lower in the eluotropic series or by changing the ratio of polar and nonpolar solvents, favoring the polar solvent. The eluotropic series, solvents arranged in order of polarity, and other solvent activity have been described in books [19,20]. The preparation of chromatoplates is relatively easy and can be accomplished by using several techniques: pouring, dipping, spreading, or spraying, The first two methods require no special equipment, but they lack the refinement needed to provide uniform films. The spray technique is messy and does not always yield films of uniform thickness. By far the most popular technique is that which uses a draw bar. Films are prepared by mixing adsorbent, binder, and water until a homogeneous slurry is obtained. Glass plates, usually 2 × 8 in. (5.08 × 20.32 cm) or 8 × 8 in. (20.32 × 20.32 cm), are aligned on a perfectly flat surface. A spreader is positioned on the end plate, charged with the slurry, and drawn across the plates with constant pressure and speed. For analytical purposes, film thickness should be in the range of 0.2 to 0.5 mm. Chromatoplates are air dried and, if desired, activated by heating at elevated temperatures. Although glass is the most common substrate, plastic and fiber glass sheets have been used successfully. TLC sheets from plastic and fiber glass can be cut and shaped with scissors. Pre-coated glass plates and plastic sheets can be purchased from several commercial sources, and, although the price per plate is increased substantially, the cost is still within the budget of most laboratories. A solution of the sample may be transferred to the chromatoplate with a micropipette or syringe. After the diluting solvent has evaporated, the plate is transferred to a developing chamber where it is irrigated with the developer solvent. If a two-dimensional technique is necessary, the plate is turned 90° and treated with another solvent. The plates are dried and then sprayed with an appropriate visualization reagent.

Methods of identification are similar to paper chromatography; R_f values or "parallel analysis" are standard techniques for TLC. Additional information may be obtained by removing spots with a spatula and subjecting them to chemical or instrumental analysis. Visual comparison with standards of known concentrations run simultaneously is often sufficient for estimating the amount of a component. If more precise quantitative information is required, instrumental methods are used. Densitometric techniques measure the density of color or acid char on the plate and relate this property to the amount of sample present. With all quantitative TLC procedures, it is important to rigidly control sample application, adsorbent quantity, and solvent composition. For an in-depth treatment of TLC theory and practice, the reader is referred to books by Truter [19], Bobbitt [20], Randerath [21],and Stahl[22].

Applications—the utilization of TLC for paint research and routine applications has been illustrated by Privett

and Blank [23] and Rybicka [24]. The former dwells on the many general applications to fats and oils that are important to the paint chemist. Privett and Blank also demonstrated the use of TLC for the determination of total saturated fatty acids in oils, and an investigation of a more basic nature illustrated the usefulness of thin films for elucidating mechanisms involved in the auto-oxidation of oils. An interesting application, as described by Rybicka, illustrates the utility of TLC for monitoring glycerolysis reactions. Periodic sampling and TLC analysis on silicic-acid-coated plates were used to show how triglyceride content is decreased, accompanied by an increase in mono- and diglycerides. Similar studies with other polyols and oils were described.

A very comprehensive survey of TLC methods as applied to lipids has been made by Mangold [25]. Included are details for the separation of glycerides, fatty acids as methyl esters, and cis- and transisomers along with other facets of lipid analysis. Many of the methods are capable of yielding information relevant to the analysis of organic coating materials. Knappe [26] demonstrated the application of TLC to a broad spectrum of coating materials including polyols, dicarboxylic acids, fatty acids, and hydrolysis products from nitrogen resins. Numerous chromatograms and comprehensive retention data were presented to illustrate applications. Techniques for the fractionation of materials used by the plastic industry, but of importance to the paint chemist, have been described [27–29]. These data include tables of R_f values of polyhydric alcohols, dicarboxylic acids, and plasticizers. An impressive list of 40 plasticizers is presented in Ref. [29]. Separations were performed on silica gel layers using methylene chloride as the mobile phase. Antimony pentachloride was the primary visualizing agent.

Potentially, TLC promises to be an extremely valuable tool for research and quality control problems, and wider acceptance by the paint industry should be seen in the near future. The commercialization of precoated TLC plates from several manufacturers should alleviate some of the reproducibility problems associated with "homemade" TLC plates prepared in the past. Used to its fullest potential, TLC techniques can be used to screen and/or separate a wide variety of relatively nonvolatile materials prior to HPLC analyses.

GAS CHROMATOGRAPHY

Of the various forms of chromatography, that using a gaseous moving phase has proved to be the most effective for the analysis of organic coating materials. As in most chromatographic processes, the separation of compounds may occur by partition or adsorption activity—GLC and GSC, respectively. The equipment for, and the execution of, both forms are similar; however, due to its versatility and effectiveness, GLC has made a much greater impact on paint analysis, and for that reason it will be emphasized and discussed at considerably greater length. A glossary of GC terms can be found at the end of this chapter.

The primary object of this discussion is to impart to the reader a basic concept of GC processes and to focus attention on the many applications to paint analysis. Within the scope of the discussion, it will be only possible to etch the surface of present GC knowledge. If the references appear to be numerous, it is because the technique has such broad application and not because it has been exhaustively investigated.

GC is a separation technique that uses a gaseous moving phase to transport volatilized components of a sample through a small diameter tube containing a solid adsorbent or a liquid fixed to an inert porous solid. As the components advance through the column, they are retarded selectively by sequential adsorption on a solid stationary phase or by solubilization in a liquid stationary phase. A sensing device, located at the exit of the column, detects the various components by responding electronically to some physical or chemical property. From the time of appearance and the magnitude of the signal furnished by the detector, information regarding the number, type, and concentration of components can be usually ascertained.

Since the advent of GC, many time consuming and laborious test procedures have been reduced to routine methods of short duration. In addition, the unique responsive capability of GC permits the accumulation of analytical information, much of which cannot be obtained by conventional techniques. In short, GC is characterized by versatility, reliability, and speed.

The outstanding popularity and performance of GC can be attributed to features that are inherent in this type of analysis. Any material that is volatile or can be converted to a volatile derivative will respond to GC. GC is extremely sensitive—as little as one nanogram of some materials can be detected. Rapid and efficient analysis is made possible by the low density and viscosity of carrier gases, which permits rapid mass transfer between phases, thereby allowing rapid flow rates. Columns can be used repeatedly; several hundred analyses on one column are not unusual. The production and interpretation of data are relatively uninvolved. On the other hand, GC has certain disadvantages. Materials remaining on a column are not detected. Owing to the empirical nature of the technique, chemical or instrumental confirmatory tests may be necessary to verify the presence of a compound, particularly when background information concerning the sample is lacking.

Ever since its introduction by James and Martin [30] in 1952, a wealth of GC information has appeared in the literature that has swelled to mammoth proportions. The retrieval of such information is readily made possible through the use of compiled classified indices such as bibliographies [31,32] and annual volumes of Gas Chromatography Abstracts [33,34]. In addition, for current developments, Preston Technical Abstract Company [35] offers a weekly abstract service consisting of tides of papers and abstracts. Reviews [36–46] reflecting specific application to organic coatings have also been published. ASTM Committee E19 on Chromatography's Chromatographic data compilations [47–50] are arranged according to compound and liquid phase; data include relative indices for a vast number of compounds obtained in different columns. Committee E19 has also been responsible for the publication of two general methods, ASTM Practice for Packed Column Gas Chromatography (E260) and ASTM Practice for Gas Chromatography Terms and Relationships (E355). ASTM Committee D01 on Paint and Related Coatings, Materials, and Applications also published Practice for Direct Injection of Solvent-Reducible Paints Into a Gas Chromatograph for Solvent Analysis

(D3271-87 (2006)) and ASTM Test Method for Analysis of Dichloromethane and 1.1,1-trichloromethane in Paints and Coatings by Direct Injection Into a Gas Chromatograph (D4457-85).

Gas-Liquid Chromatography

Various terms such as gas-partition, vapor-phase-partition, gas-liquid-partition chromatography, and vapor fractometry have been used interchangeably when referring to GLC. However, the name GC is probably the most commonly used.

GLC is characterized by the presence of a stationary liquid phase, usually a nonvolatile liquid or solid that is liquid at the operating temperature, supported by the wall of a tube or by sorption to an inert porous material such as diatomaceous earth. In GLC, the components to be separated are vaporized at the entrance of a partition column and moved through the column by a continuous flow of inert gas. For the most part, the rate of migration exhibited by components is dependent upon their degree of solubility in the immobile liquid phase. Very soluble molecules are dissolved readily by the stationary phase, and their passage through the column is retarded. Compounds that have poor or moderate solubility in the liquid phase spend more time in the carrier gas and move through the column rapidly. Ideally, the multiplicity of variable conditions can be regulated so that each compound will reach the end of the column at different times where they are detected electronically as they leave the column.

The distribution of a compound between phases is referred to as its partition coefficient. Although the partition coefficient difference may be very small in a static experiment where only one equilibrium occurs, separation is possible through magnification of that difference by a continuous series of equilibria that is the normal occurrence during chromatographic separation. Since the partition coefficient is affected directly by the solubility characteristics of the liquid phase, the equilibrium for a given compound can be shifted by using stationary phases at different chemical structures. Liquid phases of varying polarity are available in great number, and it is the exploitation of their different selectivities that accounts for the tremendous flexibility and effectiveness of GLC.

Apparatus and technique—the essential components of a gas chromatograph are shown schematically in Fig. 3. In the following discussion of equipment, it will be convenient to explain the process under its operational stages, which may be briefly summarized as follows. The flow of gas, usually from a compressed gas cylinder, is adjusted to desired levels with a series of pressure and flow regulators and split into two streams; one is allowed to flow through the reference side of a differential detector and the other is directed to the injection system, which is located immediately ahead of the column. This segment of the chromatograph, the injection port or flash vaporizer, is maintained at a temperature sufficiently high to cause instantaneous vaporization of the sample in the flowing carrier gas. Introduction of liquids and solids in solution is accomplished most often by injection through a self-sealing silicone rubber septum with a hypodermic syringe. The sample is carried immediately onto the column where the various components are separated by virtue of their different partition coefficients. As the components emerge from the partition column, they pass through a sensing device that transmits an electronic signal proportional to the concentration of the sample to a potentiometric strip recorder or an electronic integrator.

To provide maximum performance and flexibility, the injection port, column oven, and detector should all be individually thermostated. A rule of thumb is that the temperature of the injection system and detector should be at least 25°C higher than that of the column.

The choice of carrier gas is limited to a few inert gases, and this is restricted even more by the type of detector used. The most widely used carrier gases are helium, nitrogen, hydrogen, and argon.

A GC detector must be capable of sensing minute changes in the composition of the carrier gas in a reproducible and precise manner. In order to perform effectively, GC detectors must have high sensitivity, linear response, and low noise level. Secondary factors such as low cost, simplicity, and ruggedness are also desirable. The two most prominent detectors are thermal conductivity (TC) and flame ionization (FID). TC detectors, also called katharometers, consist of two filaments heated electrically and arranged in a Wheatstone bridge circuit; one filament is exposed to pure carrier gas and the other is located in the carrier gas stream emerging from the analytical column. When the carrier gas from the column is diluted with the sample, the temperature and resistance of the sensing filament increases, thereby causing a

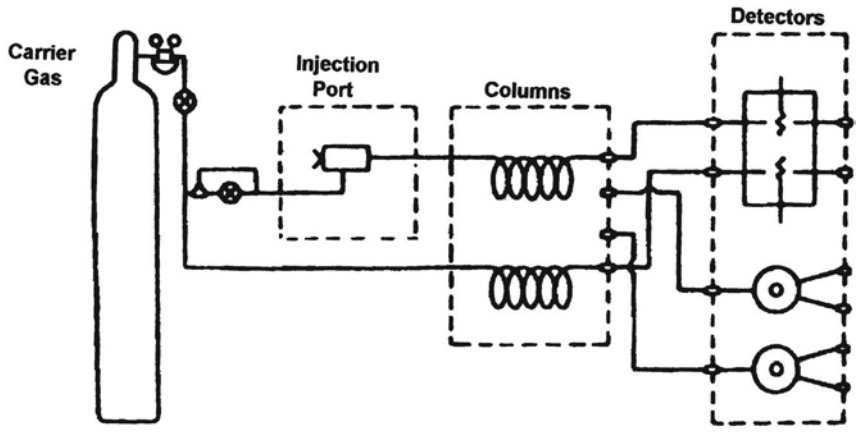

Fig. 3—Schematic diagram of a gas chromatograph.

voltage drop across the bridge, which is shown as a peak on the chromatogram. FID detectors operate on the principle that relatively few ions are formed when hydrogen is burned in air; but when organic compounds are present, ions proportional to the carbon concentration are formed. By applying a potential across two electrodes surrounding the flame, the ion current produced from the sample molecules is fed to an electrometer amplifier, the output of which is sent to a recorder. TC and FID detectors are both durable and relatively trouble free. TC detectors will respond to virtually all compounds, whereas FID detectors are sensitive to organic compounds only. One of the principal virtues of FID detectors is its high sensitivity, about 1000 times that of thermal conductivity. Testing of thermal conductivity and flame ionization detectors used in gas chromatography are discussed in ASTM Practice for Testing Thermal Conductivity Detectors Used in Gas Chromatography (E516-95a (2005)) and ASTM Practice for Testing Flame Ionization Detectors Used in Gas or Supercritical Fluid Chromatography (E594-96 (2006)), respectively.

There are other high-performance detectors that are used in conjunction with GC. Beta-ray ionization detectors use a radioactive source to ionize the argon carrier effluent from the column. Metastable argon ions collide with sample molecules, inducing a current flow that is amplified and measured. Glow discharge detectors operate on the principle that the composition of the effluent can be measured in terms of voltage across a gaseous discharge. In an electron capture detector, nitrogen is passed through an ionization chamber containing tritium as the source of ionizing radiation. All ions formed by the ionizing radiation can be collected by applying a small potential across the chamber. When the effluent from a gas chromatograph contains electron-attracting compounds, a decrease in current flow proportional to the electron affinity of the compound is observed [51,52]. The detector is highly selective for compounds containing halogen, conjugated carbonyl, nitriles, nitrates, and organometallic compounds. The function and performance of various detectors have been discussed in detail [53,54]. The use of electron capture detectors in GC is covered in ASTM Practice for Use of Electron-Capture Detectors in Gas Chromatography (E697-96 (2006)). Testing of nitrogen/phosphorous thermionic detectors for use in gas chromatography is discussed in ASTM Practice for Testing Nitrogen/Phosphorus Thermionic Ionization Detectors for Use in Gas Chromatography (El 140-95 (2005)).

Most modern instruments are equipped for linear programmed temperature operation, which consists of increasing the column temperature at a uniform rate throughout an analysis. Programmed temperature gas chromatography (PTGC) is particularly useful for the examination of complex mixtures and wide-boiling-range samples, where a single analysis of high and low boiling components at constant-temperature isothermal analysis is not practical. Generally, when the range of boiling points in a mixture is 100°C or more, temperature programming is recommended. If low temperature isothermal analysis is used, low boiling compounds will usually be separated effectively but high boiling compounds emerge as broad peaks. At high isothermal temperatures, light components emerge rapidly, causing peaks to be crowded; high boiling compounds produce favorably shaped peaks. When temperature-programmed operation is employed, a low initial temperature can be used for the separation of low boiling materials, and, by steadily increasing the column temperature, intermediate and high boiling components can be eluted in a reasonable length of time as sharp, well-defined peaks.

Although PTGC has greatly enhanced the usefulness of gas chromatography, its practice is somewhat restricted by the type of liquid phase employed. During temperature programming, a temperature is reached at which volatilization or decomposition of the liquid phase occurs, thereby causing a positive deviation of the recorder pen from the baseline. This effect is referred to as column bleeding, and in the event of severe bleeding the recorder pen may travel off-scale, obscuring any component peaks that may be present. Column bleed may be suppressed by favoring thermally stable liquid phases and through the use of short and low-loaded columns. These remedies are not always practical since a specific problem may dictate the use of conditions contrary to those described previously. A more direct way to compensate for column bleed is through the use of a dual column gas chromatograph. In this type of system, a column matching the one used for analysis is mounted in the oven compartment and connected to the reference side of the detector. As the temperature is increased, a signal is generated in the reference cell equivalent to that in the sample cell, thereby cancelling out any signal due to substrate bleeding.

Columns

The successful practice of GLC depends primarily on the proper selection and preparation of a suitable column. The availability of hundreds of liquid phases and numerous solid supports, in addition to parameters such as length, diameter, amount of liquid phase, and mesh size, offers an almost infinite number of possibilities. Fortunately, most separations can be performed on relatively few columns involving only a few liquid phases. Columns are divided into two major classes, packed and open tubular. Packed columns consist of tubing filled with size-graded support material impregnated with a nonvolatile liquid. Generally, higher-column performance is obtained with small-column-diameter and light-stationary-phase loading. Four to ten-foot (1.22 to 3.048 m) columns of 1/8 or 1/4 in. (3.175 or 6.350 mm) outside diameter containing 10 to 20 % liquid phase are common.

With Golay's development of the capillary column or open tubular column [55], the separations possible in GLC were greatly increased. These columns are prepared by coating the inside surface of small-diameter tubing with a thin layer of nonvolatile liquid. Capillary columns are generally much more efficient than packed columns, but, owing to their low capacity, high-sensitivity detectors and special sampling techniques are necessary to accommodate the small samples used. Fortunately, the split/splitless injector ports introduced by GC manufacturers in the late 1980s and early 1990s are able to handle normal-sample-size injections without much difficulty.

The readers may find the chemically cross-linked and surface-bonded stationary phases made using fused silica capillary tubing (30 m by 0.25 mm ID) quite useful to have in their gas chromatography laboratory (see Table 2).

Table 2—Commonly used stationary phases in the gas chromatography laboratory

Stationary Phase Composition	Comparable to
100 % dimethyl polysiloxane	DB-1, Rtx-1, HP-1, OV-1, SP-2100, 007-1
95 % dimethyl-5 % diphenyl polysiloxane	DB-5, Rtx-5, HP-5, OV-5, SPB-5, 007-2
80 % dimethyl-20 % diphenyl polysiloxane	Rtx-20, OV-7, SPB-20, 007-7
65 % dimethyl-35 % diphenyl polysiloxane	DB-35, Rtx-35, OV-11, 007-11
50 % dimethyl-50 % diphenyl polysiloxane	DB-17, Rtx-50, HP-17, OV-17, SP-2270, 007-17
50 % dimethyl-50 % cyanopropyl	DB-23, SP-2330, 007-CPS-1
50 % dimethyl-50 % trifluoropropyl	DB-210, SP-2410, RSL-700
50 % dimethyl-50 % cyanopropyl phenyl polysiloxane	DB-225, Rtx-225, HP-225, OV-225, 007-225
cyanopropyl-phenyl-dimethyl polysiloxane	DB-624, 007-624, AT-624, OV-624, Rtx- volatiles
86 %-dimethyl-14 % cyanopropyl phenyl polysiloxane	DB-1701, Rtx-1701, OV-1701, 007-1701
100 % biscyanopropyl polysiloxane	Rtx-2340, SP-2340, OV-225
acidified polyethylene glycol	DB-FFAP, HP-FFAP, 007-FFAP, SUPEROX-FA, OV-351, STABILWAX-DA
polyethylene glycol	DB-WAX, STABILWAX, HP-20M, 007-CW, SUPEROX II, SUPELCOWAX

Note:

Trademark	*Company*
DB	J&W Scientific
OV	Ohio Valley Specially Chemical
Rtx	Restek Corporation
STABILWAX	Restek Corporation
SUPEROX	Alltech Associates
SUPELCOWAX	Supelco, Inc.
Teflon	E. I. du Pont de Nemours & Co., Inc.

Tubing

Tubing materials should be stable with respect to the sample, packing, and carrier gas, and be of uniform diameter. Tubing made of copper, stainless steel, monel, glass, and plastic have all been used for the construction of packed columns. The two most widely used materials are stainless steel and copper-stainless steel for its inertness and copper for its low cost. The most common tubing material used in capillary column gas chromatography is fused silica, primarily due to its flexibility and inertness. Special attention was given to the wide-bore, 0.53-mm inside-diameter columns because they have been reported [47] as a packed column alternative. Readers are also referred to a 1991 review covering the fundamentals, characteristics, and selection of open tubular columns in gas chromatography [48].

Solid Support

The function of the support material is to provide a large surface area for holding the liquid phase; it should be chemically inert to the sample and partition liquid and have good handling characteristics. The principal support materials are those derived from diatomaceous earth (Table 3). They are relatively inert, have adequate mechanical strength, and will adsorb up to 40 % of the liquid phase without losing their free-flowing character. Diatomaceous earth supports can be broadly classified as to color: white or pink. White supports contain fewer active sites and therefore are considered superior for the analysis of polar compounds. Pink supports, on the other hand, are less fragile and have greater capacity for holding the liquid phase. Schuppe and Lewis [49] group the various commercial diatomaceous earth supports according to color and ASTM code.

Ideally, a support should be completely inert, but unfortunately diatomites exhibit a certain amount of surface activity. The interaction with polar compounds, usually hydrogen bonding, is mainly attributed to the presence of silanol (–Si–DH) groups located at the surface of the support. Attempts to deactivate supports have been practiced in several ways: washing with acid and alkali, saturating with polar liquids, and reacting silanol groups with reagents. Although acid and base washing have been widely practiced, both techniques are of questionable value. In fact, acid treatment has sometimes proved deleterious by promoting isomerization of certain compounds and the decomposition of the liquid phase. By far the most effective way to reduce support reactivity is by reacting the silanol groups with a silylating reagent. This treatment is more effective with white supports; the degree of deactivation varies with the type of reagent and the technique employed.

Other support materials of notable importance are glass beads, Teflon, and porous polymers. Since porous

Table 3—Commercial diatomaceous solid support materials [44]			
Solid Support			
White			**Pink**
ASTM Code 50	**ASTM Code 60**	**ASTM Code 70**	**ASTM Code 80**
Anakrom U	Chromosorb G	Gelatrom	Anakrom P
Celite 545		Gas Chrom S	Chrompak P, Regular
ChrompakW, Regular			Chromosorb P
Chromosorb W			Columpak
Chromaport			Firebrick, C-22
Diatoport W			Gas Chrom R
Embacel			GC Super Support
Gas Chrom Cl			Sterchamol
			Ultraport

polymers are generally used without a liquid phase, they will be discussed in detail under gas solid chromatography. Teflon has found its greatest use in the separation of very polar compounds such as water, acids, alcohols, and amines, but Teflon has poor handling properties and produces columns that are much less efficient as compared to columns from diatomaceous earth. Because of their low surface area, glass beads cannot hold much liquid phase, less than 0.5 %; it is this low volume of liquid phase that is responsible for some of its advantages, namely, speed of analysis and low operating temperatures. They are, on the other hand, substantially less efficient than diatomite columns. For information concerning support technology, such as types, physical properties, chemical structure, pore structure, treatment, etc., the reader is referred to detailed articles [56–58] on the subject.

Stationary Liquid Phase

The selection of liquid phase is one of the most vital judgments made in selecting a chromatographic system, for it is the degree of selectivity of the partitioning liquid that most strongly influences the separating capability of a GLC column. Theoretically, any liquid can be used as a liquid phase, but there are some limiting factors. A liquid phase must be nonreactive to the system and sample, have reasonable thermal stability, and be liquid at the operating temperature. Although materials of low vapor pressure are favored, the main criterion regarding volatility is that the liquid phase be relatively nonvolatile (vapor pressures 0.01 to 0.10 mm) at operating temperature. Finally, a liquid phase must be soluble in some volatile solvent to allow coating of the support. Terms such as substrate, partition liquid, stationary phase, and solvent are synonymous with liquid phase. Considerable effort has been expended in an attempt to permit advance prediction of the most suitable liquid phase for a given problem, but most often the analyst must rely on experience, published procedures, and certain generalizations. Although solute-liquid phase activity such as chemical interaction, hydrogen bonding, and other cohesion forces all affect the selectivity of the liquid phase, in practice the most distinguishing characteristic is polarity. The polarity of the liquid phase is determined by the ratio of polar or polarizable groups to nonpolar groups, with the retention of solutes depending on the relative polarities of solutes and liquid phase. The greater the polarity of the stationary phase, the greater is the solubility (retention) of polar solutes relative to nonpolar solutes. The solubility or lack of solubility of sample components in the liquid phase can be used to make group separations or to accelerate or retard components with respect to others in the sample. In general, nonpolar liquid phases separate nonpolar solutes by order of volatility and polar solutes by structural type; whereas, polar phases separate polar solutes by order of relative volatility and polarity and nonpolar solutes by structural type.

An enormous number of liquids, semisolids, and solids have been recommended for use as liquid phases. Schupp [54] listed over 300 materials along with their maximum temperatures, chemical names, and trade names. The seventh edition of Guide to Stationary Phases for Gas Chromatography [59] contains over 700 literature references to liquid phase use in order of application to different classes of compounds. Lists of liquid phases, arranged alphabetically in chemical classes, are available from suppliers of chromatographic equipment, and they usually include maximum temperatures and solvency. Although there are a vast number of liquid phases available, the majority of problems encountered in most laboratories can be resolved with five or six stationary liquid phases provided they represent a wide range of polarities. The following list, arranged in order of descending polarity, is representative of such a group: N,N bis(2-cyanoethyl) formamide; diethylene glycol succinate; dodecyl phthalate; polyethylene glycol (molecular weight 20 000); and apiezon grease. Books on GLC generally contain chapters devoted specifically to the discussion of partition liquids, and it is recommended that the reader consult the previously mentioned books [54] for a more complete study of liquid phase technology.

Column Efficiency

Column efficiency may be defined by considering the narrowness of a peak relative to time spent in the column. Provided there are no instrumental deficiencies, column

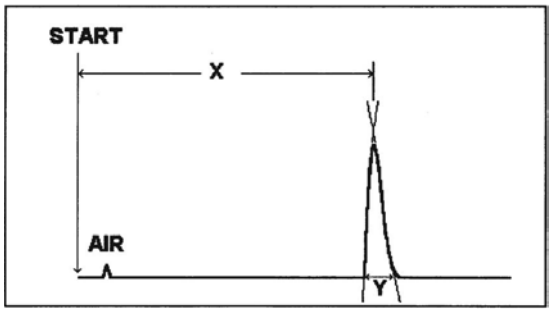

Fig. 4—Graphic calculation of column efficiency.

efficiency is a function of packing type, packing technique, and operating conditions and is usually expressed in terms of the number of theoretical plates. The plate concept, a carryover from counter-current extractions, implies a series of complete equilibria or "theoretical plates." The better the performance of a column, the higher is its number of theoretical plates. Inasmuch as distinct stages are not observed in chromatographic separations, the number of theoretical plates for a column is calculated from the relative peak sharpness shown on the chromatogram. A good packed column should have an efficiency of at least 400 plates, and it is not uncommon for a well-prepared column to have over 1000 plates. The number of theoretical plates, *N,* equals $16(x/y)2$, where x is the distance in millimeters from injection to peak maximum, and y is the baseline in millimeters cut by the two tangents as shown in Fig. 4.

Column efficiency can be expressed per unit of column length. The height equivalent to a theoretical plate (HETP) is calculated by dividing L, the length of the column in centimeters, by N; thus, HETP = L/N. High HETP indicates that the column has been poorly prepared or is not being operated under ideal conditions.

Theories [60–62] have been developed to elucidate mechanisms that cause spreading of the component molecules as they pass through the column, and an understanding of such processes is important to efficient operation of a chromatograph. Such theories take into account the interrelated multiple effects of parameters such as column diameter, column length, carrier gas, temperature, gas velocity, support size and shape, and sample size, and their ultimate effect on N. A summary and comparison of these theories have been presented [63]. A brief discussion to shorten analysis time while maintaining or improving resolution was published in 1993 [64].

Interpretation of Chromatograms

Fundamentally, the object of a chromatographic analysis is the resolution of sample components for identification and quantitative measurement. Fortunately, GC has tremendous capacity for resolving mixtures, but, unlike many other instrumental techniques, the record of an analytical run tells very little about the chemical nature of separated compounds. In addition, components in a sample mixture may not completely separate on a given column; consequently, the number of peaks on a chromatogram is not always an indication of the number of compounds in a sample. When background information concerning the sample is available and when sample components are few, the interpretation of GC data is fairly simple. However, the interpretation of a chromatogram from a multicomponent sample, where background information is limited, is a formidable task. In this section, qualitative and quantitative analysis will be briefly discussed; for a more complete treatment of the subject, the reader is referred to the work of others [65,66].

Qualitative Analysis

For a given set of operating conditions, the amount of carrier gas required to elute a compound from a column is characteristic for that compound and is not influenced by the presence of other compounds.

Accordingly, the time from injection to peak maximum is a property peculiar to a compound. This type of information, represented as retention volume (VR) and retention time (tr), has been the basis for most schemes of qualitative analysis. The use of such information may be greatly assisted by the considerable amount of published retention data such as ASTM compilations [49,50].

One of the weaknesses of gas chromatography is in the identification of unknown compounds. Dutoit [51] examined the retention indices of 135 solutes representing most chemical families on pure polar phase and pure nonpolar phase. This 1991 publication should aid the readers in the qualitative identification of GLC peaks. Another recent study regarding qualitative analysis by GLC using retention indexing was completed by Sun et al. [52]. The programmed temperature retention value databases compiled in various laboratories are listed along with reproducibility data under different chromatographic conditions.

For the purpose of illustration, the description of retention parameters will be confined to retention times; this does not, however, imply the use of retention volume to be inferior. Retention time measurements are shown on the chromatogram presented in Fig. 5. The adjusted retention time (t_R), time measured from air peak to peak maximum, corrects for instrument dead volume.

The first impulse would be to conclude that absolute retention times are adequate for identification purposes, but absolute retentions are comparable only when obtained on the same column using identical operating conditions. Instead, most retention times are calculated relative to some other compound that is used for reference. Relative retention time (r) is obtained as follows:

$$r_{c,s} = t'_{R,c} / t'_{R,s} \tag{3}$$

where c refers to component in the sample, and s indicates the reference standard. Relative retention times are independent of column length, liquid loading, and flow rate, but they are dependent on the type of liquid phase. The reference material may be one that is known to be in the

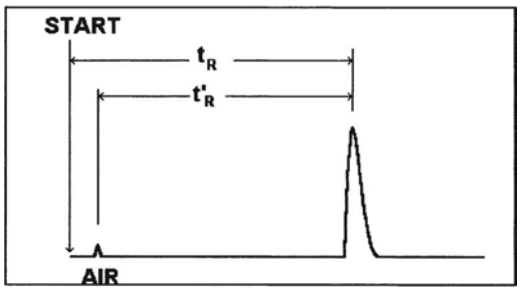

Fig. 5—Retention time (t_R) and adjusted retention time (t'_R).

original sample, or it can be mixed prior to the chromatographic analysis. In practice, relative retentions are usually obtained by computing the ratio of the distance from air peak to standard and air peak to component.

Once a peak has been tentatively identified from its retention time, the sample may be "spiked" with the suspected compound to see if it superimposes and shows up as one peak. If the two materials emerge together, this is good evidence of its presence in the original sample, but this does not constitute positive identification since more than one compound may have the same retention time for a given column. The next step is to go through the same procedure using a different column having a packing of completely different polarity. It is not likely that two materials will have the same retention time on widely different columns, but, if doubt still persists, the compounds can be trapped at the exit of the GC unit, and the isolated materials can be subjected to instrumental or chemical analysis. Walsh and Merritt [67] trapped eluted materials in a neutral solvent and applied a battery of chemical tests to determine chemical functionality. Methods have been described for direct trapping of fractions on a disk of potassium bromide and fraction trapping with subsequent transfer to a microcell; the isolated components were then subjected to infrared (IR) analysis. Although somewhat limited in versatility and flexibility, table top GC-mass-spectroscopic and GC-Fourier transform infrared units do an outstanding job of routine identification and for quality control purposes. Prices of these integrated instruments vary from $60,000 to approximately $100,000.

Success in any research laboratory is highly dependent on the timing upon which unknown chromatographic peaks are identified. While lR and mass spectroscopy (MS) have been proven to be important qualitative tools, each has its inherent weaknesses. When used together, these techniques reinforce each other, producing a richer body of useful information than either technique used alone [68]. The use of mass spectrometers as detectors for capillary column gas chromatography has also been discussed by Clement [69] in his 1992 publication. Another 1992 review [70] with several references is given on gas chromatography, including column types, injection methods, detection means, data systems, supplementary apparatus, and future prospects.

Quantitative Analysis

The analog signal generated by the presence of a compound in the carrier gas is proportional to its concentration, and quantitative analysis is obtained by conversion of this signal to some form of digital data. For the most part, quantitative data are obtained from peak area measurements, but significant use has been made of peak heights.

Peak areas can be measured by: (1) use of a planimeter, (2) cutting and weighing chart paper, (3) triangulation (A = WH/2), (4) height times width at half height (H × W at H/2), (5) ball-and-disk type of integrator, and (6) electronic digital integrator. The planimeter yields good results, but its use is tedious, and accuracy is dependent on the shape of the peak and the skill of the operator. Cutting and weighing peaks from chart paper is time consuming, and it is practically impossible to accurately cut and weigh cutouts of narrow peaks. Triangulation and height times width at half height are both relatively simple methods, and each will yield satisfactory results with symmetrical peaks, but the methods are unsuitable with asymmetric or very narrow peaks. The ball-and-disk type of integrator, which is attached to the drive mechanism of the recorder pen, has found widespread application. Since peak areas are integrated as they are recorded, the operator need only count the integrator units under the appropriate peak. With an electronic integrator, the output from a gas chromatograph is fed to the measuring unit that converts the analog signal to digital, which is eventually converted to peak areas using an appropriate algorithm. The integrated peak areas are read directly from the printer/plotters of most electronic integrators. Of the various methods for integrating peak areas, ball-and-disk and electronic integration provide the best results for applications requiring reasonable speed and precision of quantitative data. However, ball-and-disk integrators are extremely difficult to find because of the popularity of electronic digital integrators. Where cost permits, particularly in the case of routine analyses, the electronic digital integrator is preferred. Most electronic integrators made in the late 1980s and early 1990s have the capability of plotting the chromatograms in real time. Thus, a separate strip chart is no longer necessary to monitor the progress of the analysis.

Area normalization and internal standardization are methods used for converting digital data to percent composition. In the normalization procedure, the area of the component being measured is divided by the total area of all other peaks. This method assumes that all of the sample is eluted from the column.

$$\text{Percent component } C = \frac{\text{Area of } C}{\text{Total area of all peaks}} \times 100 \qquad (4)$$

If a portion of the sample remains on the column, an error proportional to the amount of material remaining on the column will be conferred on all the compounds measured.

The internal standard method is used more widely for the quantitative interpretation of a chromatogram. In this method, peaks of interest are calculated relative to a known amount of internal standard that has been added prior to chromatography. It is not necessary to determine all peaks as in the normalization method, and this can be advantageous particularly when one compound is to be determined in a complex mixture. The following calculation is used with internal standardization determinations:

$$\text{Percent component } C = \frac{CW}{BS} \times 100 \qquad (5)$$

where:
C = peak area of component,
B = peak area of internal standard,
W = weight of internal standard, and
S = weight of sample.

If the determination is to be calculated on a volume basis, simply substitute volume for weight in W and S. Complete elution of all components is not necessary; in fact, the percent of sample hang up can be determined by calculating the total percent represented by all the peaks eluted and subtracting the total from 100.

A direct weight-to-area relationship does not exist for all compounds. Detector response is a function of structure and molecular weight; the detector response for a

given compound is not the same with all detectors since various detector types operate on different principles. Once determined, however, response factors are generally interchangeable between instruments having the same type of detector. Messner et al. [71] published thermal conductivity factors for a large variety of compounds and also provided a formula for calculating factors. Deitz [72] tabulated a lengthy list of TC and FID detector response factors for various classes of compounds. For certain applications, peak height measurements are more convenient and reliable than peak area. Such is the case when peaks are tall and narrow and where errors in area measurements are likely to be maximized. Peak height determinations are affected to a greater extent by variations of operating conditions than are peak area determinations. This effect is greatly diminished through the use of an internal standard.

To increase accuracy and precision of peak area measurements, the use of electronic integrators is highly recommended. The initial cost for such an investment can easily be recovered within a short period of time primarily through labor cost savings. Current integrators are so versatile that they can perform difficult peak integration that normally would take a less experienced analyst a lot of time to perform. Some can perform reintegration and recalculation using a variety of methods. In the 1990s, most integrators are capable of being interfaced to a personal computer to enhance data crunching and for information storage and retrieval purposes. This is especially useful where data documentation is critical.

Applications—applications for GLC in the paint industry exist at almost every level of manufacture and product development. Its rapid acceptance by the industry is due to several inherent features, principally, versatility and speed. Initially, analyses were solvent oriented, but applications to virtually every class of material used in surface coatings have been reported in the literature. At present, GLC is used for a variety of analytical operations including both routine and research functions. It is unexcelled as a routine quality control tool for defining raw materials to be used for the manufacture of paint products. Batches of solvent, plasticizers, polyols, fatty acids, and other materials can be examined simply and rapidly to determine conformance to acceptable standards. Information regarding vehicle composition of a whole paint can be obtained in great detail and with reasonable accuracy.

Moreover, GLC can be used to monitor drying processes, solvent release from films, and the chemical curing of polymeric materials. In a 1991 publication, K. Takahashi [42] described a simple and sensitive method for the measurement of the leaching rate of tributyltin and triphenyltin compounds from antifouling paint by gas chromatography using flame photometric detection. Static headspace analysis by combined gas chromatography-mass spectrometry for the analysis of organic solvents in printing inks was recently studied [43].

Because of the multiplicity of published papers relevant to GC coatings analysis (well over 1000), complete coverage of all applications is beyond the scope of this chapter. A review [46] describing basic GC processes and applications includes approximately 150 references to coatings analysis. In his monograph on GC application to polymer analysis, Stevens [44] refers to several hundred analytical procedures and, in many cases, presents operating conditions, tables of retention times, and chromatograms. Readers are directed to the second part of a 1992 article by Ettre [45] on the evolution of chromatography since the development of GLC by Martin and James 40 years ago and HPLC by Moore and Horvath 25 years ago.

Table 4—Gas chromatographic methods relevant to organic coatings analysis

Subject	References
Reviews	[37–41,44–48,68,70,138]
Solvents	[76–90,137]
Oil and fatty acids	[91–101]
Resin acids	[102–104]
Alkyd and polyester resins	
Fatty acids	[105–107]
Dicarboxylic acids	[108,111–114]
Polyols	[108,112,113,115–117]
Pyrolysis	[109,110,118–126]
Plasticizers	[127–130]
Residual reactants	[131–134,142]
Volatile organic compounds (VOC)	ASTM D 3792, ASTM D 3960, ASTM D 4457
Miscellaneous	[43,135–137,139–145]

A partial list of references is shown in Table 4; examples were selected to illustrate the variety of coating problems amenable to GLC analysis. Methods directed to the analysis of oils and fats are listed separately, but most are also applicable to fatty acids isolated from alkyd resins. A compilation of ASTM methods that have been evaluated and accepted as standard or tentative procedures is presented in Table 5. Other GLC procedures are currently being evaluated for ASTM acceptability.

One facet of GLC that often goes unrecognized is the pretreatment of substances to alter their structure, thereby permitting the examination of materials that would not respond normally to GLC analysis.

Such is the case with the analysis of paint binders and very polar materials such as polyols and dicarboxylic acids. Many of the methods of sampling and techniques for preparing derivatives described by Cavagnol and Betker [73] and Schupp [74] have application to the analysis of surface coatings. Beroza and Coad [75] attack the same general problem but in a different way; for the most part, samples are altered within the instrument and not externally.

In the following discussion of analytical methods, special emphasis will be directed to the broad range of usefulness within the paint field, and, wherever possible, basic principles and equipment will be stressed.

Solvents

A major consideration in GLC is sample volatility. Materials to be analyzed must possess sufficient vapor pressure to permit vaporization at the point of sample introduction. Since enamel and lacquer solvents fulfill this requirement, it is only natural that GLC would be rapidly utilized in

Table 5—Summary of ASTM test methods for paints, related coatings, and aromatics using GC

ASTM	Title of Test Method or Practice
D2245	Test Method for Identification of Oils and Oil Acids in Solvent-Reducible Paints
D2360	Test Method for Trace Impurities in Monocyclic Aromatic Hydrocarbons by GC
D2743	Practices for Uniformity of Traffic Paint Vehicle Solids by Spectroscopy and GC
D2804	Test Method for Purity of Methyl Ethyl Ketone by GC
D3257	Test Method for Aromatics in Mineral Spirits by GC
D3271	Practice for Direct Injection of Solvent-Reducible Paints into a GC for Solvent Analysis
D3329	Test Method for Purity of Methyl Isobutyl Ketone by GC
D3362	Test Method for Purity of Acrylate Esters by GC
D3545	Test Method for Alcohol Content and Purity of Acetate Esters by GC
D3760	Test Method for Analysis of Isopropylbenzene (Cumene) by GC
D3792	Test Method for Water Content of Coatings by Direct Injection into a Gas Chromatograph
D3797	Test Method for Analysis of o-Xylene by GC
D3798	Test Method for Analysis of p-Xylene by GC
D3876	Test Method for Methoxyl and Hydroxypropyl Substitution in Cellulose Ether Products by GC
D3893	Test Method for Purity of Methyl Amyl Ketone and Methyl Isoamyl Ketone by GC
D4367	Test Method for Benzene in Hydrocarbon Solvents by GC
D4457	Test Method for Analysis of Dichloromethane and 1,1,1 Trichloroethane in Paints and Coatings by Direct Injection into a GC
D4492	Test Method for Analysis of Benzene by GC
D4735	Test Method for Determination of Trace Thiophene in Refined Benzene by GC
D4747	Test Method for Determining Unreacted Monomer Content of Latexes Using GC
D4773	Test Method for Purity of Propylene Glycol Monomethyl Ether, Dipropylene Glycol Monomethyl Ether, and Propylene Glycol Monomethyl Ether Acetate
D4794	Test Method for Determination of Ethoxyl or Hydroethoxyl Substitution in Cellulose Ether Products by GC
D4827	Test Method for Determining Unreacted Monomer Content of Latexes Using Capillary Column GC
D5008	Trace Method for Ethyl Methyl Pentanol Content and Purity Value of 2-Ethylhexanol by GC
D5060	Test Method for Determining Impurities in High-Purity EthylBenzene by GC

Table 5—Summary of ASTM test methods for paints, related coatings, and aromatics using GC (*Continued*)

ASTM	Title of Test Method or Practice
D5135	Test Method for Analysis of Styrene by Capillary GC
D5310	Test Method for Tar Acid Composition by Capillary GC
D5399	Test Method for the Boiling Point Distribution of Hydrocarbon Solvents by GC
D5713	Test Method for Analysis of High Purity Benzene for Cyclohexane Feedstock by Capillary GC
D5910	Test Method for Determination of Free Formaldehyde in Emulsion Polymers by LC
D5917	Test Method for Trace Impurities in Monocyclic Aromatic Hydrocarbons by GC and External Calibration
D5974	Test Method for Fatty and Rosin Acids in Tall Oil Fractionation Products by Capillary GC
D6133	Test Method for Acetone, p-Chlorobenzotrifluoride, Methyl Acetate, or t-Butyl Acetate Content of Solvent-borne and Waterborne Paints, Coatings, Resins, and Raw Materials by Direct Inhection into a Gas Chromatograph
D6142	Test Method for Analysis of Phenol by Capillary GC
D6144	Test Method for Analysis of AMS (Alpha Methyl Styrene) by Capillary GC
D6229	Test Method for Trace Benzene in Hydrocarbon Solvents by Capillary GC
D6387	Test Method for Composition of Turpentine and Related Terpene Products by Capillary GC
D6438	Test Method for Acetone, Methyl Acetate, and p-Chlorobenzotrifluoride Content of Paints, and Coatings by Solid Phase Microextraction GC
D6526	Test Method for Analysis of Toluene by Capillary Column GC
D6563	Test Method for Benzene, Toluene, Xylene (BTX) Concentrates by GC
D6886	Test Method for Specification of the Volatile Organic Compounds (VOCs) in Low VOC Content Waterborne Air-Dry Coatings by GC
D7011	Test Method for Determination of Trace Thiophene in Refined Benzene by GC and Sulfur Selective Detection
D7057	Test Method for Analysis of Isopropylbenzene (Cumene) by GC (External Standard)
D7090	Test Method for Purity of Isophorone by Capillary GC
D7266	Test Method for Analysis of Cyclohexane by GC (External Standard)

this area. Solvents may be encountered in two forms: as raw material to be formulated into a surface coating or as an ingredient of a coating. In the latter event, the analysis is complicated by the presence of pigment and binder, which usually necessitates the isolation of solvent through distillation. To alleviate problems associated with solids or nonvolatile components of the paint or coating,

a removable glass liner or glass insert can be installed in the injection port of the gas chromatograph. Such glass liners can be occasionally solvent-cleaned or oven-cleaned overnight at 400°C. Another, but less desirable alternative. is through the use of a precolumn. The pre-column should be made from the same stationary phase as the analytical column [76].

An important aspect of production control is the analysis of individual solvents for impurities. Relatively small amounts of impurity may seriously affect the performance characteristics of a paint, and such impurities can be easily detected and determined using GLC. Batches of solvent can be rapidly screened by subjecting them to GLC analyses and comparing the resulting chromatograms to those obtained from reference materials of acceptable quality [77]. Relative amounts of each solvent can be quickly ascertained from ratios of peak heights or peak areas. If significant deviation from the reference material is observed, a more thorough and precise GLC analysis can then be conducted. In 1993, Vonk [78] described the use of wide-bore fused silica columns for the analysis of solvents.

Petroleum fractions, such as mineral spirits and VM&P naphtha, are extremely complex mixtures of hydrocarbons, and it is virtually impossible to completely separate all the components. Nevertheless, valuable information regarding the nature and identity of such solvent systems may be obtained by comparison with reference chromatograms obtained using identical operating conditions. No attempt is made to identify the individual peaks; instead, observations are made to determine if the unknown and control have similar distillation ranges and if peaks are proportional. Chromatograms of this type are referred to as "fingerprints" and will often suffice for quality control purposes.

The percentage of aromatic species in mineral spirits may be determined by using columns prepared from highly selective liquid phases such as N,N-bis(2-cyanoethyl) formamide and 1,2,3-tris(2-cyanoethoxy) propane. These very polar liquid phases are capable of eluting high boiling aliphatic solvents well in advance of low boiling aromatics, thereby providing the means for aliphatic-aromatic group separation. Such columns provide the basis for the analysis of aromatics in enamel thinners and solvents [79,80] yielding information that relates to the photochemical reactivity of hydrocarbon solvents, a factor of importance in air pollution studies.

The problem of determining solvents in whole paints and lacquers by GLC is compounded by the presence of non-volatiles, and special provisions must be made for sampling. No universal method for isolating solvent from paint and lacquer is available [81–85]. Vacuum distillation and collection in a cold trap [86] works well in many cases, but this scheme is time consuming and difficulties arise when very light or very heavy solvents are present. Introduction of a coating from a syringe onto an adsorbent pad [36] in the injection port has been used, but viscous samples require dilution, and thermally unstable resins are decomposed in the injection port, resulting in the appearance of extraneous peaks on the chromatogram. To avoid or significantly minimize thermal degradation of certain resins, it is advisable to decrease the injection port temperature below its decomposition temperature. A good injection port temperature for most solvent analysis is 200°C. As previously indicated, use of a removable glass liner or insert is a must if direct injection of the whole paint is to be performed. Again, the glass insert can be occasionally cleaned using an appropriate solvent or by overnight oven cleaning at 400°C. Precipitation of lacquer resins with pentane and subsequent analysis of the supernatant liquid by GLC works well with most automotive lacquers [77], but the nonuniform occlusion of certain solvents has been reported. For the most part, the means of sample handling will be determined by the type of material encountered and the extent of analytical information desired.

Several comprehensive schemes have been proposed that are particularly useful for the analysis of unknown samples. Haken and McKay [87] used GLC in conjunction with solubility tests in various media along with functional group analysis for the characterization of solvent systems. The New York Society for Paint Technology published a paper [81] on the subject of solvent analysis that included a comprehensive tabulation of retention data for a broad spectrum of solvents. A procedure for the identification of plastic and lacquer solvents was described by Haslam et al. [86]. The solvents were isolated by vacuum distillation in a sealed "H-tube" and subsequently separated on tritolyl phosphate and paraffin wax columns. Chromatographic data were supplemented by infrared spectroscopy where necessary.

Since no single column will separate all solvents, separation on one liquid phase can be very misleading. When examining an unknown solvent mixture, it is best to conduct the analysis on at least two liquid phases of different polarity, and in some cases supplementary chemical or instrumental testing will also be necessary.

GLC has also been used to study the retention of solvents in paint films during drying processes [88,89]. It has been demonstrated that solvent retention is related to the chemical structure of the film and solvent, as well as the boiling point of solvents. Perrone [90] also described a GC method for the determination of residual solvents in pressure sensitive tapes as a quality control step in the manufacturing process [91–99].

Oils

The drying and nondrying oils used in the production of paints and varnishes can be identified through the application of GLC. The GLC analysis is preceded by the saponification of sample and isolation of the fatty acids. Free fatty acids may be examined directly [100], but they are generally analyzed as their methyl esters, which are more volatile, less polar, and less susceptible to isomerization. Any of the several acid-catalyzed esterification techniques, for example, hydrochloric acid (HCL), sulfuric acid (H_2SO_4), or boron trifluoride (BF_3) in methanol, will provide adequate conversion to the ester; the BF_3-methanol reagent, however, offers the advantages of a high yield combined with rapid ester conversion. The difficulty in handling BF_3 gas can be circumvented by using boron trifluoride etherate in methanol. The reagent is easy to prepare, stable, and will convert fatty acids to their corresponding methyl esters within a few minutes.

Many of the fatty acids found in oils are of the same carbon chain length, differing only in position and number of double bonds [101–104]. Most polyester liquid phases will differentiate between C_{18} fatty acids, but polyesters

having the highest oxygen-to-carbon ratio provide the best separations. Of the polyester liquid phases, diethylene glycol succi-nate has received the most attention. Six- to-eight-foot (1.83 to 2.44 m) columns containing 10 to 20 % polyester on white diatomaceous earth supports are most common.

Zielinski et al. [105] considered the analysis of reacted and unreacted oils and made provisions for their complete analysis. Fatty acids were identified from the relative retention time ratio (RTR) values. RTR values were defined as the numerical ratio of the corrected retention time of a given methyl ester peak to that of the methyl palmitate peak. With the exception of licanic and eleostearic acids, all the fatty acids can be readily separated and identified.

Linseed, soybean, tall, safflower, and cottonseed oils can be identified from their characteristic fatty acids distributions. With other oils, identification may be achieved from an inspection of only one or two acids. For example, marine oils contain respectable amounts of palmitoleic and myristic acids, castor oil consists mostly of ricinoleic acid, coconut oil is rich in lauric acids, and oiticica and tung oils contain appreciable amounts of licanic and eleostearic acids, respectively.

Complete details for the identification of oils in organic coatings by GLC may be found in ASTM Test Method for Identification of Oils and Oil Acids in Solvent-Reducible Paints (D2245) [106].

A further extension of GLC to fatty acid analysis is demonstrated in a method for dimer acids [107]. Dimers are relatively nonvolatile, but their elution as methyl esters is made possible by using a short column acid composed of a thermally stable liquid phase, silicone grease, on silanized Chromosorb W. Monomeric fatty acids are eluted as one peak, while dimer acids emerge further along the column as a well-defined Gaussian peak.

Resins

The GLC analysis of resins constitutes a special problem inasmuch as the analyst must rely on some means of forming volatile products, either by derivative formation or through thermal decomposition [108–114]. Thermal decomposition techniques will be discussed in greater detail in the following section; this section will be concerned with methods for converting nonvolatile resinous materials to volatile derivatives.

Alkyd and polyester resins account for a large portion of polymeric material used in organic coatings. The identification of the oil component in alkyd resins by GLC has already been described. The remaining classes of material, dicarboxylic acids and polyols, can be analyzed by chemically degrading the resin so as to regenerate the acids and alcohols, which are then derivatized and subsequently analyzed by GLC. If butylamine is used to degrade the resin, polyols may be analyzed qualitatively [115] as their acetates or qualitatively [116] and quantitatively as trimethylsilyl ethers [117]. The latter method involves a minimum of sample manipulation, and it is applicable to all of the polyols normally found in alkyd resin. Both procedures are relatively uninvolved and capable of analyzing more than one polyol simultaneously.

When alkyd or polyester resins are subjected to a catalyzed equilibrium reaction in a large excess or methanol, methyl esters of mono- and dicarboxylic acids are formed in good yield.

MeOH(large excess) + alkyd or polyester + methyl ester + glycol

A method [111] has been developed for the identification of mono- and dicarboxylic acids in alkyd and polyester resins where lithium-methoxide was employed as the transesterification catalyst. Two columns, one polar and the other nonpolar, were used to obtain retention data. Identification was made possible by comparing the relative retention times of peaks from a sample to those obtained from pure compounds. Percival [108] reported a similar method using sodium methoxide as the catalyst; semiquantitative results for polyols and dicarboxylic acids were presented.

Pyrolysis

Thermal degradation, when used in conjunction with GLC, can be applied to the analysis of a wide range of polymeric materials. This technique, commonly referred to as pyrolysis, has been the subject of numerous papers. One of the most recent reviews regarding pyrolysis gas chromatography, their advantages and problems in polymer characterization, was published in 1992 by Ahmadi et al. [109]. Pyrolytic GLC is a most convenient way of analyzing small quantities of high-molecular-weight material without the necessity of resorting to chemical pretreatment. Under proper conditions the products of thermal degradation are unique for the material being analyzed, and if conditions are controlled carefully, highly reproducible results are obtained. Data, however, are sometimes difficult to interpret, and reproducibility between laboratories is not always good.

Early pyrolysis work was conducted in a system external to the gas chromatograph, with the pyrolyzate being collected in a cold trap. Pyrolysis products were introduced into a gas chromatograph and chromatographed by conventional means. Ever since its inception, pyrolytic GLC has undergone a series of refinements with the ultimate development of integrated pyrolytic-GLC systems. Curie point pyrolysis coupled with GC-MS, headspace GC-MS, and preparative HPLC were used to determine the compounds of an uncured polyester resin containing a cross-linking accelerator, an acrylate copolymer, surfactants, additives, and marble powder [110]. Of the many techniques described in the literature, two are most prominent.

In one method, a filament of high-resistance wire is coated with the sample resin, and the sample is pyrolyzed by energizing the filament with a predetermined amount of current. In a modification of the "filament technique," a quartz or ceramic sample holder is placed inside the heating coil to prevent catalysis, which may occur at the surface of the wire. In both variations, pyrolysis products are carried onto the column as they are formed, thus preventing the occurrence of secondary reactions between highly reactive chemical species. Pyrolysis temperature can be controlled by calibrating various settings of a variable voltage source with a thermocouple [118].

The second type of pyrolysis [119] employs a microoven to decompose the sample. In this technique the oven is preheated to the desired reaction temperature and the sample is then introduced by means of a moveable boat or cup. The unit can be designed so that several samples

can be readied for analysis and introduced one at a time by external sample manipulation. Generally, the carrier gas is not allowed to flow over the sample until pyrolysis is complete, at which time valves are positioned so as to direct the carrier gas flow over the boats, thereby carrying the pyrolysis products onto the column.

As compared to the filament technique, the micro-oven offers better reaction temperature control and a means of weighing the sample and residue, but it is more susceptible to secondary reaction of pyrolysis products.

Since polymer composition may vary over a wide range, it is difficult to choose column and chromatography conditions to cover all substances. Some polymers yield highly polar species (for example, acetic acid from polyvinyl acetate or amines from nitrogenous resins) that may be lost by adsorption on the column. Columns that perform well with polar substances are not always suitable for the separation of less polar materials. Therefore, optimum conditions should be determined for different classes of polymers. When samples are completely unknown, best use is made of pyrolysis when the general type of resin is determined by prior chemical or instrumental testing. Kim [120] reviewed the fundamentals of gas chromatography and pyrolysis and their applications in the analysis of fibers and polymers. Generally, the fragmentation of polymers will proceed by three basic pyrolytic reactions. Cross-linked polymers tend to carbonize, and as a result they produce pyrograms that are very difficult to relate back to the starting material. Such is the condition with alkyd resins. Secondly, some linear polymers will rupture between the side chain and the polymer backbone. This type of pyrolysis can be useful if the decomposition products are characteristic of the side chain. Pyrolysis of polyvinyl acetate typifies this type of bond schism; acetic acid is the principal decomposition product. The final and most useful type of pyrolysis occurs when the polymer backbone ruptures, producing monomers of the polymer. This type of decomposition is favored by quaternary-substituted carbons on the polymer backbone. For instance, good yields of methacrylate monomer are formed from the pyrolysis of polymethacrylate polymers, whereas polyacrylate polymers give low yields of acrylate monomer.

If experimental conditions are controlled carefully, the reproducibility of pyrolysis patterns is good. Thus, if sufficient reference chromatograms are developed, an unknown resin can be identified by matching the sample pyrogram with one from a reference library. Since, in many cases, decomposition produces a pattern of peaks that are not individually identified, the resulting chromatogram is employed as a "fingerprint." Jain et al. [121] demonstrated the use of pyrolytic GLC for the identification of small samples of paint. Characteristic pyrograms were obtained from different types of paint vehicles and those with the same vehicles but different pigments. The method was recommended for use in the forensic field where, very often, chips or traces of paint are the only physical evidence. Groten [122] investigated a broad spectrum of polymeric materials and found that they all produced characteristic pyrograms. McKinney [123] compiled a bibliography on pyrolysis gas chromatography for the period 1960 to 1963 that includes a subject and author index. A comprehensive treatment of pyrolysis chromatography, with special reference to paint resins, was presented by Hillman [124]. The study included 22 pyrograms of various types of coating materials in addition to a discussion of the effects of operating conditions and polymer structure on the resulting chromatograms.

As mentioned before, alkyd resins do not yield well-defined pyrograms that can be used for compositional analysis. Pyrolysis of alkyd resins is most useful for the examination of minute chips or flakes of paint. If an adequate amount of wet sample is available, alkyd resins may be examined best by gas chromatography of the fatty and dibasic acid methyl esters [105,111] and the trimethylsilyl ethers of the polyhydric alcohols [117]. Styrenated and acrylated alkyds, however, give good yields of monomer from the modifying resin, and with proper calibration the concentration of modifying resin can be ascertained.

When the pyrolysis is limited to certain classes of resins, for example, methacrylate and polystyrene, high yields of monomer are obtained that can be equated with the copolymer composition of the polymer through the use of calibration mixtures. Since copolymers do not give the same pyrograms as physical mixtures of the same composition, physical mixtures cannot be used for the quantitative analysis of copolymers. A random rupture of bonds occurs when acrylate is pyrolyzed; yields of monomer are low, accompanied by the esterification alcohol and gases. A scheme for the identification of copolymer composition of thermosetting acrylic resins has been presented [108]. In this method, a filament was coated with the resin solution and dried prior to decomposition. Twelve monomers were identified by combined analysis on polar and nonpolar columns [126].

Plasticizers

One of the most desirable properties of a plasticizer is low volatility, and for this reason it would be expected that the analysis of such materials by GLC would not be easy. Indeed, the vapor pressures of many plasticizers are so low that they have been recommended as stationary liquid phases for GLC analysis where moderate operating temperatures are adequate. However, by a suitable choice of operating conditions, most nonpolymeric plasticizers may be chromatographed without great difficulty.

In general, reasonable emergence times of high boiling compounds may be achieved by the use of short columns, rapid flow of carrier gas, high operating temperatures, or low-liquid-phase concentration. Since each of these operating conditions can produce undesirable effects such as poor resolution, reduced column longevity, and tailing, a compromise must be reached that will allow the resolution of high boiling mixtures within a reasonable time span. A 9 in. (22.86 cm) silicone grease column [127] was found to be adequate for the quality control of incoming stocks of butyl benzyl phthalate. Differences in the manufacturing processes of this plasticizer leads to products of variable composition, and, although a high yield is the desired end product, appreciable amounts of dibutyl and dibenzyl phthalate are sometimes encountered. When incorporated with acrylic resins, dibutyl phthalate tends to distill out of a lacquer on exposure, a condition that may ultimately lead to resin embrittlement.

A method for the analysis of plasticizers was presented [128] in which a 6 ft (1.82 m) silicone grease column was used to separate a broad range of plasticizers. A rapid flow of carrier gas, 120 mL/min, and a high terminal column temperature, 290°C, were used in conjunction

with temperature programming for the separation of low, medium, and high boiling plasticizers [129–134].

Miscellany

Ghanayem and Swann [135] separated glycols on polar columns without resorting to derivative formation. A method of this type is useful where the purity of low-boiling, uncombined polyol is under consideration. High-boiling polyols, however, normally require derivatization prior to the chromatographic step. The ever-increasing popularity of aerosol packaging has generated considerable interest in methods for the chemical analysis of aerosol propellants. The performance characteristics of various propellants may vary over a broad range; flammability, toxicity, vapor pressure, and solvency are some of the factors that determine their usefulness. It is practically impossible to identify propellants using conventional methods; they are, however, susceptible to GLC analysis. A two-column method [136] has been devised for the identification of propellants in aerosol-packaged paint. In this method, a 22 ft (6.70 m) silicone grease column is used at ambient temperature for the separation of fluorinated compounds, chlorinated hydrocarbons, and aliphatic hydrocarbons. A 6 ft (1.82 m) porous polymer column is used for the separation and identification of carbon dioxide. The concentration of each propellant may be approximated from the ratios of peak heights or peak areas. Obtaining a representative sample from an aerosol can could, prior to solvent analysis, present some difficulties to inexperienced analysts. Rastogi [137] suggested freezing the aerosol can in liquid nitrogen, puncturing the can, and allowing the propellant to evaporate as a sample preparation method.

The many applications of GLC to paint analysis are too numerous to mention; indeed, the number is vast and continues to grow. Eiceman et al. [138] reviewed the fundamental developments in gas chromatography for the period 1990 and 1991 and noted the attention given to the characterization of liquid phases and prediction of retention behavior. A review of the usual methods of quantification by headspace gas chromatography for liquid samples was presented by Nagai [139] in 1991.

In today's laboratory environment where analysts are required to multitask, autosamplers are helpful not only for productivity reasons but also for increasing accuracy and precision. The design, operation, and troubleshooting of GC autosamplers was discussed by Hinshaw [140]. Moreover, the labor cost associated with troubleshooting could be prohibitive when the analytical laboratory relies solely on the GC instrument manufacturer. It is critical for the analysts to be fully informed and educated about all aspects of problem solving, including the chromatographic hardware. A paper [141] covering trace-level sampling, principles of splitless injection, post-injection effects, and troubleshooting splitless injection was published in 1991.

Gas—Solid Chromatography

GSC represents a gas chromatographic technique where components are separated on a solid rather than on a liquid phase. Its application to the analysis of coating materials has been extremely limited, and for this reason only a very brief description of GSC processes will be presented with special emphasis being directed to new developments and potential applications to paint analysis.

Instrumentation and interpretation of data are basically the same as in GLC, the only departure from GLC convention being the absence of a liquid stationary phase. Initially, GSC methods were used primarily for the analysis of very volatile, inert materials, but with the introduction of new packing, the technique has been extended to the analysis of a much broader spectrum of chemical types. Alumina, silica gel, molecular sieve, organoclay, and porous polymers are the most widely used GSC packing materials. GSC with silica gel, alumina, or organoclay preclude the analysis of polar solutes since polar solutes are irreversibly adsorbed on surface-active groups. Of the GSC packing mentioned, porous polymers are the most recent, and, owing to their versatility, they offer the best potential for GSC analysis of coating materials [142–145].

Porous Polymer Packings—porous polymer beads represent a unique advance in column technology by making use of polymer synthesis to produce columns for specific applications. Porous polymer beads are derived from the same family of polymers used in gel-permeation chromatography; they were first introduced as a GC packing by Hollis [146], who demonstrated their application to various chemical species.

The porous polymer beads used by Hollis were prepared from styrene, t-butylstyrene, and ethylvinylbenzene cross-linked with divinylbenzene. By varying the monomer ratios and polymerization conditions, the properties of the polyaromatic beads can be varied with regard to chemical structure, pore structure, particle size, and surface area. Consequently, beads of different performance characteristics can be synthesized. Porous polymer beads from different sources have been studied [147]; their physical properties and performance characteristics have been described in great detail.

Technically, the use of porous polymer beads packings should not be classed exclusively as GSC since partition and diffusion, as well as adsorption, all contribute to their effectiveness. Most likely, adsorption predominates at low temperatures and partition at high temperatures. Porous polymer beads have good mechanical strength, which permits their being packed by conventional vibration techniques. Most beads can be used up to 250°C with little or no bleeding, and this characteristic is particularly important when high-sensitivity detectors are used in conjunction with temperature programming. Unlike diatomaceous earth packings, porous polymer beads are hydrophobic, eluting water very rapidly with little or no adsorption. The potential uses of such packings are still being explored, but excellent results have already been achieved for the analysis of polar compounds [148], these chemical types being difficult to chromatograph on conventional GLC columns [149].

Finally, the readers may find the list of ASTM practices relevant to chromatography shown in Table 5 useful in their practice of chromatography [150].

GAS CHROMATOGRAPHY GLOSSARY

The following definitions of terms used in GC were compiled by Brenner and Olson [149] and the International Union of Pure and Applied Chemistry under the Chairmanship of Dr. Ambrose [150].

adsorbent (active solid)—Solid, granular material used to pack columns and on the surface of which sample components are held by adsorptive forces.

adsorption chromatography—See gas-solid chromatography.
adsorption column—Column used in gas-solid adsorption chromatography. The column material consists of an active solid (adsorbent).
air peak—The peak of a substance that is not retarded by the column material, thus indicating the time necessary for the carrier gas to travel from the injection point to the detector.
attenuator—An electrical element containing a series of resistances that may be selected by a switch to produce the reduction of input voltage to a recorder by a fixed factor.
band—See peak.
band area—See peak area.
baseline—The line drawn by the recorder pen when no sample is being measured in the detector.
capillary column (open tubular column)-Tubing of small diameter, usually 0.25 to 1.0 mm inside diameter, in which the inner walls of the tube are used to support the stationary liquid.
carrier gas—The gas, usually inert, that constantly flows from a pressurized source through the chromatograph, impelling the sample through the system.
chromatogram—The graphic recording of the detector response versus time or volume of carrier gas.
column—A metal or glass tube packed or internally coated with the column material through which the sample and carrier gas flow and in which the chromatographic separation is performed.
column material—The material contained in the column. In adsorption chromatography, the column material is the adsorbent itself; in partition chromatography, the column material consists of a stationary phase distributed on an inert solid support or coated on the inside wall of the column.
component—A pure compound contained in the sample mixture.
detector—A measurement device, usually electrical, that emits a signal in the presence of a component that is eluted from a chromatographic column.
elution—The "washing" of a component through and out of the column by the carrier gas.
filament element—A type of thermal conductivity device in which a fine tungsten or similar wire is used as the variable resistance element in the cell chamber.
flow programming—A technique in which the carrier gas flow rate is gradually increased in order to expedite the elution of the higher boiling components.
gas chromatography (GC)—Collective noun for all chromatographic methods in which the moving phase is a gas. The term "chromatography" implies that a stationary phase is present in addition to the moving phase. These methods are also called vapor-phase chromatography (VPC).
gas-liquid chromatography (GLC)—Chromatographic method in which the stationary phase is a liquid distributed on a solid support. The separation is achieved by partition of the components of a sample between the phases. This method is also called gas-liquid partition chromatography (GLPC).
gas-solid chromatography (GSC)—Chromatographic method in which the stationary phase is an active solid (adsorbent). The separation is achieved by adsorption of the components of a sample. This method is also called gas-solid adsorption chromatography.
integrator—A mechanical or electromechanical device for producing a continuous summation of detector output with respect to time, yielding a measurement of included area of a chromatographic band.
ionization detectors—Chromatographic detectors in which the measurement of a sample is derived from the current produced by the ionization of sample molecules induced by thermal, radioactive, or other excitation sources.
katharometer (catharometer)—See thermal conductivity cell.
Liquid phase—A liquid that is relatively nonvolatile at the column temperature and is sorbed on the solid support where it acts as a solvent for the sample. The separation achieved differs with differences in solubility of the various components of the sample in the liquid phase. This is also called the stationary phase or substrate.
moving phase (mobile phase)—The carrier gas within the column, in which sample component molecules progress down the length of the column.
partition chromatography—See gas-liquid chromatography.
peak—The portion of the chromatogram recording the detector response while a single component emerges from the column. (If the separation of a mixed sample is incomplete, two or more components may appear as one peak.)
peak area—The included area formed by the ascending and descending arms of a chromatographic-recorded band and the baseline of the chart.
potentiometric recorder—A readout device in which a pen, whose deflection is proportional to the voltage output of the chromatographic detector, writes on a paper chart that is moving at a constant speed.
pyrolysis—A technique in which nonvolatile samples are thermally decomposed in the absence of oxygen in the inlet system and the volatile products are admitted to the chromatographic column.
relative retention—The ratio of the retention time of a component to the retention time of a second component chosen as a standard.
resolution—The degree of separation between peaks.
retention index—The number of carbon atoms (multiplied by 100) of a hypothetical normal paraffin, which under the given conditions would have a retention time identical to that of the substance of interest.
retention volume—The product of the retention time of a component and the volumetric flow rate of the carrier gas.
retention time—The elapsed time from injection of the sample to recording of the peak maximum of a component band.
sample—The gas or liquid mixture injected into the chromatograph for analysis.
sample injector—A device by which a liquid or gaseous sample is introduced into the apparatus. The sample can be introduced directly into the carrier gas stream or into a chamber temporarily isolated from the system by valves that can be changed so as to

instantaneously switch the gas stream through the chamber.

separation—The elapsed time between elution of two successive components, measured on the chromatogram as the distance between the recorded bands.

solid support—The granular material upon which the thin layer of liquid in a partition column is held.

solute—The individual fractions of the sample dissolved in the liquid phase during their travel through the column. This is also used as another term for the sample itself.

solvent—Synonym for the liquid phase.

span of a recorder—The signal level (number of millivolts) required to produce a change in the deflection of the recorder pen from zero to 100 % on the chart scale.

splitter—A T-fitting attached to the column to divert a portion of the flow. An inlet splitter allows introduction of very small samples to a capillary column. An effluent splitter may be used to permit parallel operation of two detectors.

stationary phase—See liquid phase.

substrate—See liquid phase.

tailing—A form of band distortion in a chromatogram in which the trailing edge returns to the baseline relatively slowly, producing an asymmetrical band.

temperature programming—A technique in which the column temperature is gradually increased in order to expedite the elution of the higher boiling components.

thermal conductivity—A physical property of materials that is the ability to conduct heat from a warmer to a cooler object.

thermal conductivity cell—A chamber in which an electrically heated element is contained that, by its change in resistance, will reflect changes in thermal conductivity within the chamber atmosphere.

thermistor bead element—A type of thermal conductivity detection device in which a small glass-coated semiconductor sphere is used as the variable resistive element in the cell chamber.

vapor-phase chromatography (VPC)—See gas chromatography.

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Electron Microscopy Overview with Coating Applications

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INTRODUCTION

ELECTRON MICROSCOPES ARE FREQUENTLY USED in the analysis of coatings and their components because of their high resolution and multifunctional capabilities. The two common types are the scanning electron microscope (SEM) and the transmission electron microscope (TEM). In various operating modes and with specialized detectors, these instruments can be used to examine surface texture and internal structure, determine particle size and shape, provide elemental analysis, and reveal crystallographic orientation and identity.

The resolving power of electron microscopes is orders of magnitude greater than that of light-optical microscopes, partly due to the shorter electromagnetic wavelength (higher energy) of electron illumination. Modern SEMs with field-emission electron guns have the ability to resolve better than 1 nm between objects and commercial TEMs can resolve better than 0.2 nm. However, the actual resolution obtained is highly dependent on the nature and preparation of the sample. Contrast develops in SEM by electrons emitted at or near the surfaces of bulk specimens and, therefore, topography and composition are examined. Contrast develops in TEM by electrons transmitted through thin specimens and, therefore, variations in structure and composition are examined. Due to the improved resolution of modern SEMs, TEMs are no longer needed to see coating components 50 nm or smaller. In this chapter, SEM will receive more attention than TEM for this reason, along with its greater availability and documented coatings applications.

Types of signals generated in a sample by a vertically incident electron beam are illustrated in Fig. 1. An SEM typically has detectors for secondary electrons (SEs), backscattered electrons (BSEs), and X rays positioned above the surface of bulk specimens. The TEM collects elastically and inelastically scattered electrons, and sometimes X rays from thin (ca. 100 nm) specimens. Hybrid TEMs have some SEM capabilities. They may collect BSEs and SEs from the incident-beam side of thin specimens, a variety of transmitted electron signals from the opposite side of the sample, and X rays from both sides. These are known as scanning transmission electron microscopes (STEMs) or analytical electron microscopes. Their greatest strength is their ability to focus a fine electron probe on very thin samples, achieving high spatial resolution in elemental and structural analysis.

SEMs and TEMs were both invented in the 1930s in Germany [1]. Ernst Ruska shared the 1986 Nobel Prize in Physics for designing the transmission electron microscope and improving electron optics. Soon after its invention, TEM became widely used to image replicas of surfaces at resolution far better than was possible with the first SEM and, therefore, further development of SEM continued at a slow pace. An important step was the invention of an efficient secondary electron detector by Everhart and Thornley in 1960. In 1965, the Cambridge Instrument Company introduced the first commercial SEM. SEM was quickly applied to the study of coatings, as evidenced by American Chemical Society Symposia on SEM of polymers and coatings in 1970 [2] and 1973 [3].

Some of the greatest recent improvements in SEM and TEM design and operation were made possible by the rapidly increasing power and decreasing cost of personal computers. Manufacturers (and after-market suppliers) have moved to using standard personal computer (PC) interfaces and operating systems to control microscope functions. Better computers and software have driven an almost complete transition from analog to digital beam control, correction, and acquisition. Image archiving, processing, and analysis functions are common options. Intensive image processing and crystallographic computations are performed quickly during an imaging session. One or more PCs can integrate these and other functions, such as energy dispersive spectrometer (EDS) analysis and motor stage control.

This chapter has three main parts: SEM, TEM, and further applications to coatings. The SEM section begins with a description of the electron-optical column including the electron gun, lens system, and scan coils. This is followed by a discussion of image formation and signal collection. The function of these components must be understood in order to create ideal operating conditions for SEM and to correctly interpret SEM images. Also included is a discussion of X-ray microanalysis, used to identify and measure the elements present in a sample. The SEM section also has an overview of sample preparation, including conductive coatings and cross-section analysis. In the TEM section is a brief discussion of contrast and electron optics. The last section discusses some additional applications of electron

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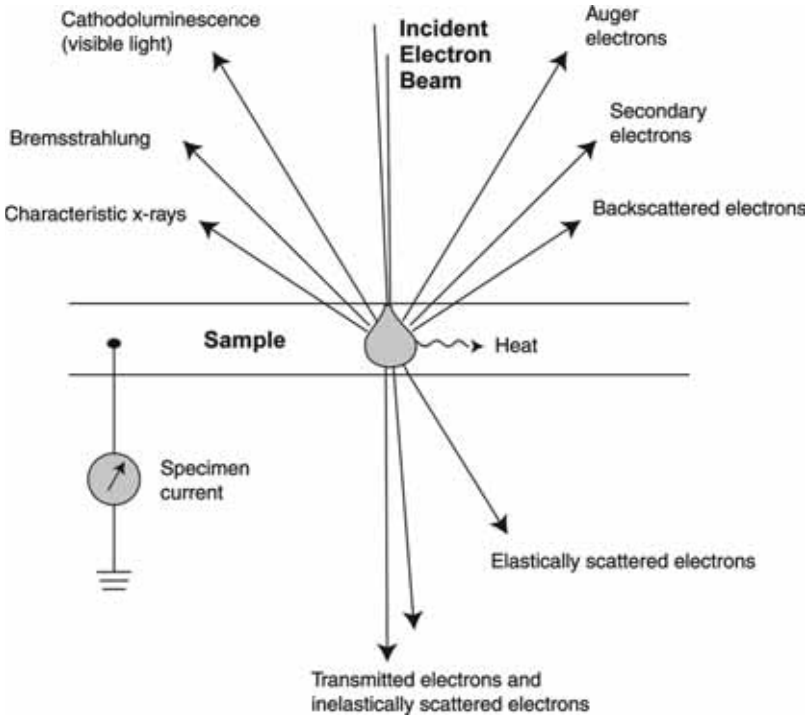

Fig. 1—Electron beam interactions with a sample and signal types generated. A typical thick SEM sample will have the teardrop-shaped interaction volume. Reproduced with permission from Thermo Fisher Scientific.

microscopy to coatings, from pigment sizing and identification to structure and wear.

SCANNING ELECTRON MICROSCOPY

The main specifications that control the performance of an SEM are the type of electron gun and whether the sample chamber will have variable pressure capabilities (in addition to the standard high-vacuum sample environment). In configuring an SEM, there are a wide variety of choices in signal detection systems. These have to be balanced against the size and geometry of the sample chamber. Vacuum systems for SEMs have become more complex due to the need for higher vacuum in the electron gun and lower (weaker) vacuum levels in the sample chamber. Two excellent texts are available to the reader desiring more detail on SEM and X-ray microanalysis [4,5].

The SEM can image surfaces at magnifications from about 10 to 200,000 times. Depth of focus is large, so rough surfaces may be fully focused. The types of signals that can be collected include SE, BSE, and characteristic X rays. As the electron beam scans the sample, the signal from each spot is collected, amplified, and synchronously displayed on the monitor with intensity proportional to the collected signal. The same scan generator deflects the electron beam across both the sample and the monitor and therefore the image displayed is a magnified view of the scanned area. In digital SEMs, the scans are digitally stepped with control over step size and dwell time per pixel.

To clearly see a feature of interest requires sufficient contrast, magnification, and resolution. Each of the signal types noted above has its own contrast mechanisms. Although SEMs commonly have magnification ranges above 100,000 times, obtaining a useful image at those magnifications requires sufficiently fine resolution. Spatial resolution is the ability to differentiate two closely spaced objects, measured by their distance of separation. An instrument with 3 nm spatial resolution will not provide sharp images of 3 nm objects. Instead, it will be able to differentiate larger objects spaced as closely as 3 nm apart, if they respond ideally under the electron beam.

A schematic diagram of the SEM is shown in Fig. 2. Electrons are drawn out of the gun by the electric field between the source and the anode. The condenser lenses form the beam into a finely focused probe. The scan coils cause the probe to scan across the sample in a raster. The final lens focuses the beam on the sample. Any combination of BSE, SE, and characteristic X rays can be detected. Details of the function of each component in the SEM are discussed below.

Electron Guns

The ultimate resolution of an ideal sample imaged in the SE mode of SEM is substantially controlled by the type of cathode in the electron gun, or source. The resolution is improved by making the probe diameter at the specimen surface smaller. This beam diameter can be expressed in nanometers as

$$d_{\min} = KC_s^{1/4}\lambda^{3/4}(1 + i_p/B\lambda^2)^{3/8}$$

where K is a constant near one, C_s is the spherical aberration of the lens, λ is the electron wavelength in nanometers, i_p is the probe current in amperes, and B is the electron gun brightness (in amperes per centimeter squared—steradian) [4]. To decrease the beam diameter (improving resolution) one can use an electron gun with higher brightness (current density). In any SEM, lowering the probe current (using condenser lens controls) and decreasing wavelength (by increasing accelerating voltage) should decrease probe size.

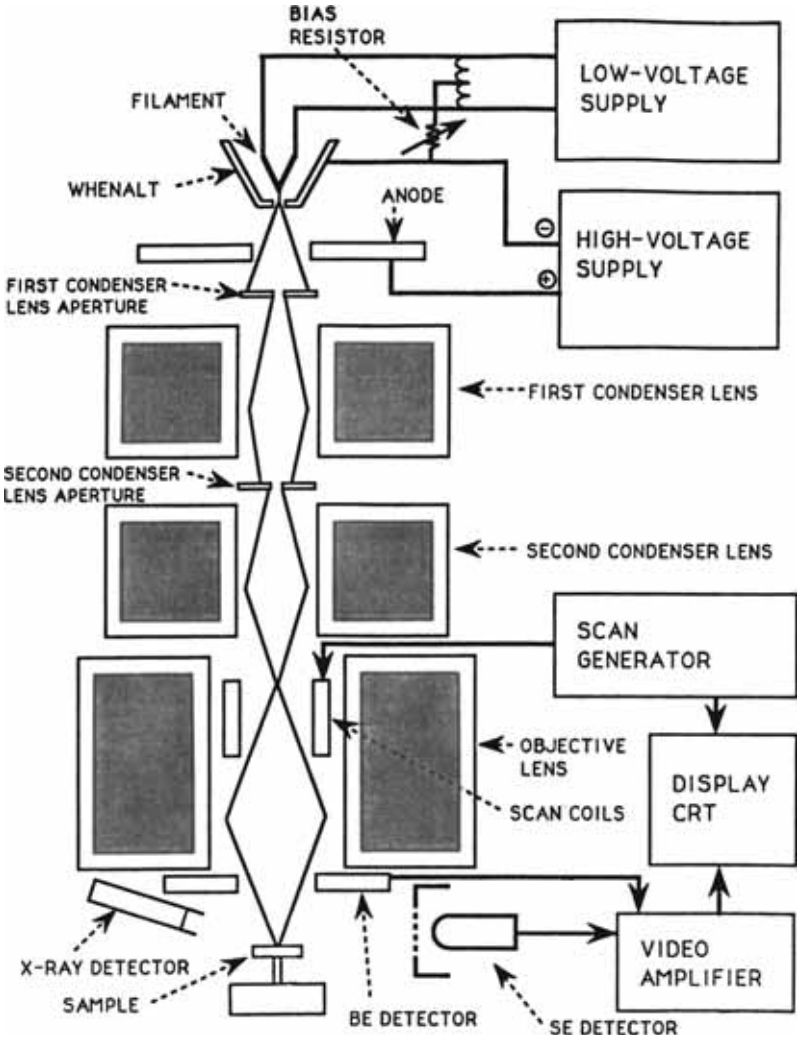

Fig. 2—Schematic diagram of an SEM with a thermionic electron gun. The "objective" lens is actually a final condenser lens. Adapted from Thomas [6] with permission from John Wiley and Sons.

An SEM can be designated conventional or field emission (abbreviated FESEM or FEG SEM), depending on which gun type is incorporated. Characteristics of electron sources are summarized in Table 1. A conventional SEM may have either a tungsten filament or a lanthanum hexaboride (LaB_6) crystal cathode, the most common thermionic cathode materials. Thermionic excitation occurs when a filament is heated to near its potential-energy barrier, allowing electrons to overcome their work function and eject themselves into the vacuum. Tungsten cathodes consist of a wire bent like a hairpin. They are easy to operate and need only moderate vacuum to prevent oxidation. However, they require frequent replacement (ca. 50–100 h). LaB_6 cathodes consist of a crystal of that compound mounted in refractory metal strips or an intermediate carbon-ceramic support. Compared to tungsten, LaB_6 has higher current density, and a smaller diameter of the first crossover, resulting in better resolution (Table 1). Another advantage of LaB_6 cathodes is their significantly longer lifetimes. However, LaB_6 guns require a somewhat higher vacuum to prevent contamination and reactions of LaB6 with oxygen-containing residual gases [5]. This adds to the expense and complexity of the gun vacuum system.

Field emission electron guns deliver orders of magnitude higher current density (brightness) than conventional SEM sources, but require a larger capital investment. FESEMs are made with either cold or thermal field emission design. Field emission occurs when a huge potential gradient ($>10^7$ V/m) is applied to a tungsten tip of about 0.1 μm in diameter, causing electrons to tunnel through their potential barrier. No thermal energy is needed to lift the electrons over the barrier. The combination of high current density and small diameter of the first crossover in field emission (FE) guns makes possible ultrahigh resolution (<1 nm) SEM imaging. The diameter of the first crossover from a field emitter is only about 10 nm and therefore only one condenser lens is needed to demagnify the probe enough for high-resolution imaging. Gas molecules that strike the tip cause the work function to rise and the emission to fall. Field emitters that operate at room temperature (known as "cold field" emitters) require vacuum better than 10^{-8} Pa. Even in a clean vacuum, gas molecules eventually cover the tip. The tip is cleaned by rapid heating (flashing) at about 2300 K.

A second type of high current density source is thermal field emission, including the Schottky design. This cathode

TABLE 1—Performance parameters for electron sources in SEM[a]

	Tungsten	Lanthanum Hexaboride	Cold Field Emission	Schottky Thermal Field Emission
Gun vacuum, Pa	10^{-3}–10^{-4}	10^{-5}	10^{-8}	10^{-7}
Lifetime, hours	50–100	≥1000	thousands	thousands
Source size	50 μm	10 μm	2 nm	20 nm
Brightness, A/cm^2-sr	10^5	10^6	10^8	10^8
Signal stability, (% drift/hour)	1	2	5[b]	1–2
Maximum probe Current, A	2×10^{-5}	2×10^{-5}	5×10^{-9}	5×10^{-7}
Energy spread, electron-volts	2	1	0.1	0.2
SE resolution @ 30 kV, nm	3.5	2.5	0.5	1

[a]Approximate values. Adapted from sources including Goldstein et al. [4] with permission from Springer-Verlag.
[b]Stability commonly improved by correction circuitry.

contains a zirconium oxide (ZrO) coated tungsten crystal maintained at 1800 K. The high temperature avoids the flashing required to clean cold FE tips and accommodates a slightly weaker gun vacuum. The ZrO coating lowers the work function, easing electron emission [4]. Schottky emitters can produce higher beam currents, valuable in some backscattering and x-ray analysis applications.

SEM at low accelerating voltages (below 5 kV) has the advantages of less specimen damage and less surface-charge buildup, when lower beam currents are used. There is improved representation of surface details because the primary electron beam does not penetrate as deeply, and there is a smaller region of secondary electron emission. Low-voltage SEM had been limited in resolution mainly by large chromatic aberrations in final lenses, which arise from the large energy spread of electron beams from thermionic cathodes. This problem has been overcome by FE cathodes, whose energy spread is an order of magnitude smaller than in thermionic cathodes (Table 1). The merits of low-voltage SEM for surface imaging and EDS were discussed by Boyes [7].

Magnetic Lenses and Scan Coils

The purpose of the condenser lens system in the SEM is to deliver electrons from the first crossover to the specimen plane in a small-diameter, high-intensity beam. SEMs with thermionic electron guns have two demagnifying condenser lenses plus a final condenser lens (Fig. 2). The first condenser is placed halfway between the second condenser and the electron gun, and the second is placed halfway between the gun and the specimen. Two condenser lenses instead of one are advantageous because more electrons are collected and focused into the probe, and the probe diameter is smaller. The spray aperture in each condenser lens intercepts scattered electrons and decreases spherical aberrations. The first spray aperture is usually fixed and the final aperture is selectable to varying diameters. While a smaller probe diameter improves resolution, it is not always advantageous because it reduces both the probe current and the signal-to-noise ratio. Higher probe currents are needed for EDS and some BSE detectors. The operator must decide which combination of aperture and condenser lens currents fits the requirements of resolution and signal detection.

The lens closest to the sample is often incorrectly called the "objective" lens. It is more accurately called the final condenser lens. There is no objective lens in an SEM because, unlike a TEM and compound light microscope, all SEM lenses are on the same side of the sample as the illumination source (electron gun). The purpose of the final lens is to provide the operator with a fine control for the focus of the beam at the sample surface.

The scan coils, located within or above the final lens, deflect the electron beam across the sample in a raster pattern. The image signal from a selected detector is simultaneously displayed on the monitor in the same positional coordinate system. Magnification is the ratio of a feature's length in the image to the length of that same feature in the sample. The distance between the bottom of the final lens and the top of the sample is known as the working distance. The depth of focus is inversely proportional to the working distance. Probe diameters are small when the beam is focused at short working distances. Therefore, high-magnification imaging should be done at short working distances, and low-magnification imaging should be done at long working distances (if more depth of focus is desired).

Image Formation

Most SEMs are equipped to detect SEs, BSEs, and characteristic X-rays as the electron beam scans across sample surfaces. The SE signal is produced when bound electrons are removed as a result of inelastic scattering of the electron beam. The intensity of the SE signal depends partly on the orientation of the sample feature with respect to the primary electron beam, which is why SE images provide topographic contrast. X-ray detection is discussed in a later section.

BSEs result from elastic scattering of the primary electron beam. Electrons are elastically scattered when they penetrate the electron clouds of target atoms and change direction without losing energy. An electron is backscattered after a series of direction-changing elastic events that cause the electron to exit the sample. The probability of a backscatter event depends on the size of the nuclei and, therefore, backscatter contrast depends on the distribution of an average atomic number in the sample. BSE images of flat specimens show higher atomic number phases as brighter. The depth in a sample from which BSE information emerges ranges from about 80 nm for gold to about 600 nm for aluminum if the accelerating potential is 20 kV [5]. Since BSEs can come from deep in the sample (lower

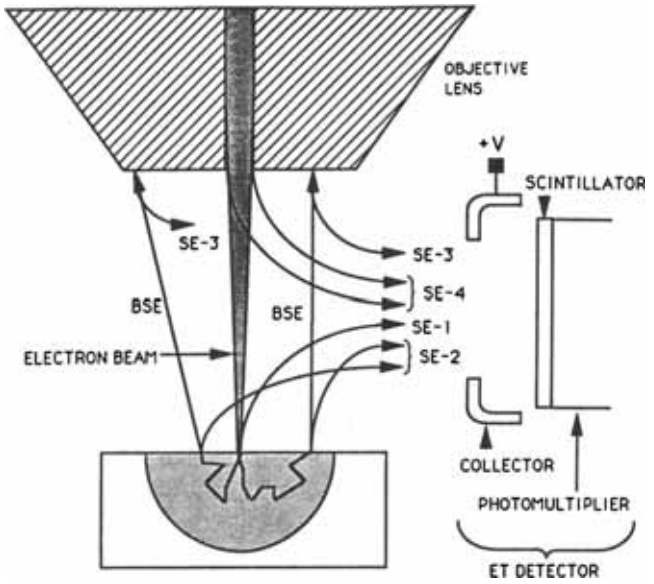

Fig. 3—Types of secondary electrons collected by the ET detector. SE1 carries high-resolution topographic information. Adapted from Reimer [5] with permission from Springer-Verlag.

in the teardrop in Fig. 1), the spatial resolution is generally poorer than in SE images. The BSE signal strength drops rapidly below 10 kV, and its behavior changes significantly below 5 kV.

Although some BSEs reach the Everhart–Thornley (ET) detector used for SE collection, it is an inefficient way to collect BSEs. BSE detectors are generally either of the solid-state or scintillator design. They are retractable or permanently mounted above the sample (labeled "BE Detector" in Fig. 2). A solid-state detector is a disk-shaped detector placed just below the final lens with a hole in the center for the electron beam. Scintillator-type detectors have an aluminized layer on a light pipe connected to a photomultiplier. They take up more space but respond better at fast scan rates.

Most SEM images are acquired with secondary electrons using the ET detector, shown in Fig. 3. SEs have low energy (<50 eV) and escape from the near-surface to provide more surface-sensitive data with higher resolution than BSEs. The ET detector collects mainly SEs, with a small contribution of BSEs. The major components of the ET detector are a collector grid, a scintillator, and a photomultiplier. SEs are pulled toward the scintillator by a small positive potential on the collector grid. A 10 to 12 kV bias on the scintillator coating accelerates SEs enough to cause photon emission when they strike the scintillator.

Secondary electrons are classified into four types, shown schematically in Fig. 3. SE1s are generated by direct interaction with the primary beam and therefore carry the highest resolution information. SE2s are generated by backscattered electrons as they exit the sample surface and therefore contribute subsurface atomic number contrast. Since SE2s come from a large electron diffusion zone around the primary beam, they degrade spatial resolution. SE2s cannot be detected separately from SE1s, but operating parameters (like lower accelerating potential) can lower their contribution.

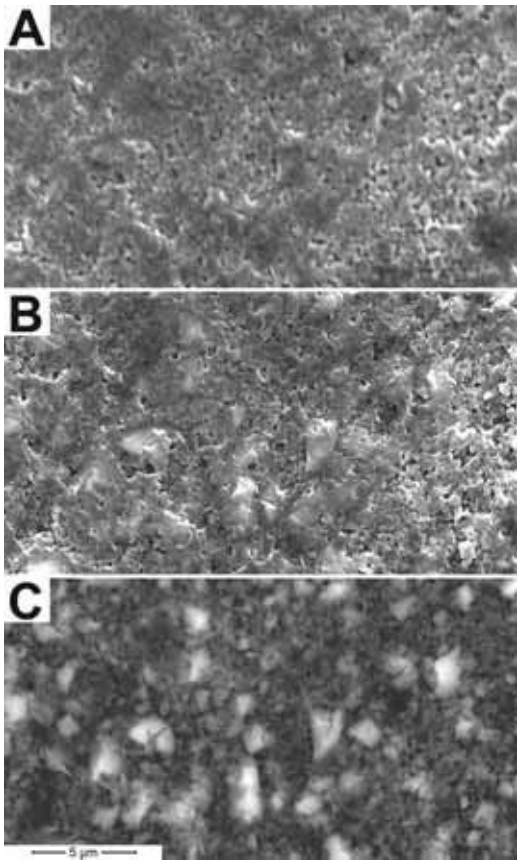

Fig. 4—Three SEM images of the same area of a coated paperboard used for food packaging. (A) SE image at 5 kV; (B) SE image at 20 kV; (C) BSE image at 20 kV. Bar = 5 μm. Photos by S. A. Wight, National Institute of Standards and Technology (NIST).

SE3s are generated by backscattered electrons that strike the final lens pole piece and the specimen chamber walls. SE4s are generated when the primary beam strikes internal column parts. SE3s generated at the final lens pole piece can be reduced with a shield made of low SE-emitting material, such as carbon-coated aluminum, placed just below the final lens. A +50 V bias applied to the shield prevents the escape from the shield of any SE3s. Reimer [5] discussed these signal types in detail. Peters [8] reviewed procedures for high-resolution SE image formation.

To demonstrate the importance of SEs and BSEs in generating contrast in the SEM, three micrographs of the same area of a coated paperboard used in food packaging are shown in Fig. 4. The coating contains kaolin clay and calcium carbonate pigment in an organic binder. Micrographs in Figs. 4(*A*) and 4(*B*) were recorded at 5 and 20 kV accelerating potential, respectively, with an ET detector. In Fig. 4(*A*) at 5 kV, the surface looks porous but uniform with pigment particles barely visible in the binder due to the low energy BSEs, therefore weak signal from SE2 and SE3, and dominance of SE1. In Fig. 4(*B*), pigment particles are becoming visible from within the coating blend due to a combination of SE2, SE3, and BSE. This is possible because of the greater exit depth of BSE at 20 kV. Comparison of Figs. 4(*A*) and 4(*B*) demonstrates the strong dependence of accelerating voltage on the appearance of SEM

images. Sometimes more than one accelerating voltage is needed for coating characterization.

The micrograph in Fig. 4(*C*) shows the same area as Figs. 4(*A*) and 4(*B*), this time recorded with a solid-state BSE detector at 20 kV. Since no SEs were detected, the binder near the sample surface generated little signal. Instead, contrast was mostly generated by the distribution of pigment particles within the coating. This example illustrates the importance of understanding signal generation in the SEM in order to correctly interpret images. Observation of only Figs. 4(*B*) and 4(*C*) might lead one to the false conclusion that the binder does not cover the pigment particles. The SEM was operated at normal (high) vacuum, with a thin gold coating added to the sample for electrical conductivity.

X-Ray Microanalysis

Inner shell ionization is the event that triggers characteristic X-ray production. An X-ray photon is produced when an electron from an adjacent shell drops to an inner shell to replace the ejected electron. Each element has its own set of characteristic X-rays and therefore elements present in a sample can be identified by their wavelength or energy if a spectrum of emitted X-rays is collected. That is the basis of X-ray microanalysis.

There are two common types of X-ray detectors: the wavelength dispersive spectrometer (WDS) and the EDS. In WDS, a small portion of the emitted X-rays hit a crystal. X-rays that satisfy Bragg's law for the crystal are diffracted to a proportional counter. X-ray spectra are collected by varying the crystal type and its position on the focusing circle. The advantages of WDS are excellent energy resolution (avoiding elemental overlaps), lower limit of detection (about 100 ppm instead of 1000 ppm), and high a signal-to-noise ratio. However, WDS uses higher beam currents than EDS (more sample damage and larger probe size), and is very sensitive to surface roughness. Also, simultaneous multielement acquisition requires more than one detector.

Before EDS was introduced to SEM in 1968, X-ray microanalysis was primarily done with WDSs using dedicated electron microprobes. EDS has poorer energy resolution than WDS (ca. 140 eV versus 20 eV), but the whole energy spectrum can be recorded simultaneously and therefore the elemental components can be quickly identified. Today, EDS detectors are routinely installed on SEMs. In EDS, X-rays pass through a thin window to a lithium-doped silicon crystal. The energy of incoming X-rays is measured from the number of electron-hole pairs generated in the crystal by each X-ray photon. A beryllium (BE) window (ca. 8 μm thick) usually separates the vacuum in the microscope from that around the liquid nitrogen cooled Si(Li) crystal. The BE window blocks out most X-rays from elements lighter than atomic number 11 (sodium). Windowless and ultra-thin window detectors extend the range down to $Z = 4$ (BE). Since the 1990s, durable atmospheric thin windows have been replacing Be windows, allowing full-time light element detection [9]. Silicon drift detectors have now become the preferred choice over Si(Li) for new EDS detectors because of their rapid acquisition speed, ability to handle high count rates, and freedom from liquid nitrogen cooling.

Accurate quantitative analysis requires careful control of conditions and an understanding of the beam interaction volume. In quantitative X-ray analysis with EDS, the X-ray intensities of each element in a sample are measured and compared to the measured intensities of well-characterized standards. The concentration of each element in the sample is the ratio of the X-ray intensity of each element in the sample to that in the standard. Still, corrections are needed to account for the different ways X-rays are generated in the sample compared to the standard. These include backscattering and the stopping power (Z), X-ray absorption (A), and fluorescence (F). Together, these corrections are known as the ZAF correction. EDS analytical systems available from commercial vendors have computer programs that calculate ZAF corrections, or the alternative $\phi(\rho z)$ corrections [9]. Quantitative EDS analysis without standards has its limitations, but has been effectively applied [10].

In X-ray mapping a compositional image is created with elemental windows selected from an EDS or WDS detector. Labana and Wheeler [11] mapped the spatial distribution of elements in a corroding metal-coating interface of painted phosphated steel using an electron microprobe. Elemental concentrations were determined quantitatively from individual spot analyses using the wavelength dispersive detectors. With modern EDS hardware and software, full spectrum mapping allows extensive re-display and quantification of chemical data.

EDS elemental X-ray maps can be very useful in tracing production defects or failures in coatings. Fig. 5 from Germani [12] shows a cross-section of paint that was applied to a metal sign. The SEM/BSE image (upper left) reveals the location of the primer, white ink, and clear topcoat layers. The clear topcoat suffered delamination upon outdoor exposure. The failure at the ink-topcoat interface was attributed to chlorine migration into the clear coat from the ink (see the chlorine X-ray map). The titanium signal is from titanium dioxide pigment. Silicon in the primer may come from a mineral pigment and from a deglossing agent in the topcoat.

Crystal Orientation by SEM

Electron diffraction in the TEM is an established approach to the determination of crystal structure in electron microscopy. However, BSEs in an SEM can also be used to generate diffraction patterns. As with X-ray diffraction and other forms of electron diffraction, Bragg's Law controls the constructive interference of energy waves from a crystalline material. Electron diffraction from the focused beam on a poly-crystalline sample generates light and dark Kikuchi bands containing information on the crystal orientation and identity. Reimer et al. [13] compared approaches such as high energy electron diffraction, electron channeling patterns, and electron backscatter diffraction (EBSD).

EBSD holds great potential for the study of coatings. The patterns come from within tens of nanometers of the surface [14]. They can be used to map the orientation of crystallites and their grain boundaries and to identify the crystalline phase. Modern EBSD systems include a tilted mount, retractable camera, and specialized software to enhance and analyze the patterns. Low-cost high-speed computers allow rapid automated calculations and integrated image displays.

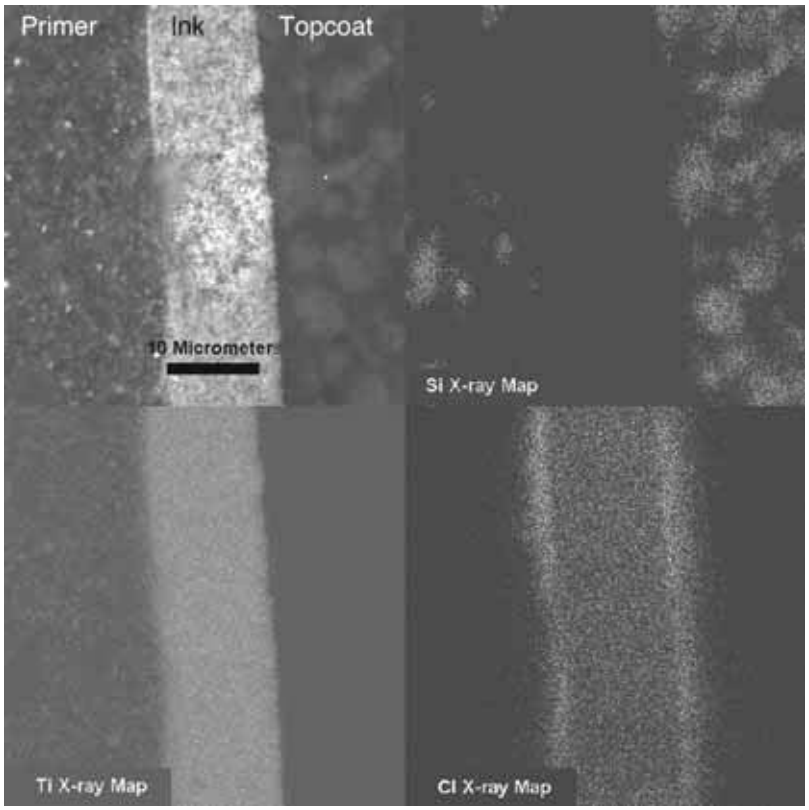

Fig. 5—SEM/BSE image and three elemental X-ray maps of a paint cross section. Bar = 10 μm. Reproduced with permission from M. S. Germani, Ph.D., Micro Materials Research, Westmont, IL, [12].

Conductive Coatings

Historically, all electrically nonconductive materials have been given a thin conductive coating prior to SEM analysis. Application of a 10 to 20 nm coating, after mounting the sample on a conductive base, provides a pathway for electron flow to prevent charge buildup. Metal coatings also increase SE yield and signal strength, indirectly improving feature resolution. With the advent of variable pressure SEMs (VPSEMs) and the operation of SEMs at low accelerating potential, there are now some situations in which a conductive coating may not be needed at all.

For routine SEM imaging with secondary electrons, gold or gold-palladium coatings are applied. When the main objective is analysis using the X-ray or BSE detector, carbon coating may be more appropriate. Carbon has low X-ray (and electron) absorption and its low-energy characteristic X rays are normally not in the range of sample peaks. Metal coatings can generate their own X-ray background and characteristic peaks in critical ranges. They can also suppress the BSE contrast inherent in the specimen. Carbon coatings will generally not produce the level of feature resolution or charge dissipation obtained with metal coatings. Carbon is usually deposited by thermal evaporation under high-vacuum, but some low-vacuum methods are also available.

Coating techniques for SEM include thermal evaporation, plasma-magnetron sputtering, and dc glow discharge. Films are formed by thermal evaporation when a metal wire or carbon rod is heated to its melting point in a high vacuum ($<10^{-3}$ Pa). Films formed by thermal evaporation have large grains compared to other techniques and may not reach areas of the sample that are shadowed from this point source. As the resolution of SEMs improved, the grain size of metal coatings became a limit to resolution. Coating techniques that produce thinner, continuous films with smaller grains were needed. Plasma-magnetron sputtering is one of them.

In magnetron sputtering, films are formed when ionized, inert gas atoms strike a metal cathode to eject metal atoms, which deposit on the sample. Ionization efficiencies and, hence, sputtering rates are increased with an annular magnetic field that surrounds the cathode to concentrate electrons in the cathode area [15]. Films made with magnetron sputtering have smaller grains than thermally evaporated films. The magnetron sputter-coater is now standard equipment in most SEM labs. Care should be taken not to allow rotary-pumped coaters to reach their ultimate vacuum. Otherwise, pump oil can disrupt nucleation when it contaminates the target and the sample. State-of-the-art magnetron coaters are evacuated with oil-free turbomolecular pumps and equipped with cold stages because low sample temperatures decrease grain size. Au/Pd alloy targets produce finer grain coatings than pure gold, but some users avoid them due to the additional peaks that appear during X-ray microanalysis.

Metal film thickness can be measured to ensure that only enough metal is deposited on the sample to form a continuous film. The quartz microbalance is the most widely used instrument to measure film thickness on electron microscopy specimens. Methods of film-thickness determination were discussed by Flood [16].

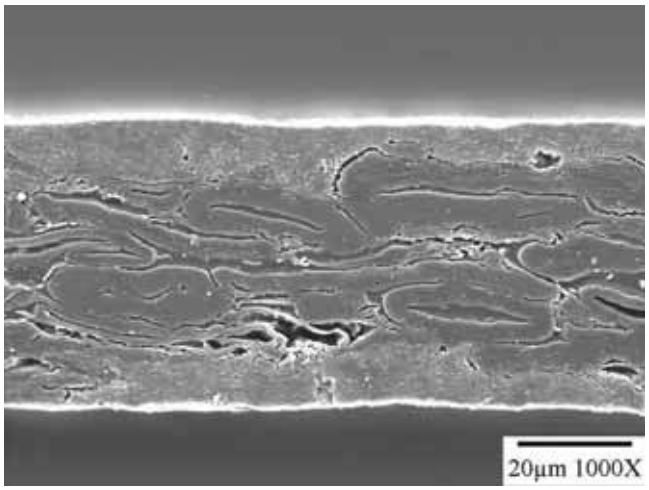

Fig. 6—Polished and etched cross section of lightweight clay-coated paper. Secondary electron SEM image. Bar = 20 μm. Photo by G. Maghiari, IPST.

Extra care is required to coat samples with ultrathin (1 to 4 nm) continuous films needed to take advantage of the high resolution at magnifications over 50,000 times, available from FESEMs. Magnetron coaters made to accommodate a chromium target and a greater range of controls are commercially available. More recently, a method of osmium coating through DC glow discharge has proven to provide excellent high-resolution images [17]. The osmium tetroxide dissociates in the glow discharge and ionized osmium molecules form an amorphous metal film on the sample surface. Safety considerations for the toxic osmium tetroxide have been addressed in the design.

Sample Preparation and Cross Sections

If samples are not dry and a cryogenic or variable pressure SEM is not available, some method of stabilization and drying will be necessary. This might simply entail drying in an oven or vacuum oven. If such drying will alter the microstructure, then freeze-drying or critical point drying may be used. Other approaches include exchanging the solvent with epoxy or making a cast/replica of the surface. Dry samples are trimmed to a size adequate for the microscope stage and attached to a planchet (mount) with conductive paint or tape.

When cross-sectioning is needed for analysis of internal structure or composition, several methods are available. Sometimes a broken or fractured edge is sufficient. Cut faces are usually too rough or smeared to reveal essential features. If the material is soft or plastic, freeze-fracturing in liquid nitrogen may work. The best sections are usually prepared with a microtome or by grinding and polishing. Dried paint and other coatings are normally embedded in epoxy prior to microtomy or metallographic polishing.

Microtomes are designed to cut sections of specified thickness ranges. Depending on the design, they may have metal, glass, or diamond knives. Rotary microtomes cut thick sections (ca. 20 μm) for light microscopy. Some ultra-microtomes have "thick" settings for sections approximately 2 to 10 μm thick, and "thin" settings for 50 to 200 nm TEM sections. Although microtomes do not generally work well on very hard materials, ultramicrotomes can be used to prepare ultrathin TEM sections of silicon wafers and ceramics [18]. For SEM, one only needs a cleanly cut block face, although the sections cut from it can be analyzed. Improved resins and microtomes have made cross-sectioning of paints less difficult. Derrick et al. [19] used glass knives in an ultramicrotome to produce 5 μm-thick paint sections.

Cross sections are often used to determine the thickness, composition, and structure of coating layers with SEM. Coated papers have historically been sectioned by microtome, but grinding and polishing (after epoxy embedding) have become more common due to improved procedures and the larger sample area exposed [20]. Fig. 6 shows an SE image of a polished and etched section of coated paper with excellent detail. Sometimes BSE imaging is used to display the compositional contrast of coating layers and components. ASTM Test Method D5235 [21] (method withdrawn) describes a grinding-polishing method for preparing and measuring cross sections of coatings on wood, using light microscopy. With modification, this procedure might be used for SEM, especially VPSEMs that do not require dry specimens.

On the leading edge of cross-section technology is focused ion beam (FIB) preparation for TEM and SEM. These systems are quite expensive but have been extensively used in semiconductor analysis. Typically, the FIB workstation has a gallium ion source that is used to thin and shape a small area of interest. This method has enabled the production of well-resolved images of thin ink layers on printed paper [22]. Dual beam FIB/SEM instruments allow the operator to guide and observe the sectioning of a sample. Layered fuel cell electrodes were prepared and analyzed this way [23]. By imaging the surface during progressing ion milling, the authors were able to build a three dimensional model of the structure. In another FIB/SEM study [24], structural components and defects in carbon fiber composites for nuclear fusion devices were characterized.

Cryogenic SEM

Electron microscopes operating in the normal high-vacuum mode have a pressure lower than 10^{-3} Pa in their specimen chambers. This limits conventional SEM to dry samples. When volatile samples like paints are placed in the SEM specimen chamber their solvents quickly evaporate, contaminating the electron column, damaging the vacuum pumps, and causing the electron beam to scatter. One solution is to lower vapor pressures by freezing and examine samples in an SEM equipped with a stage cooled by liquid nitrogen. The technique is known as cryogenic SEM (cryo-SEM), described by Sheehan [25–27] for examining paper-coating formulations. The reader is also referred to Echlin [28] for more on techniques of cryo-electron microscopy.

The procedure of cryo-SEM is to fast-freeze each sample and transfer it into a vacuum chamber attached to the SEM specimen chamber. There each sample is fractured, sometimes etched, and then coated with a thin metal film. Then the sample is transferred to a cold stage in the SEM. The challenges of high-resolution cryo-SEM are to freeze fast enough to prevent noticeable growth of ice crystals, transfer without condensing water vapor on the fracture

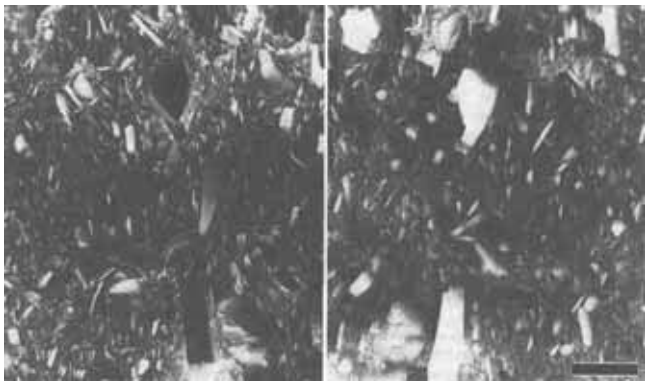

Fig. 7—Cryo-SEM image of complementary fracture faces of a coating formulation. Bar = 1 μm [26]. Reproduced with permission from Microscopy Society of America.

surfaces, coat frozen-hydrated samples with an ultrathin, continuous metal film, and image in the SEM without too much buildup of contaminants.

Wet microstructures of coating formulations can be examined with cryo-SEM after freezing and fracturing. Complementary fracture faces of a frozen-fractured pigment/latex coating formulation are shown in Fig. 7. Kaolin and calcium carbonate particles can be identified by their morphologies. The dark areas between the particles are ice. Close examination of the complementary faces shows that fractures propagated around the pigment particles.

Environmental and Variable Pressure Scanning Electron Microscopy

Cryo-microscopy is one approach to imaging volatile samples in the SEM. VPSEM, including the environmental SEM (ESEM), is another. Before the advent of the ESEM, some operators mechanically limited the vacuum level (ca. 20–200 Pa) in the SEM sample chamber and imaged their materials exclusively with a BSE detector. Usually a scintillator-type BSE detector was used because of its greater topographic contrast and better response at high scan speeds than solid-state detectors. In recent years, SEM vendors began to offer variable pressure capabilities on many microscope models, some advertising a resolution of 5 nm in variable pressure mode.

A revolutionary development in SEM in the 1980s allows the imaging of wet, volatile specimens without freezing. It is known as ESEM [29]. With the ESEM, samples are imaged in a gaseous environment at pressures up to 2.7 kPa. This is made possible by a combination of a differentially pumped vacuum system, small travel distances for the electron beam in moderately pressurized gas, and (most importantly) a biased current detector known as the gaseous secondary electron detector. The gas in the specimen chamber promotes SE signal multiplication and neutralizes charge buildup on samples. Therefore, a conductive coating is not required for imaging electrically insulating samples. ESEM SE resolution approaches that of conventional high vacuum SEM operation. To obtain optimum images from some samples, a conductive coating may still be needed to boost SE contrast. EDS elemental analysis can be performed in VPSEM/ESEM modes, but the spread of the electron beam in the gaseous environment makes spot analysis by EDS more difficult to control and quantify [30].

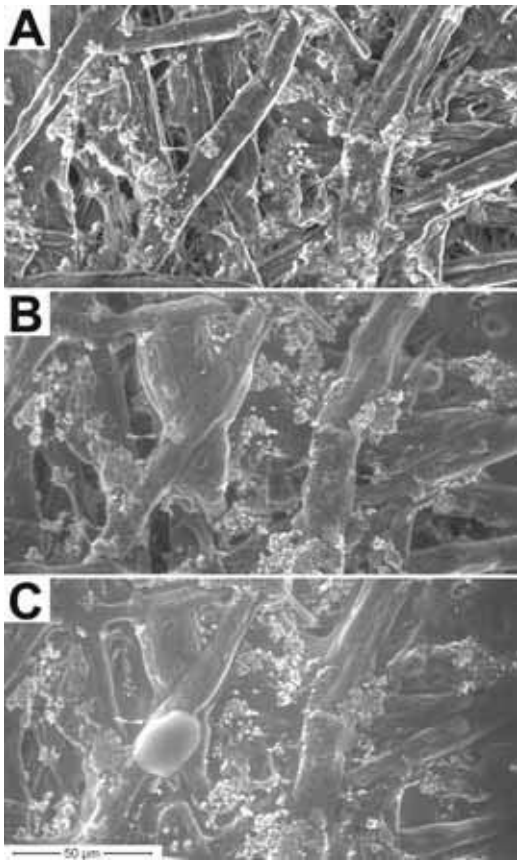

Fig. 8—ESEM micrographs of the same area on uncoated writing paper as water condenses. (A) ambient dryness, 20°C, 293 Pa; (B)condensation and fiber damage, 7°C, 933 Pa; (C) water drops and films, 7°C, 1093 Pa. Bar=50 μm. Photos by S. A. Wight, National Institute of Standards and Technology (NIST).

The main advantage of ESEM compared to conventional SEM is that hydrated samples can be examined in their natural states at water-saturated vapor pressures. This also makes possible dynamic imaging of wetting and drying by controlling sample temperature and water vapor pressure. Other experimental gases can be used in the ESEM sample chamber instead of water vapor.

Care must be taken with ESEM of hydrated specimens to avoid specimen damage by radiolysis products of water. Water molecules are radiolyzed by the electron beam into mainly hydrogen and hydroxyl radicals, which diffuse into specimens and sometimes damage them [31,32]. Radiation damage from free radicals in hydrated specimens was documented in TEM by Leapman and Sun [33]. Molhave et al. [34] concluded that water vapor enhanced irradiation induced destruction of carbon nanotubes in both SEM and TEM.

Fig. 8 demonstrates real time water condensation in an ESEM sample chamber. Fig. 8(*A*) is an ESEM image of writing paper (with wood pulp fibers) in its natural state at 20°C and 293 Pa pressure. Accelerating potential was 10 kV and no conductive coating was used. Water was condensed in the same area by raising the pressure to 933 Pa and lowering the stage temperature to 7°C (Fig. 8(*B*)). Beam damage, perhaps enhanced by radiolysis, can be seen in the prolonged exposure used for this demonstration. In

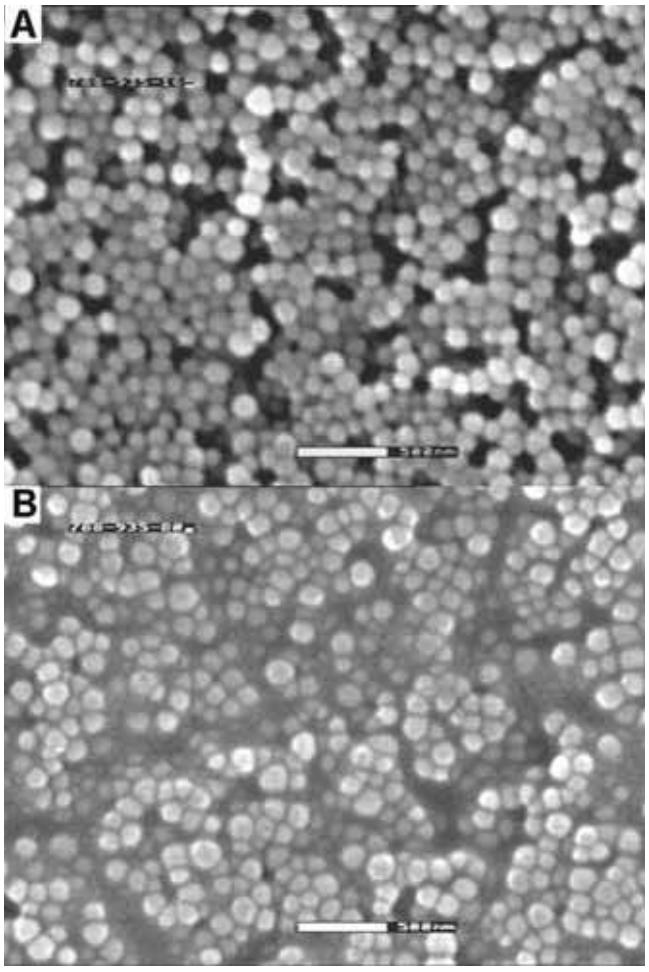

Fig. 9—ESEM micrographs of two coatings containing 0.10 μm plastic pigment with latex levels of (A) 14 wt. %; (B) 44 wt. %. Bar = 500 nm. Reproduced from Xiang and Bousfield [35] with permission from JPPS.

Fig. 8(*C*), at 7°C and 1093 Pa, water droplets and films can be seen.

A paper coating formulation with plastic pigment and a high latex content is susceptible to damage and difficult to image in a conventional SEM [35]. ESEM images in Fig. 9 compare 0.10 μm plastic pigment in mixtures with 14 % and 44 % latex binder by weight. They show the packing of pigment particles and filling of interparticle pores. Few pigment-size pores are open at the 44 % binder level.

TRANSMISSION ELECTRON MICROSCOPY

The TEM produces images from electrons that have been transmitted through ultrathin sections of samples, or naturally thin particles. The spread of the beam in a sample is minimized by the thin specimen, allowing a higher spatial resolution than SEM. Modern TEMs can resolve better than 0.2 nm. Contrast mechanisms include scattering, diffraction, and phase contrast. The useful thickness of amorphous samples at 100 kV is 100 to 3000 nm. For metal foils and crystalline materials at 100 kV, it is about 50 to 200 nm [36]. With added STEM capabilities, compositional and structural data can be collected from a spot 1 nm or less in diameter.

Types of Contrast

Electron beam interactions that lead to contrast in the TEM are shown in Fig. 1. In ultrathin samples, the beam does not spread into the teardrop shape shown for a bulk specimen. Electrons are elastically scattered by coulombic interactions with positively charged nuclei as they travel through TEM specimens. Scattering contrast is also known as amplitude contrast, or mass-thickness contrast, because the amount of scattering depends on specimen thickness and atomic number. Scattering contrast in TEM can be imaged in the bright-field mode and in the dark-field mode. In the bright-field mode, electrons that are scattered at larger angles are intercepted by the objective aperture. Others pass through the objective aperture and form the image. In the dark-field mode, only the electrons that are scattered at large angles are used to form the image. This is accomplished by tilting the electron beam off axis or by moving the objective aperture off axis. In STEM, an annular dark-field detector collects that signal.

Another type of contrast caused by elastic scattering is known as phase contrast, the result of interference between the scattered and the unscattered electrons. Phase contrast varies as the objective lens focus is varied above or below the specimen. Diffraction contrast results when Bragg reflections from crystalline planes interfere with the primary beam. The interference image gives information about crystal structures. A TEM can be switched to diffraction mode to provide electron diffraction patterns for phase analysis.

Inelastic interactions in TEM include plasmon excitations and inner-shell ionizations. Some TEMs are equipped with electron spectrometers that measure the energy loss spectrum, known as electron energy loss spectroscopy. Electronic structures are indicated by plasmon losses, whose energies are less than 50 eV. Chemical compositions are indicated by losses from inner shell (K, L, and M) ionizations [36].

Optics

A schematic of an electron-optical column of a TEM is shown in Fig. 10. It is similar to an upside-down view of a compound light microscope, with the illumination source being an electron gun. The electron-optical column of the TEM differs from the SEM in several ways. First, the electron beam is not scanned across the sample (except in STEM mode). The condenser lens system illuminates the entire area to be imaged. Second, the TEM has a projector lens system that focuses the transmitted electrons onto a phosphor screen, where the image can be viewed. Third, higher accelerating potentials (80 to 500 kV) in TEM are needed to transmit electrons through thin samples. Accelerating potentials in SEMs range from about 300 V up to 30 kV.

The two condenser lenses work together in the normal TEM imaging modes. The first condenser lens (C1) controls the spot size, while the second condenser lens (C2) is used to adjust brightness. In the STEM mode, where a finely focused probe is required, C2 is essentially turned off, and the upper part of the objective lens is used as a third condenser lens to focus the beam.

The objective lens forms, focuses, and initially magnifies the image. In most TEMs the specimen is inserted

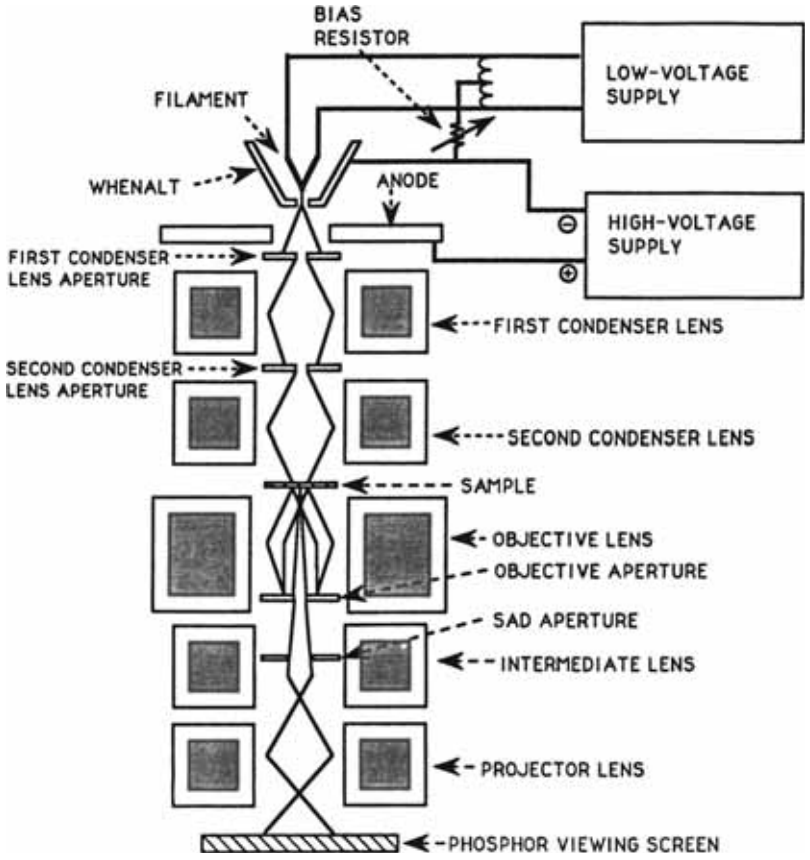

Fig. 10—Electron-optical column of the TEM. Adapted from Thomas [4] with permission from John Wiley and Sons.

into the objective lens section of the column. The objective aperture blocks scattered electrons in the bright-field mode, discussed earlier. Contrast is increased if a smaller objective is selected, but the signal strength will decrease accordingly.

The projector lens system projects the transmitted electrons onto the phosphor viewing screen or photographic emulsion. A wide variety of digital cameras are now available for image collection below the column or through a side-mounted camera port. Digital image collection has all but replaced film photography in TEM.

ADDITIONAL COATING APPLICATIONS

Pigment Particle Size and Identification

There are numerous non-microscopic methods for determining particle size distribution. Given a large, well-dispersed pigment population, these automated methods generate statistically valid measurements in very little time. Each approach, including microscopy, measures "size" differently and is likely to generate somewhat different results. Microscopic size measurement is a powerful approach when the shapes of particles need to be determined or when they are fixed in a dry coating. Particle-size measurements are more fully explored in a separate chapter of this manual.

The microscope is especially useful for measurement of plate-like and needle-shape particles that do not obey Stokes' law on which the sedimentation sizing methods are based. However, microscopic methods can be slow and laborious. In the past, particle-size analysis was performed by manually measuring particles with the aid of a reticle or grid on the microscope display or with a ruler using printed micro-graphs. Today, with size-calibrated digital images collected on electron microscopes, selected dimensions can be easily measured with the click of a mouse. Automated image analysis is possible if individual particles can be made to stand out unambiguously from their background by a combination of the right sample preparation, signal selection, and image processing. It must be understood that the particle images represent two-dimensional projections or slices of three-dimensional objects. True diameters may not be presented, and preferred orientation of particles in a coating will affect their shape within the section.

Pigments of known morphologies can be identified easily with both SEM and TEM. Some pigment particles are smaller than 0.1 μm and therefore conductive coatings must be ultrathin in order not to blanket morphologies of the particles before SEM imaging. Pigment particles can also be identified in SEM by their EDS spectra if the particles are larger than a few micrometers. Identification of smaller particles in SEM with an EDS is hampered by the large generation volume of X rays.

Fig. 11 shows images of kaolin clay taken with SEM (Fig. 11(*A*)) and TEM (Fig. 11(*B*)). The different contrasts in the SE mode with the SEM and in the bright-field mode with TEM are clear. The SE contrast is topographical and the TEM contrast depends on mass-thickness. In both, the pseudohexagonal, plate-like habits of particles are indica-

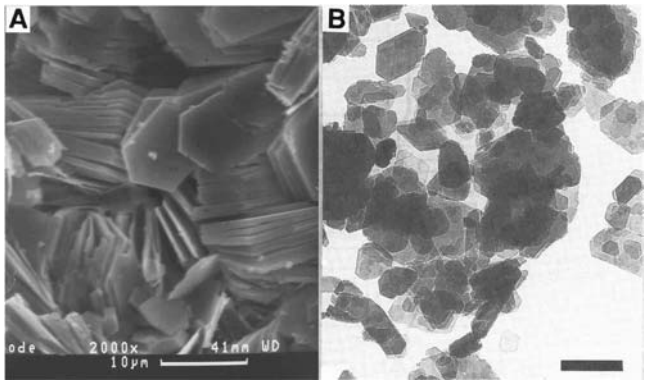

Fig. 11—Different kaolin clays imaged in (A) SEM. Bar = 10 µm. Photo by D. R. Rothbard; TEM. Bar = 0.5 µm. Photo by R. P. Gursky.

tors of the presence of kaolin. Clay identifications should be confirmed using other detection modes that provide chemical and structural data.

Contact diameters of various sizes of latex have been measured with SEM [37] and TEM [38], and compared to theoretical predictions. Demejo et al. [39] imaged with high-resolution SEM extents of latex deformation resulting from particle-substrate adhesion and compared their results to theoretical predictions.

Failures and Defects

Pits, cracks, and loss of adhesion can be readily examined with SEM. Some contaminants can be identified by their morphologies and others by their characteristic X rays using EDS. Here are some examples: SEM examination of a paint film that failed rapidly in a salt spray test revealed a textured surface that rusted rapidly in the pitted areas. When the paint was applied with a smooth finish, it passed the salt spray test. Poor scrubbability in a latex paint was due to lack of coalescence, readily apparent after SEM examination revealed many cracks in the film. Loss of adhesion on metal reflectors was due to insect eggs that pulled the paint off as the eggs dried. A glossy varnish, which turned out flat, was found to be laden with diatomaceous earth from a broken filter [40].

Quach [41] used SEM with EDS to identify contaminants responsible for adhesive failures. Welding splatter was identified as a cause of chipping of paint on a steel building chord. EDS was also used to identify plaster dust, fly ash, and sulfur dioxide as contaminants that caused adhesive failure in other samples.

Structure and Wear

Bishop and Silva [42] examined leaching of pigment in cross sections of antifouling paint films. Cross sections were made by fracturing in liquid nitrogen. They found a linear correlation between the leached matrix thickness and the volume fraction of pigment. Examination of complimentary fracture faces was required to see if leached pigment or fracture was responsible for voids. They also showed that the insoluble matrix of microtome-sectioned films was distorted.

Fay et al. [43] used SEM and EDS in an investigation of antifouling paints, to monitor the concentration and distribution of biocides. SEM images were used to document paint erosion after synthetic seawater exposure, in terms of texture and film porosity. The authors assumed they were obtaining quantitative EDS elemental analysis to the hundredths of a weight percent, which is an overinterpretation of standardless EDS analysis in an inhomogeneous medium.

SEM examination of weathered paint films showed the onset of chalking when binder wears away from between pigment particles [44,45]. However, the conclusion was that SEM images point to the cause of chalking, but gloss measurements are a more quantitative and economical method for routine weatherability evaluation.

Nylon coatings are used in such applications as printing rollers and marine hardware because of their wear and weather resistance. Thermally sprayed nylon 11 coatings with 7 and 12 nm silica pigment were sectioned and analyzed by SEM [46]. SEM was used to determine the structure of the raw materials and finished coating. Cross-section images, supported by EDS, showed nylon polymer cells surrounded by bead-like silica-rich interfaces.

FIB sectioning was mentioned earlier with respect to SEM preparation. It is used as much, if not more, for TEM. The method was applied in a TEM study of plasma spray coatings on aluminum and the interface between them [47]. Oxidative wear of a nano-structured TiAlN/VN coating was studied by TEM and EDS after FIB preparation [48]. The authors were able to detect a 20–50 nm thick wear induced tribofilm on the surface.

A combined analytical approach was used to examine the structure and composition of thermal barrier coatings (TBCs) designed for engine and turbine components [49]. Light microscopy, SEM, TEM, EDS, and X-ray diffraction methods were applied. Thick TBCs are commonly modified to increase their lifetime. The modification methods and their effects on structure and performance were compared.

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Infrared Spectroscopy

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INFRARED (IR) SPECTROSCOPY IS ONE OF THE most powerful analytical methods available in the coatings industry. It can be applied to both liquid and solid samples, and can be used to analyze both bulk samples and surfaces. Although perhaps the most fundamental uses of infrared spectroscopy are the elucidation of molecular structure and the identification of unknowns, it has great utility in the coatings industry as a problem solving tool. For instance, IR spectroscopy can be used not only to determine if the specified epoxy coating was actually used on a project experiencing coating failure, but can also be used to determine if the coating was mixed in the proper ratio of Part A to Part B, and maybe even to determine if it was applied over an organic contaminant such as grease or oil. In some cases, it can be used to determine a coating's degree of cure, or to examine surfaces for exudates, or to determine if the correct amount of plasticizer is present in a brittle lacquer. In short, IR spectroscopy is an essential component of the modern coatings laboratory.

THEORY OF INFRARED SPECTROSCOPY

Spectroscopy can be simply defined as the study of the interaction of light with matter. Since there are many different types of light, or electromagnetic radiation, it stands to reason that there must also be many types of spectroscopic techniques.

The classical interpretation of the nature of electromagnetic radiation, put forth by Christian Huygens in the late seventeenth century, ascribed to it a wavelike nature. In this view, light (radiation) consists of oscillating electric and magnetic fields moving through space at right angles to one another, with a characteristic frequency and wavelength (see Fig. 1). The wavelength (λ) is defined as the distance between successive maxima or minima (a cycle), while the frequency *(ν)* is the number of cycles per second. For electromagnetic radiation moving through a vacuum, the relationship between wavelength and frequency is as follows:

$$c = \gamma\nu$$

where c is the speed light (3.0×10^8 m/s). From this relationship, it can be easily seen that wavelength and frequency are inversely proportional to one another. In other words, as frequency increases, wavelength decreases, and vice versa. Although frequency is often expressed in cycles per second, or hertz, in infrared spectroscopy it is usually expressed in wavenumber, or reciprocal centimeter units, abbreviated cm^{-1}.

The wave theory of light was able to explain many, but not all, phenomena. This lead to the development in the early to mid twentieth century of quantum mechanics, which provided the very useful relationship that the energy of light *(E)* is directly proportional to its frequency, as follows:

$$E = h\nu$$

where h is Planck's constant (6.6×10^{-34} Js).

The electromagnetic spectrum is depicted in Fig. 2. As shown in this figure, the different types of electromagnetic radiation have different frequencies, and hence different energies. As a consequence of this, they interact differently with matter. For example, the very high frequency gamma rays, shown at the far left of the table, are sufficiently energetic to disturb the structure of the nucleus of an atom and cause radiation sickness, while the low frequency microwaves are only able to affect the rotation of molecules, and are useful for less destructive tasks such as heating water. Infrared radiation is roughly in the middle of the table, and is energetic enough to interact with the internal vibrations occurring in molecules.

Molecules are in a constant state of motion. Not only does this include translational motion through space, but it also includes the stretching and bending of the chemical bonds holding the various atoms of a molecule together. These stretching and bending vibrations occur within very discrete ranges of frequency, depending on the type of atoms and the type of chemical bonds holding them together. For example, Fig. 3 depicts some of the vibrations which can occur in a simple fragment of a molecule consisting of a carbon atom bonded to two hydrogen atoms. As shown in Fig. 3, if the carbon–;hydrogen bonds stretch in and out together, this occurs at a frequency of about 2850 cm^{-1}. If the bond lengths stay the same, but the angle of the bonds change in a bending or scissoring type action, this occurs at a frequency of about 1470 cm^{-1}.

If the frequency of infrared light focused through or on a sample identically matches the frequency of one of these molecular vibrations, the sample can absorb some of this light. In practice, the sample is scanned over a wide range of frequencies, typically from about 4000 to 400 cm^{-1}, and a spectrum is produced showing the frequencies at which the infrared light is absorbed. Since these correspond to the frequencies of the internal molecular vibrations occurring

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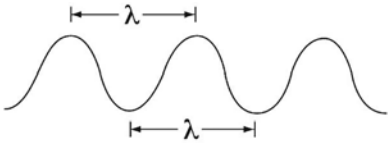

Fig. 1—Electromagnetic wave. Courtesy of Spectroscopy Atlas.

in the sample, and since these vibrations are indicative of the type of atoms and how they are bonded together, an infrared spectrum provides a great deal of information on the chemical structure of the molecule.

The infrared spectra of methyl ethyl ketone (MEK) and toluene, two common solvents used in the paint industry, are shown in Fig. 4. Since MEK and toluene have dramatically different molecular structures, their spectra are also dramatically different. Indeed, every compound has a unique infrared spectrum, which is sometimes referred to as a "fingerprint." Sometimes differences are dramatic and sometimes they are subtle, but as Fig. 4 demonstrates, infrared spectroscopy can be a very powerful tool in the identification of unknowns.

A quick examination of the spectra in Fig. 4 shows that they have many bands, including those near 2900 cm^{-1} due to the carbon–hydrogen stretching vibrations discussed above. The very strong band near 1720 cm^{-1} in the spectrum of MEK is due to a carbon atom double bonded to an oxygen atom (a carbonyl group). While all of these bands correspond to one type of vibration or another, and therefore provide a great deal of information about the structure of the molecule, it is not always necessary to be able to assign every single band to a particular type of molecular vibration. Indeed, in some cases this would be extremely difficult. There are many excellent collections of infrared spectra, such as "An Infrared Spectroscopy Atlas for the Coatings Industry" [1], which enable one to identify a compound without having to laboriously assign every single peak to a particular vibration. There are also electronic databases available which allow spectral searching on the computer.

Although many compounds can be positively identified simply by matching up the spectrum of the unknown to a spectrum contained in a reference collection, it is still desirable to have at least a general understanding of where the major bands from the more common functional groups

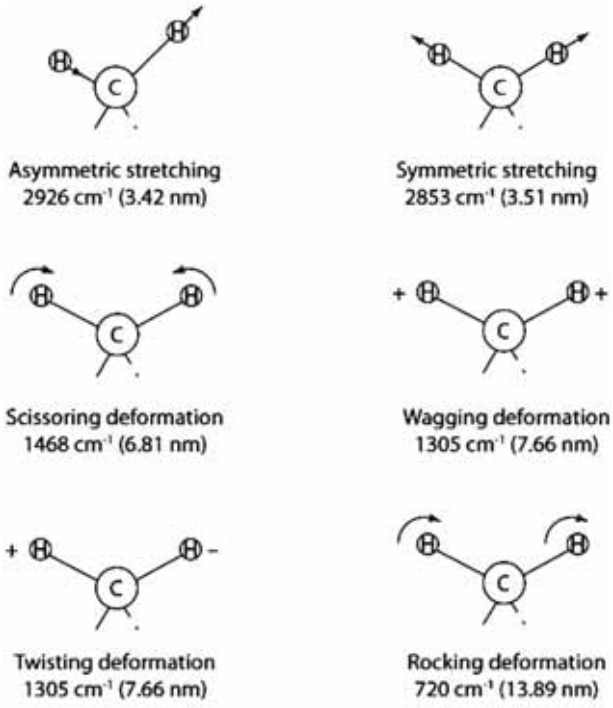

Fig. 3—Bending and stretching vibrations of a CH2 group. Courtesy of Spectroscopy Atlas.

absorb infrared radiation. This would be a very formidable task were it not for the fact that it has already been done. Because the frequencies of the stretching and bending vibrations of any pair of atoms is only modestly affected by their proximity to other atoms in the molecule, one can always expect, for instance, that the C═O stretching vibration will occur between roughly 1650 to 1750 cm^{-1} and the carbon-hydrogen stretching vibrations will always occur between approximately 2950–2850 cm^{-1}, regardless of the structure of the rest of the molecule. Because of this, and after a great deal of research, tables known as correlation charts have been developed which show where the various functional groups absorb infrared light. These tables are indispensable in the interpretation of infrared spectra, and can be found in many texts on infrared spectroscopy [1,2].

Not only do correlation charts tabulate where certain vibrations occur, they often provide information about

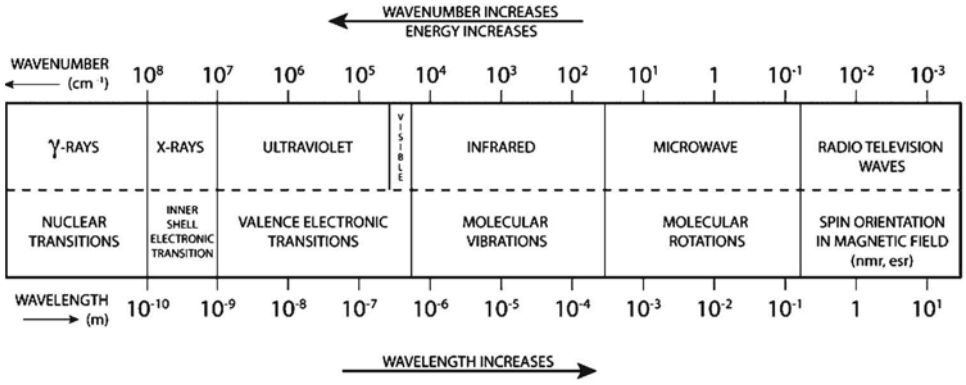

Fig. 2—Electromagnetic spectrum. Courtesy of Spectroscopy Atlas.

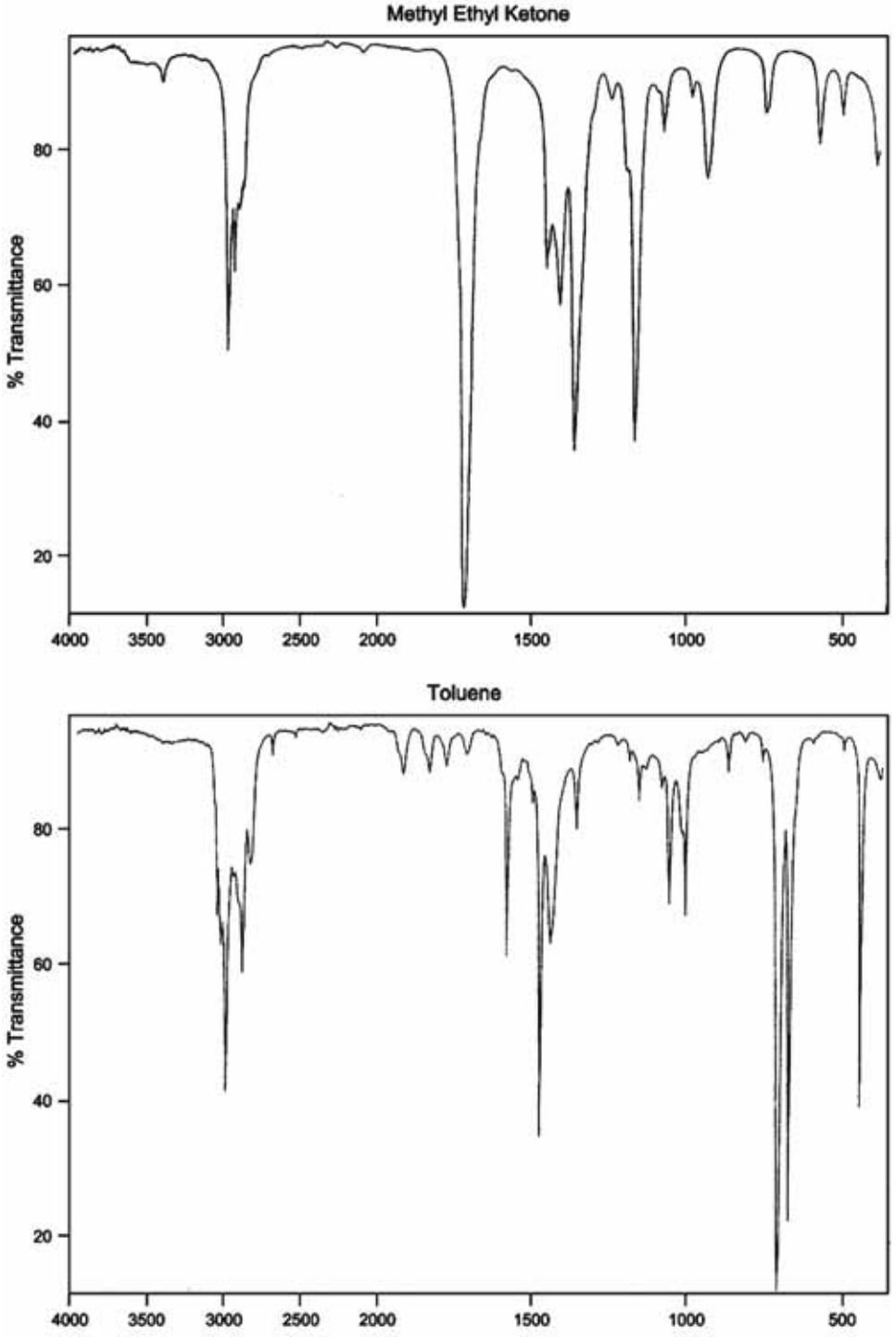

Fig. 4—Infrared spectra of methyl ethyl ketone (top) and toluene (bottom). Courtesy of Weldon Laboratories.

the strength of the absorption band. Indeed, not every vibration in a molecule is "infrared active," and there are various rules, called "selection rules," which can predict whether or not a particular vibration will actually absorb infrared radiation. While the selection rules are beyond the scope of this chapter, a simplification of them is that, for a particular vibration to absorb infrared light, and hence result in a band in the infrared spectrum, the vibration must produce a change in the molecule's dipole moment. A dipole moment arises from a partial separation of electric charge, and is related to the difference in electronegativity (the tendency of an atom to hold on to an electron) between the vibrating atoms. The dipole moment will not change during a symmetrical vibration of a symmetrical molecule, and no infrared band will result. If the change in dipole moment is small, the corresponding band will be weak. If it is large, the corresponding band will be strong. Many times, the intensity of a particular band is nearly as important as its frequency in assigning it to the correct structure or functional group.

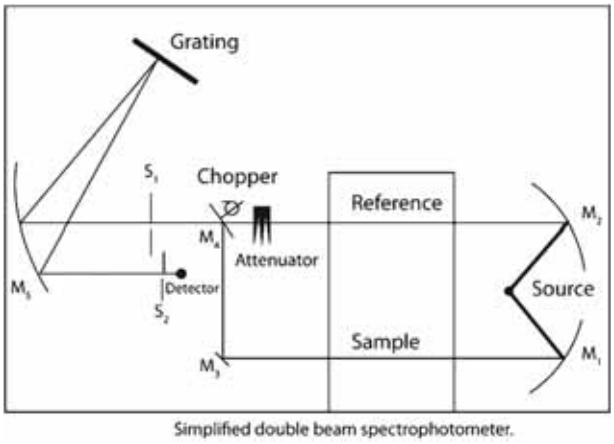

Fig. 5—Simplified double beam dispersive spectrometer.

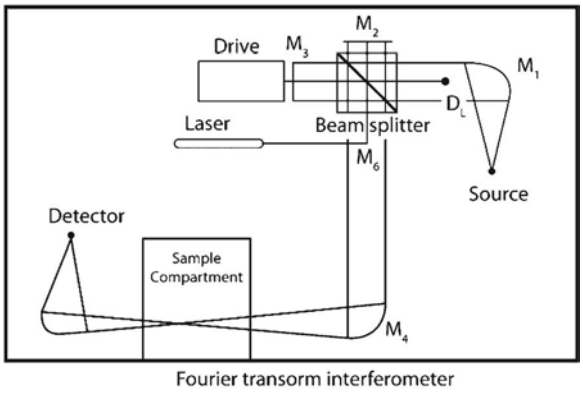

Fig. 6—Simplified fourier transform interferometer.

INSTRUMENTATION

There are two basic types of infrared spectrometers, dispersive and fourier transform. Dispersive instruments are seldom used anymore, but may still be available in some laboratories.

Dispersive Spectrometers

The development of dispersive spectrometers in the 1940s brought infrared spectroscopy into everyday use in the analytical laboratory. A simplified version of such an instrument is shown in Fig. 5. This design directs an infrared beam through the sample, and compares its intensity to that of a reference beam which bypasses the sample. The source of infrared light is an electrically heated wire or ceramic rod, which produces a continuum of infrared light spanning a wide range of frequencies. The two spherical mirrors, M_1 and M_2, direct this radiation along two paths, one of which goes through the sample (the sample beam), and one which bypasses the sample (the reference beam). The beams are "chopped" so that the detector alternately views one beam and then the other, such that the intensity of radiation in the sample beam, at any frequency, can be ratioed to that of the reference beam. The means of selecting a certain frequency of infrared light to examine is the monochromator, which consists of narrow slits (S_1 and S_2) and some type of dispersive element (either a prism or a diffraction grating).

For decades, dispersive instruments were employed for infrared spectroscopy. However, they tended to be slow (the author can well remember waiting 20 min for a spectrum to be completed), and detection limits were somewhat poor. Because of the loss of energy in the monochromator, certain accessories were often difficult to use, limiting the type of samples which could be run. Fourier transform units addressed these problems.

Fourier Transform Spectrometers

Nondispersive, or Fourier transform spectrometers, started becoming popular in the 1970s, and are by far the most common type in current use. Although they still require a source of infrared radiation and a detector, they do not disperse the radiation into individual frequencies, and hence do not require a monochromator. Instead, all of the infrared radiation is simultaneously passed through the sample, after having passed through an interferometer, as shown in Fig. 6.

As shown in Fig. 6, mirror M_1 collimates the energy from the IR source onto a beamsplitter, where the energy is divided between a stationary mirror M_2 and a moving mirror, M_3. The location of the moving mirror is tracked by a small helium neon laser, such that the difference in path length between the two beams is accurately known. The two beams are then recombined, and subsequently focused through the sample compartment and then on to the detector.

The output of the detector is not an infrared spectrum as we know it, but rather what is known as an interferogram (Fig. 7), which is basically a plot of detector response versus mirror travel, and contains all the information about constructive and destructive interference as a function of path length difference. It also contains all the spectral information concerning the sample, since the different frequencies of light will have been attenuated to one degree or another by the sample. In order to convert the abstract interferogram into the more commonly recognized infrared spectrum, a mathematical procedure known as the "Fourier transform" is employed by the instrument's computer. It took the advent of small, fast computers to bring the advantages of Fourier transform spectroscopy into the commercial laboratory.

Fourier transform infrared (FTIR) has some important advantages compared to dispersive IR, not the least of which is speed. Rather than taking several minutes to acquire a spectrum with a dispersive instrument, an FTIR can obtain a reasonably good spectrum in a few seconds.

Perhaps an even more important advantage of FTIR is sensitivity. Because there is no monochromator, all of the infrared radiation is passed through the sample at once, as opposed to a small amount at a time with a dispersive instrument. As a result, detection limits are roughly 10 to 100 times better with FTIR. As a consequence of this, certain types of samples can be run with FTIR which could not be run on a dispersive instrument. Furthermore, there are certain accessories which "waste" considerable amounts of energy, and were therefore difficult to use with dispersive instruments. These accessories, such as attenuated total reflectance attachments, are easily used with FTIR equipment, and greatly enhance the versatility of the technique.

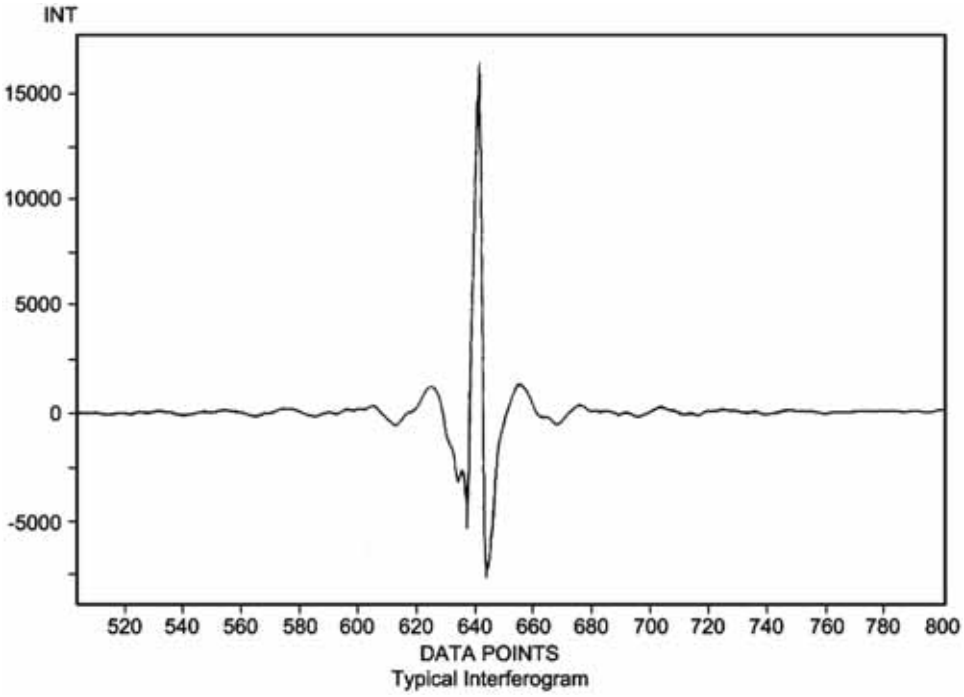

Fig. 7—Typical interferogram.

SAMPLE HANDLING

In the coatings industry, samples will usually be run in the form of a solid, although liquid samples will occasionally be encountered. There are several ways of obtaining spectra of both solids and liquids, and the choice will often depend on the type of question being asked of the analyst.

A common way of obtaining an infrared spectrum of a solid sample is by the use of the pressed pellet technique. Shavings or scrapings of the sample, such as a dried paint chip, are ground in a mortar and pestle, or by the use of a small mechanical grinding mill, along with a carrier which is essentially transparent to infrared radiation in the region desired. Two very common carriers are potassium bromide and sodium chloride powder. A ratio of roughly 1 mg of sample to 100 mg of potassium bromide is common. The ground sample is then placed in a special die and subjected to perhaps 10 000 lbs of pressure in a laboratory hydraulic press (inexpensive hand presses can also be used for the occasional sample). This fuses the sample into a relatively transparent pellet, which is then placed in the optical path of the spectrometer for analysis.

The pellet technique is extremely useful and can be used for a variety of samples. It works best for samples which are relatively hard and brittle, since they are easiest to grind. However, even relatively flexible samples can be run by this method, with enough patience. Sometimes the use of a few drops of a fast evaporating solvent, such as methylene chloride, during the grinding operation can help to break apart stubborn samples.

Often, especially in a laboratory dealing with failure analysis, or even for routine identification of paint samples from a jobsite, the samples will consist of more than one coat of paint. Care must be taken in the analysis of such samples. Usually, if the chips are thick enough, or if the various coats are of different colors, scrapings of the individual coats can be obtained with the use of a low power stereo microscope. However, if the samples are very small and/or brittle, this may not be possible.

Potassium bromide pellets can result in good quality spectra, require little sample, and can often be made in a few minutes. Since the sample as a whole is being analyzed, the spectrum will be representative of all of the ingredients in the sample, such as resins, cross-linkers, additives, and pigments. However, it must be kept in mind that potassium bromide and sodium chloride are hygroscopic. Even if stored in a desicator (a highly recommended practice), a small amount of moisture is almost inevitable. This will result in a band near 3300 cm^{-1}, and a much weaker one near 1620 cm^{-1}. Bands due to water are usually only a minor problem so long as one is cognizant of them.

A more intractable problem with pellet spectra is light scattering due to small, opaque particles dispersed in the pellet as a result of certain types of pigmentation in the coating. Some of the most difficult samples to analyze include zinc-rich primers and coatings pigmented with aluminum flake or carbon black. These particles act like minute mirrors, resulting in light scattering and severely sloping baselines.

Another way to obtain a transmission spectrum of a solid is by the mull technique. In this technique, a small amount of sample is dispersed by grinding it in a high purity mineral oil, such as Nujol. The paste is then spread across a salt plate, or sandwiched between two plates, and a transmission spectrum is obtained. Mulls do not suffer from the disadvantage of trace water, but the oils used will have bands of their own which will show up in the spectrum. Often, two different types of dispersing media are required to obtain spectra over the entire region of interest.

The pellet and mull techniques discussed above result in a spectrum of the bulk sample, since the infrared radiation is passing through the sample (a transmission spectrum). In many cases this is exactly what is needed to characterize the coating or solve the particular problem. However, sometimes it is desirable to obtain a spectrum of a surface, rather than of the bulk sample. This might be the case if one is concerned about the possibility of oil on the back of a delaminated coating, or of a surfactant exudate on the surface. The technique of choice for investigating these types of problems is attenuated total reflectance (ATR).

In ATR, the sample is pressed firmly against the face of a special crystal having a high index of refraction. The infrared radiation is focused into this crystal at such an angle that total internal reflection takes place at the sample/crystal interface, resulting in what is called a "standing wave." This standing wave penetrates and interacts with only the first few microns of the sample surface, resulting in a reflectance spectrum (as opposed to a transmission spectrum) which is very sensitive to the surface composition of the sample. The technique works best with soft, flexible samples which can be easily pressed against the face of the crystal, and can be difficult to do with hard, brittle samples, especially if they have uneven surfaces. The technique is described in more detail by Mirabella [3].

ATR is one of those "energy guzzling" techniques which has greatly benefited by the use of modern Fourier transform spectrometers. While ATR spectra have been collected for decades using traditional dispersive spectrometers, the sample size had to be relatively large, and the process was rather lengthy. With FTIR instruments, samples as small as 1mm^2 can be rapidly analyzed.

One of the most obvious advantages to the ATR technique is not having to grind the sample. Therefore, inconsistent particle size and light scattering effects are eliminated, as are bands due to moisture in the grinding medium. Soft, flexible samples, which would be difficult to grind, are usually routine for ATR. Furthermore, sometimes valuable information can be obtained from a surface spectrum which can not be obtained from a transmission spectrum.

There are, however, several disadvantages to ATR. For one thing, most collections of reference spectra are in transmission, not reflectance. While similar, there can also be substantial differences between the two types of spectra.

Furthermore, ATR spectra can be influenced by such things as the angle of the incident beam of infrared radiation, and the degree of contact between the sample and the crystal. The angle of incidence will affect the depth of penetration of the standing wave into the sample, and hence the appearance of the spectrum. The degree of contact between the sample and the crystal will also affect not only the depth of penetration, but also the strength of the signal. And, as mentioned above, brittle, wavy samples can be difficult to analyze. An additional complication is the possibility of a layering, or stratification, of the various ingredients in the coating. Although this does not happen often, it is possible that the ATR spectrum of the front of a sample will look different than the spectrum obtained from the back of the sample due to this stratification effect.

Although the above techniques are the most common ones for obtaining spectra of solid samples, they are certainly not the only ones. Diamond anvil cells can be used to produce very thin films of small samples for transmission spectroscopy, extremely thin films on very reflective surfaces can be investigated by specular reflectance techniques, and spectra can also be obtained of samples based on the acoustic vibrations they emit from the heating effects of the infrared beam (photoacoustic spectroscopy). FTIR microscopes even allow spectra to be obtained from samples as small as a few microns. Again, Mirabella's text [3] is recommended for additional information on these techniques.

While paint chips are a common staple of the modern analytical coatings laboratory, liquid samples are also routinely encountered. By far the simplest technique for obtaining a spectrum of a liquid sample, provided it does not contain water, is to spread a small amount on a salt plate (such as a potassium bromide crystal), allow the solvent to evaporate, place the crystal in the optical path of the instrument, and obtain a transmittance spectrum. This is generally referred to as a "cast film" spectrum. A similar technique is described in ASTM Standard Test Method for Infrared Identification of Vehicle Solids From Solvent-Reducible Paints (D2621).

If one wishes to obtain a spectrum which is representative of the sample as a whole, including solvent, a drop of sample may be sandwiched between two crystals and a so-called "neat" spectrum easily obtained. A neat spectrum is a very simple, rapid tool for quality control, allowing a spectral library to be easily made of all batches of a particular coating. If the sample contains fast evaporating solvents, the procedure should be accomplished as quickly as possible. Both fixed and variable path length cells can also be used to obtain spectra of liquid samples, but they are more difficult to clean.

Obtaining spectra of water based samples in the above fashions can be difficult, as water dissolves most of the common crystal materials, as well as contributing bands to the spectrum. Silver chloride discs, which are insoluble, can be used, but it is often difficult to acquire high quality spectra with them. Some of the suppliers of infrared equipment produce what are essentially thin "plastic" disposable cards to which liquid samples, both solvent based and water based, can be applied. One should, of course determine which bands the cards themselves contribute to the spectrum.

Sometimes it may be desirable to obtain an infrared spectrum of a liquid sample after first removing the pigment. Certain inorganic pigments have very strong, broad bands which can obscure much useful information from the resin components of the coating. The pigment can usually be removed by centrifugation, which is often made easier by diluting the sample with a volatile solvent such as acetone or methyl ethyl ketone. The clear supernatant contains the resin and solvent. A small drop of this is spread across a salt plate, the solvent removed, and a transmission spectrum obtained of the cast film.

The above technique does not work so well with latex samples, even if they are thinned with water. It may be possible to first break the emulsion by sonication, or to obtain a good separation using a very high-speed centrifuge. However, a technique which works well for many types of latex

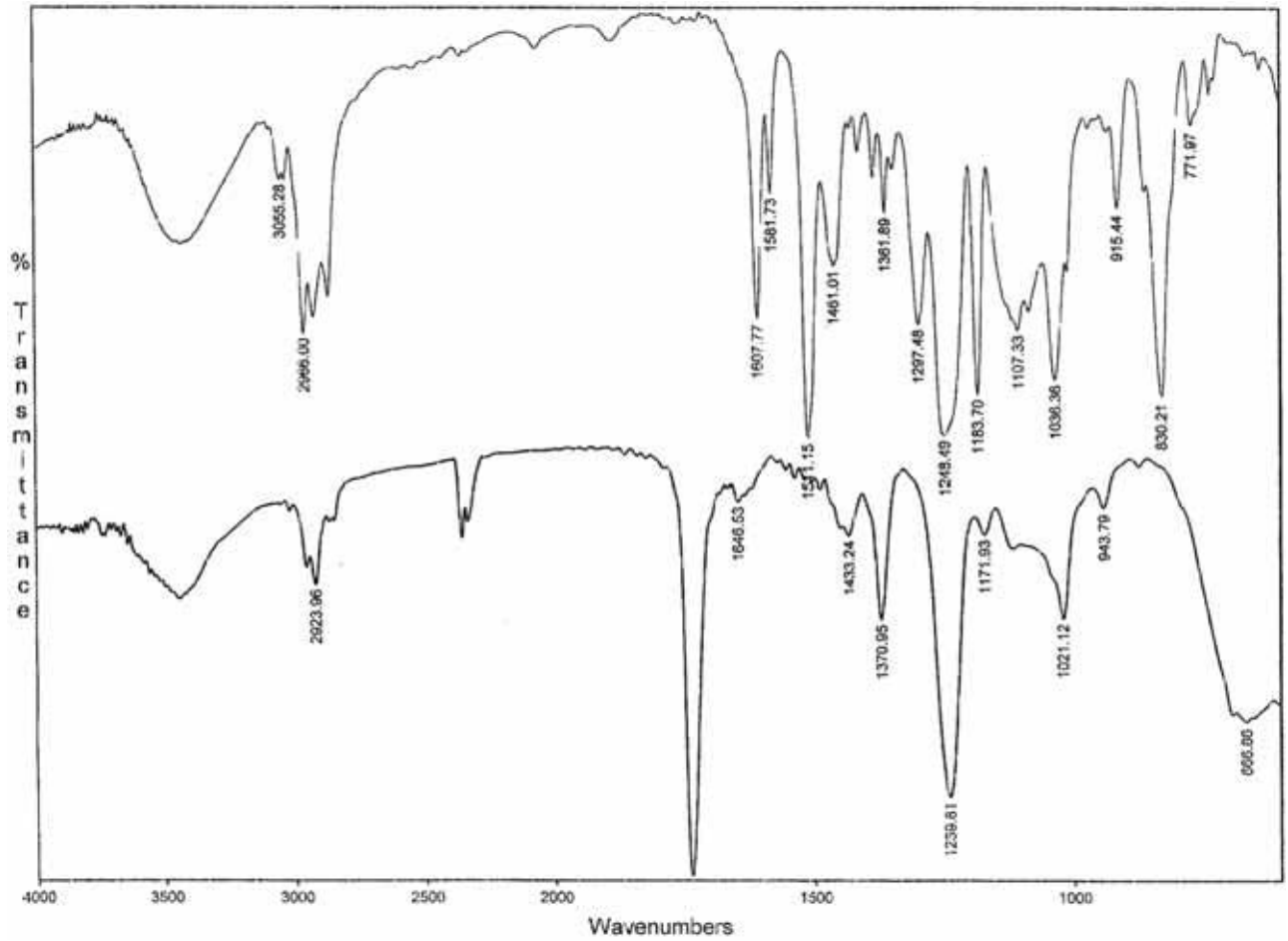

Fig. 8—Infrared spectra of epoxy (top) and a vinyl latex (bottom). Photograph courtesy of Weldon Laboratories.

samples is to first apply them to a glass slide and allow a brief time (perhaps 15–60 min) for the bulk of the water to evaporate. Usually, scrapings of the dried coating can be easily re-dissolved in a suitable organic solvent, which is then centrifuged as described above. The technique described by ASTM Standard Practice for Qualitative Identification of Polymers in Emulsion Paints (D3168) may also be useful in certain situations.

While the ATR technique previously described is usually associated with solid samples, liquid samples, especially if they are viscous, can often be applied directly to the ATR crystal. There are also other ATR accessories available from various vendors which allow liquid samples to be conveniently analyzed.

INTERPRETATION OF INFRARED SPECTRA

By far the most important component in the interpretation of infrared spectra is the experience of the spectroscopist. However, whether experienced or a novice, correlation tables are indispensable in the process of spectral interpretation. These tables list the locations of infrared bands due to the various functional groups, and often provide information into the relative intensities of the various bands. There are many texts which contain such tables [1,2], and the operational software which is supplied with many spectrometers contains digital versions. One simple but important rule is that, while the presence of an expected peak may indicate the presence of a certain functional group, the absence of an expected peak almost certainly indicates the absence of the functional group. It should also be kept in mind that a coating is not a pure compound, but can be a complicated mixture of several ingredients, each of which is contributing its own unique spectrum to the overall spectrum of the coating. Thus, although the Spectroscopy Atlas [1] is an indispensable reference collection, it is not a collection of spectra of paints and coatings, but rather of the raw materials which go into making them. ASTM D2621 also contains many useful reference spectra of alkyds, but again these spectra are of unpigmented resins.

In addition to digital correlation tables, there are also software packages which allow the spectrum of an unknown to be searched against a digital database. These databases provide a quick way to eliminate the majority of possibilities, and can often rapidly point the investigator in the right direction. Although there are various algorithms employed, the goal is to generate the best matches to the spectrum of the unknown. While sometimes very helpful, one should never blindly accept the result of such a computer search, since even matches with a high score of similarity can be wrong. One reason for an erroneous match is that most of the digital libraries only contain spectra of pure compounds or raw materials, whereas the actual coating sample may contain several such ingredients.

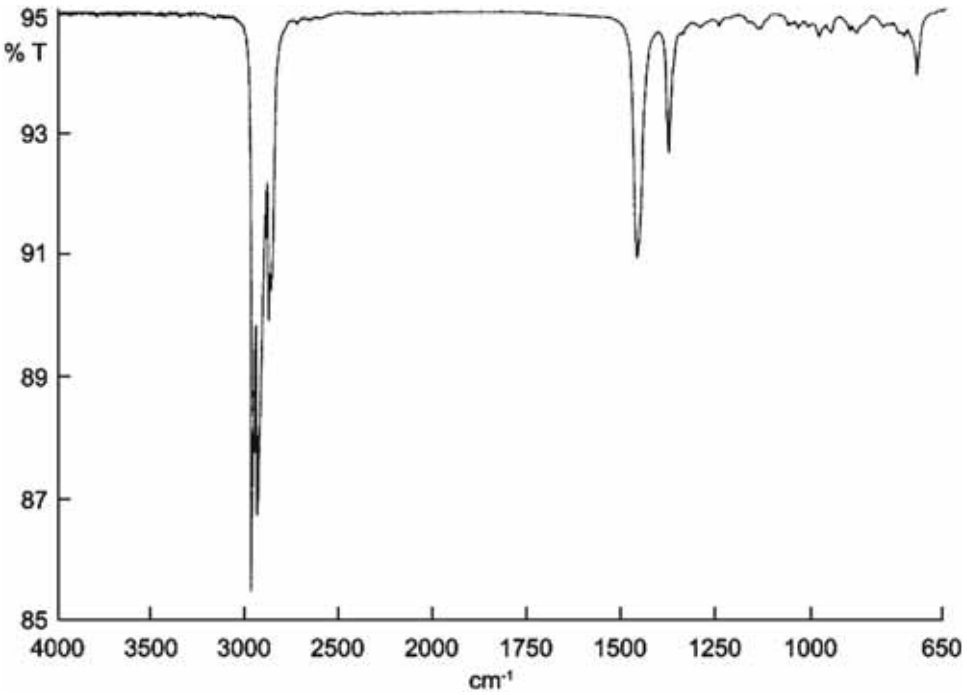

Fig. 9—Infrared spectrum of the layer found floating on top of paint.

Many instrument software packages contain some form of spectral subtraction, or "difference" spectroscopy capability. The developers of this software like to point out its ability to remove or subtract the spectral features of known or unwanted components, such that small amounts of hidden or "masked" materials can be identified. The procedures are usually interactive in nature, ideally allowing bands from known constituents to be eliminated to reveal the spectral features of a contaminant or other minor ingredient otherwise obscured.

While spectral subtraction may be very useful in certain circumstances, when applied to most coating problems the results should be viewed with a great deal of caution, especially when attempting to detect compounds at low concentrations. One of the major fallacies underlying the technique is the unspoken assumption that the spectral features of all of the ingredients in a complex, concentrated mixture are purely additive in nature, and that the presence of one compound does not interact with another and therefore affect the shape or locations of bands. Sometimes this is true and sometimes it is not.

APPLICATIONS OF INFRARED SPECTROSCOPY

There are many uses of infrared spectroscopy in the coatings laboratory, ranging from routine quality control procedures to sophisticated problem solving investigations.

Quality Control Applications

It is not unusual for a paint manufacturer to run some simple quality control checks on their incoming raw materials, such as the viscosity of a resin solution or the refractive index of a solvent. Some manufacturers extend this QC monitoring to include infrared spectra of certain raw materials, particularly resins. As discussed in the section on sample handling, it is a very easy matter to obtain a spectrum of a resin or resin solution, especially if it is unpigmented. Establishing acceptance or rejection criteria is another matter, however, and unless there is a substantial difference in appearance of the spectra, it would probably take some time until the manufacturer has acquired enough data to begin to establish these criteria for a particular product. Nevertheless, the analytical procedure is very simple and rapid, and if problems did crop up later with a certain product, one would then be able to examine the spectrum of the resin which went into that particular batch and compare it for deviations against other such resins which resulted in successful batches.

In addition to obtaining spectra of raw materials, some manufacturers also obtain spectra of the finished product. While an infrared spectrum of a finished paint sample will not be able to provide information about very slight differences in formulation, such as the type or level of an additive, it will certainly reveal any major errors very quickly. While not foolproof, it certainly provides another level of quality control over the more traditional approach of simply obtaining the sample's viscosity and weight per gallon. Indeed, a system for testing incoming raw materials, manufactured intermediates, and finished products has been developed [4].

Problem Solving Applications

The technical service department of any paint company is routinely faced with such problems as "what are these gel particles in the paint?," "why does this batch take so long to cure?," "why did this furniture lacquer crack?," or "why did this epoxy delaminate?." Infrared spectroscopy is an excellent tool in helping to solve these types of problems, and many more.

One of the simplest, most direct uses of infrared spectroscopy is in the generic identification of a coating. Many

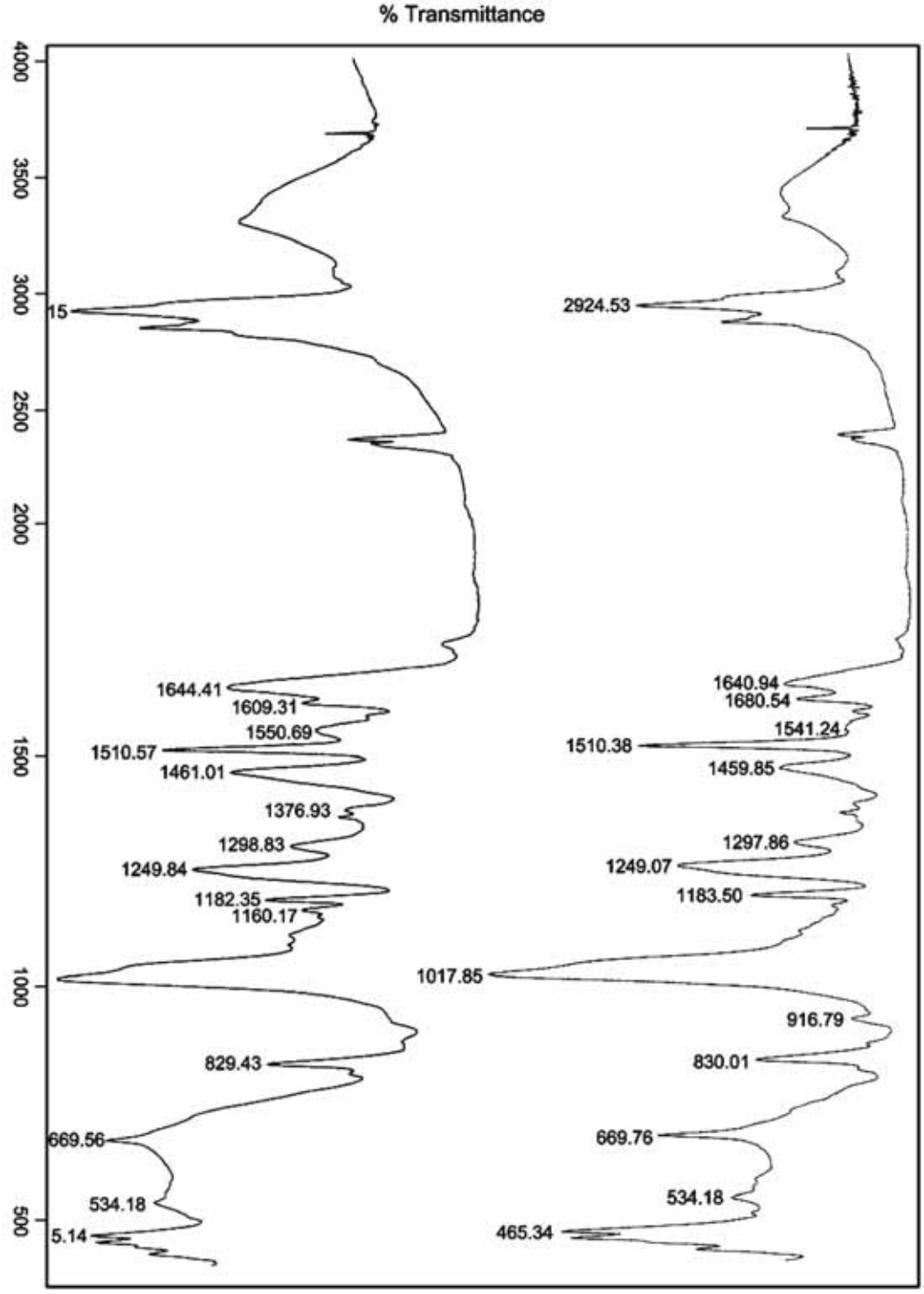

Fig. 10—Spectra of a polyamide epoxy at the proper mix ratio (top) and with an excess of Part B polyamide component (bottom). Note the difference in relative intensity of the 1640 and 1610 cm-1 bands. Courtesy of Weldon Laboratories.

times a coating does not perform as expected because the wrong paint was used, or perhaps because the "correct" paint was unknowingly applied to an existing coat of paint with which it is not compatible. Fig. 8 shows the spectra of an epoxy and a vinyl latex. It is obvious that the spectra are quite different. Therefore, if an epoxy was to have been used but an alkyd was applied instead, or if an epoxy was applied over an acrylic latex with which it is not compatible, such problems can be easily and rapidly detected by infrared spectroscopy.

Another common problem results when a component separates while standing in the shipping container. Fig. 9 shows the spectrum of such a "float" found on the surface of a paint can. Using a micropipette, the material was

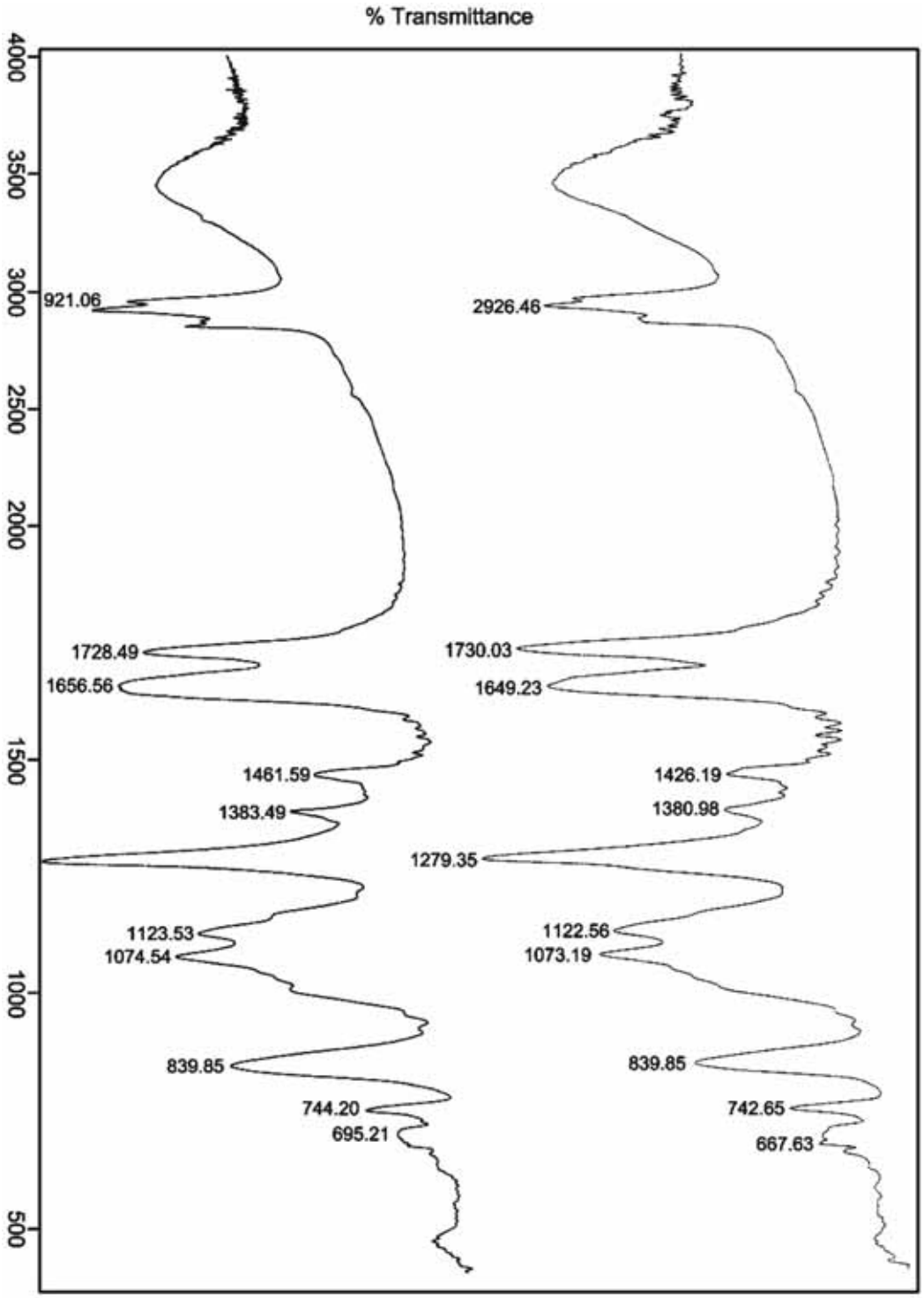

Fig. 11—Spectra of nitrocellulose lacquers with correct amount of plasticizer (top) and with inadequate plasticizer (bottom). Note the difference in relative intensity of the 1730 and 1650 cm-1 bands. Courtesy of Weldon Laboratories.

removed and spread onto a potassium bromide plate. Even though there was only a small amount of material, the spectrum was good enough to identify the layer as a mineral oil. This clue led to the discovery that a shipment of cans had not been adequately degreased prior to use [5].

A common failure mode involving two component coatings, such as a polyamide cured epoxy, is failure of

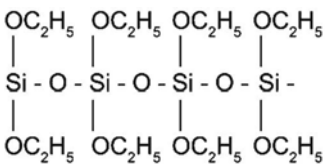

Fig. 12—Structure of ethyl silicate pre-polymer.

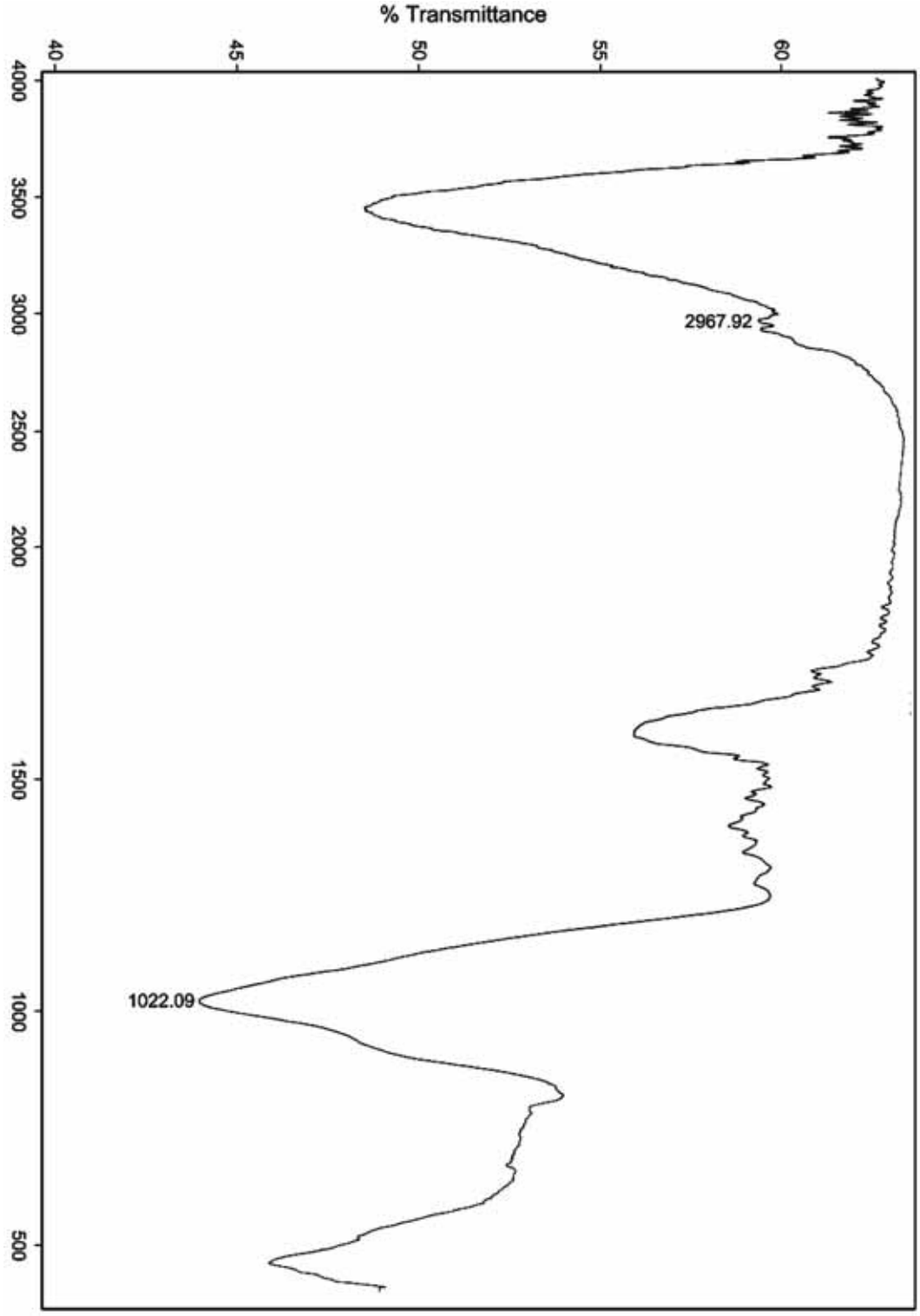

Fig. 13—Spectrum of an ethyl silicate inorganic zinc-rich primer. Courtesy of Weldon Laboratories.

the applicator to mix the Part A and Part B components in their proper ratio prior to applying the coating. One of these components will contain the epoxy resin, while the other will contain the polyamide curing agent. Failure to mix the components in their proper ratio, often 1:1 by volume, can result in coatings which do not cure properly and which have inferior physical and chemical properties. Infrared spectroscopy can often determine the approximate mix ratio of such a coating. The procedure involves preparing drawdowns in the laboratory of the coating at different mix ratios, and examining the spectra to see if there are any pairs of bands which change in relative intensity in a consistent fashion with changes in mix ratio. As Fig. 10 shows, as the mix ratio of this particular epoxy changes,

the relative intensities of several bands change, including those near 1640 and 1610 cm^{-1}. The 1640 band is due to the carbonyl vibration from the polyamide curing agent, while the 1610 band relates to the epoxy resin. It is not surprising that the ratio of these two bands changes as a function of mix ratio. The spectrum of the jobsite sample is then compared to the spectra of the standards to determine its approximate mix ratio.

It should be pointed out that, based on the author's experience, the above technique for obtaining mix ratios of two component coatings is only approximate, being good to only two significant figures. Not only is there an error associated with precisely mixing various volumes—or even weights—of viscous coatings to prepare the standards, and errors associated with reproducibly grinding the various samples for preparing potassium bromide pellets, but Beer's law, which relates the intensity of a band to the concentration of the species responsible for it, is only strictly valid for analytes in dilute solutions. This is certainly not the case in failure analysis, where the samples are at high concentrations in a solid matrix.

Another problem where infrared spectroscopy proved useful was that of a nitrocellulose furniture lacquer which developed long, hairline cracks. Nitrocellulose is an excellent resin for lacquers, as it dries quickly and produces a hard finish with good gloss and clarity. Unfortunately, it is also brittle, and usable coatings are only made by the addition of a plasticizer. Although there are many types of plasticizers available, one of the most common for nitrocellulose lacquers is a non-drying alkyd such as a coconut oil alkyd.

Fig. 11 shows the spectrum of a satisfactory lacquer which did not develop cracks, and the spectrum of the brittle, complaint batch. Nitrocellulose has a very strong, characteristic band in the infrared near 1650 cm^{-1}, while the band near 1730 cm^{-1} is due to the coconut oil plasticizer. In comparing the relative intensity of these two bands, it is apparent that the good lacquer contains a much greater ratio of plasticizer to nitrocellulose than does the brittle sample.

In certain cases, infrared spectroscopy can be a very effective tool in problems involving the lack of cure of a coating. Urethane coatings are very amenable to cure studies by infrared spectroscopy [6] since the isocyanate structure has a very distinctive band near 2300 cm^{-1} which disappears upon curing as the isocyanate reacts with the polyol component, or with atmospheric moisture.

Inorganic zinc-rich primers are another coating type whose cure can be monitored by infrared spectroscopy. Such primers consist of roughly 80 %–90 % zinc dust pigment dispersed in a binder which is usually based on a low molecular weight ethyl silicate (actually an ethoxy silicate), as shown in Fig. 12.

Because of their very high loading of zinc dust pigment, which is actually above the coating's critical pigment volume concentration (CPVC), the primers provide outstanding corrosion protection due to their galvanic effect (the zinc pigment will oxidize to protect the underlying steel, in much the same fashion as galvanizing). However, failures in the form of delamination or splitting of such primers have occurred when topcoated with such coatings as epoxies, often due to inadequate curing of the zinc-rich primers prior to topcoating [7].

Fig. 13 shows the infrared spectrum of a typical inorganic zinc-rich primer. It is dominated by a strong, broad band near 1000 cm^{-1} due to the stretching vibrations of the silicon-oxygen bonds in the inorganic polymer. There are also much weaker bands near 2900 cm^{-1} due to the carbon-hydrogen stretching vibrations of the ethoxy groups on the low molecular weight prepolymers. When these coatings cure they do so by reaction with atmospheric moisture, which cleaves the oxygen-silicon bond holding the ethoxy groups to the silicate backbone, resulting in the formation of silanol groups which subsequently condense with one another to form the high molecular weight, cured inorganic polymer. The bottom line is that as the coating cures the ethoxy groups are cleaved and evaporate in the form of ethyl alcohol. Since these groups are the only source of carbon-hydrogen functionality, as the coating cures the intensity of the carbon-hydrogen bands will decrease relative to the intensity of the silicon-oxygen band. This fact can be used to follow the degree of cure of such coatings [8], including the analysis of failed jobsite samples.

The above are just a few examples of the power of infrared spectroscopy as a problem solving tool in the coatings industry. Even if the technique does not unequivocally solve the particular problem at hand, it can often eliminate certain possibilities and point the investigator in the right direction.

SUMMARY

Infrared spectroscopy has been a powerful technique for organic and analytical chemists for over 50 years. Modern computer controlled fourier transform instruments and associated sampling accessories have made the technique increasingly rapid and sensitive, and have extended its capability to samples which would have been difficult if not virtually impossible to analyze many years ago. Although the technique has applications in quality control, its real utility is as a problem solving tool. Depending on the experience and ingenuity of the analyst, IR spectroscopy can provide solutions to a wide variety of problems concerning the composition of materials and systems in the coatings industry.

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Methods for Polymer Molecular Weight Measurement

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THE BINDERS USED IN COMMERCIAL COATINGS are organic polymers, the molecular weights of which greatly influence the properties of the final coating [1]. As a necessary result of the manufacturing processes, synthetic polymers are mixtures of compounds of similar molecular structure but varying molecular weight. For an exact understanding of the system, one must know the molecular weight and weight (or mole) fraction of each species, in other words, the molecular weight distribution. For many practical purposes, an average value of molecular weight suffices. The final cured paint film is a cross-linked system resembling a single massive molecule, where the concept of molecular weight has little meaning. Molecular weight determination is thus applied only to coating formulation ingredients.

Many procedures have been used to determine molecular weight. We limit our discussion to the most practical methods, for which commercial instrumentation is available at reasonable price. Archaic methods and research methods are omitted, as are those techniques which are suitable for determination only of low molecular weight compounds.

MOLECULAR WEIGHT DEFINITIONS

While the molecular weight of a single molecule is a simple concept, there are several ways to calculate the molecular weight of a mixture. The most useful values are number average molecular weight, $\overline{M}_n$ and weight average molecular weight, $\overline{M}_w$

$$\overline{M}_n = \frac{\sum_i n_i M_i}{\sum_i n_i}, \quad \overline{M}_w = \frac{\sum_i w_i M_i}{\sum_i w_i}$$

where M_i denotes the molecular weight of component i, n_i is the number of moles of component, i and w_i symbolizes the total weight of component i and is thus equal to $n_i M_i$. Weight average molecular weight is necessarily equal to or higher than number average molecular weight. A mixture of equal numbers of two molecules, one weighing 100 and the other weighing 1000, has a $\overline{M}_n$ of 550 and a $\overline{M}_w$ of 918. The polydispersity of this mixture, $\overline{M}_w / \overline{M}_n$, is 1.7. This indicates that most of the mass of the example mixture consists of higher molecular weight material, but that comparatively small molecules are also present. The higher the value of $\overline{M}_w / \overline{M}_n$, the broader is the distribution of weights of molecules in the sample. Two other measures of molecular weight have found acceptance because they can be directly measured by certain techniques: z-average molecular weight, $\overline{M}_z$, and viscosity average molecular weight, $\overline{M}_v$

$$\overline{M}_z = \frac{\sum_i w_i M_i^2}{\sum_i w_i M_i}, \quad \overline{M}_v = \left[\frac{\sum_i w_i M_i^a}{\sum_i w_i M_i}\right]^{1/a}$$

For the above-mentioned mixture of molecules of weight 100 and 1000, the z-average molecular weight is 991. Clearly, if the actual distribution of M_n, M_w, or M_z is known, the distributions and average values of the other two parameters may be calculated. The exponent a is obtained from the Mark–Houwink equation and is specific to polymer type and branching as well as the temperature and solvent of the measurement system [2].

Which molecular weight value is of greatest significance, number average, weight average, z-average, or viscosity average, depends upon the particular application of the polymer mixture. Knowledge of M_n and M_w is sufficient for most purposes. M_n is often critical to stoichiometry of curing reactions and controls some properties. For coatings, many of the properties of the final product are controlled by M_w, with M_w/M_n also playing an important part.

METHODS FOR DETERMINATION OF NUMBER AVERAGE MOLECULAR WEIGHT

End Group Analysis

Some polymers used in coatings have reactive end groups which participate in the curing reactions. Assuming that the degree of branching is known and that the end of each polymer chain has such a group, methods for routine quality control may be based on determination of end groups. Since each molecule has the same number of end groups, the result is a number-average molecular weight. Polyurethane raw materials fit this description, and "wet chemical" methods are well-established for rapid and accurate analysis of these compounds. Hydroxy-terminated compounds are analyzed by determination of hydroxyl number [ASTM Method for Testing Polyurethane Raw Materials: Determination of Hydroxyl Numbers of Polyols (D4274)]. Isocyanate-terminated prepolymers are analyzed by ASTM

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Test Methods for Polyurethane Raw Materials: Determination of Isocyanate Content of Aromatic Isocyanates (D5155). End group analysis is not limited to polyurethane raw materials. Amine or carboxylic acid functional groups may be determined by acid–base titration, often in nonaqueous solvents, but the parameters of solvent, titrant, and apparent pH at the end point must be worked out for each compound.

End groups may also be determined by spectroscopic methods, usually infrared, near infrared, and nuclear magnetic resonance spectrometry. For example, see ASTM Test Methods for Polyurethane Raw Materials: Determination of Primary Hydroxyl Contents of Polyether Polyols (D4273), and ASTM Standard Practice for Polyurethane Raw Materials: Determining Hydroxyl Number of Polyols by Near Infrared Spectroscopy (D6342).

Even polymers which are not usually thought of as possessing functional end groups may be analyzed. This is because molecules are often terminated by fragments of the catalyst which initiated the reaction. An example is polyacrylonitrile, which may be terminated by a sulfate or sulfonate group. The analyst familiar with the mechanism of polymerization can sometimes devise a way to measure molecular weight based on determination of these residues.

Accurate measurement of $\overline{M_n}$, by end group analysis is limited to polymers of molecular weight less than about 20 000, since the end group concentration is too low for precise measurement above this range.

Colligative Properties Analyses

$\overline{M_n}$ may be determined based on colligative properties, i.e., based on measuring changes in solvent properties which are due to the number of molecules dissolved. These properties include vapor pressure, freezing point, boiling point, and osmotic pressure. By derivation from fundamental equations [2–5], it can be shown that, at low concentration, the relationship between a colligative property and molecular weight reduces to

$$\overline{M_n} = \frac{KC}{\Delta X}$$

where K is a constant specific for the solvent, C is the weight/volume concentration of the polymer, and ΔX represents the observed change in the colligative property.

K is best determined experimentally, rather than calculated. For the best accuracy, several measurements are made so that the value of

$$\frac{\Delta T}{C}$$

can be extrapolated to find the limit at zero concentration. These techniques are more often used in research laboratories than for quality control purposes. Boiling point elevation and freezing point depression are rarely used for polymers since instrumentation suitable for observation of small temperature differences is not commercially available.

Small molecules have a disproportionate effect on the number average molecular weight. For example, the presence of 0.1 wt % water contaminating a 20 000 $\overline{M_n}$ polymer will result in return of a colligative property value of 9500 for $\overline{M_n}$. This effect is amplified as polymer $\overline{M_n}$ increases. Thus, moisture and solvent must be completely removed prior to analysis. Commercial polymers are first purified by extraction or by dissolution and precipitation to remove additives such as stabilizers and lubricants.

For determination of molecular weight by membrane osmometry, a solution of the test substance is separated from pure solvent by a semi-permeable membrane, i.e., a membrane which is permeable to low molecular weight solvent molecules but impermeable to molecules of the test substance. Because of the lowered activity of solvent containing the polymer, solvent molecules will tend to travel across the membrane from the pure solvent. The pressure which must be applied to the solution to equalize this flow is equivalent to the osmotic pressure. Because the change in osmotic pressure is dramatic compared to the small temperature changes observed with the other colligative property methods, membrane osmometry is useful for higher molecular weights, up to about $\overline{M_n} = 10^6$, although accuracy fades at the highest values. The technique cannot be used for low molecular weights because commercial membranes are not sufficiently selective: typically, manufacturers quote cutoff values of 5000 to 20 000 for various membranes, indicating that molecules below that value can permeate the membrane. This property can actually be an advantage in that it is not necessary to purify the polymer to remove low molecular weight additives: their concentration is quickly equalized on each side of the membrane, so that their presence does not affect the molecular weight value. Elevated temperatures may be used with less soluble polymers, but choice of membranes becomes limited as the temperature is increased and as less common solvents are selected.

Vapor pressure osmometry actually is unrelated to osmometry, consisting simply of the measurement of vapor pressure depression in order to determine molecular weight. Commercial instruments measure the vapor pressure indirectly: the vapor pressure difference between a dilute polymer solution and pure solvent is measured by monitoring the temperature difference between drops of each liquid in equilibrium with solvent vapor. Although in principle this is an absolute measurement, in practice these instruments are calibrated with standards of known $\overline{M_n}$. Vapor pressure osmometry complements membrane osmometry in that it is suitable for materials with $\overline{M_n}$ in the range below 20 000, with accuracy dropping off at higher molecular weights because of the very small temperature differences observed.

The experimental procedure is described in ASTM standard D2503 (Test Method for Relative Molecular Mass (Molecular Weight) of Hydrocarbons by Thermoelectric Measurement of Vapor Pressure), although the manufacturer's instructions for the specific apparatus must be considered definitive.

DETERMINATION OF WEIGHT AVERAGE MOLECULAR WEIGHT BY LIGHT SCATTERING

Unlike $\overline{M_n}$, $\overline{M_w}$ is not affected much by the presence of small quantities of low molecular weight impurities. The only common method for direct determination of $\overline{M_w}$ is light scattering. Light is scattered by polymer solutions in a manner which is well understood theoretically and which depends upon the size of the polymer molecules in solution. Classical measurement of $\overline{M_w}$ by light scattering

is described in an ASTM standard [Standard Test Method for Determination of Weight-Average Molecular Weight of Polymers by Light Scattering (D4001)]. Until the 1980s, this technique was performed only by specialists because of the attention to detail required for accurate values: (1) Traces of dust and other particles needed to be laboriously filtered from the solutions; (2) Measurements needed to be taken manually at several scattering angles.

Modern laser light sources make possible measurement of light scattered at angles less than ten degrees [2]. At such low angles, the equations defining the relation of M_w to scattered light are reduced such that measurement at a single fixed angle is sufficient. Simple measurement of a set of dilute solutions of the polymer to determine scattered light and the concentration dependance of the solution refractive index (RI) suffice to determine M_w. Instruments are also available which make measurements at multiple angles automatically, so that the radius of gyration as well as the molecular weight of the substance may be determined. With either the low-angle or multiple-angle instruments, operation is no more tedious than if a single measurement were made on each solution. An advantage of the laser light sources is that their intensity makes the sample size requirement lower, so that much less solution need be filtered free of particulates. If the instrument is designed so that the sample solution flows through the cell, interference from particulates is apparent as random sharp spikes, which may be corrected electronically before performing molecular weight calculations.

Light scattering is not suitable for analysis of polymers of M_w lower than about 20 000. However, the low-range sensitivity increases as the RI difference between solvent and polymer increases. Methods for molecular weight determination for light scattering are well described in the literature [2–5], but the instructions of the instrument manufacturer are most relevant.

SIZE EXCLUSION CHROMATOGRAPHY

Size exclusion chromatography (SEC) is a type of high performance liquid chromatography (HPLC) in which separation is made on the basis of the size of the molecules in solution [6, 7]. It is often called gel permeation chromatography (GPC) since the separating medium was historically a swollen polymer gel. The stationary phase is now most often a rigid packing containing pores of the same order as the size of the molecules in the sample. As a sample of a disperse polymer is pumped through the HPLC column, smaller molecules penetrate further into the stationary phase than do larger molecules, with the result that smaller molecules elute after those that are larger.

SEC determines size in solution versus standards. Because the interaction of a polymer with a solvent changes as a function of molecular weight, size in solution does not necessarily have a constant relationship to molecular weight over a large molecular weight range. Thus, SEC is not an absolute method for determining either M_n or M_w. In spite of this, it is today the most widely used procedure for determination of both. SEC has the very great advantage that the polymer need not be purified of additives, oligomers, and residual monomers before analysis. Indeed, SEC can sometimes be used for the determination of these components simultaneously with the characterization of the polymer itself.

SEC Instrumentation

SEC instrumentation consists of a basic HPLC system, including a constant volume pump, injector, column set, detector, and computerized data handling system. (HPLC is discussed in detail in Chapter 71.) The *pump* must be capable of delivering solvent with greater precision than is necessary for ordinary HPLC, preferably within 0.1 %. This is because the SEC calibration curve is semilogarithmic, with small differences in elution volume resulting in large differences in apparent molecular weight. Alternatively, some device may be used to continuously monitor flow rate so that experimental data may be replotted in terms of elution volume rather than elution time. Another approach is the use of an "internal standard," usually of very low molecular weight, to permit correction of experimental retention times. Such devices are rarely used nowadays, since the variations they introduce are of the same magnitude as the variations in flow of modern, well-maintained HPLC pumps. Control of the *temperature* of the system is very desirable since fluctuations in ambient laboratory temperature add variation to retention times and, more seriously, cause drift in the baseline of the refractive index detector. Ideally, the entire unit is encased in a constant temperature chamber. Unfortunately, these enclosures usually must be constructed by the user because of the limitations of commercial units. Many users make do with temperature control of only the column chamber and the detector, which suffices if the laboratory temperature remains reasonably constant.

SEC *columns* are usually filled with styrene/ divinylbenzene copolymer and are always purchased prepacked. Several instrument manufacturers supply columns of a uniform high performance. For increased resolution, more than one SEC column is used in series, with as many as four or five 30 cm columns being preferred by many operators. These may consist of diverse columns, each containing packing of a specific pore size, or each may contain packing of broad pore size distribution.

Various *detectors* are used in SEC. The most common is based on detection of changes in RI of the solvent as the solute elutes. This property is closely related to concentration and such a detector is suitable for any material with an RI which differs from that of the solvent. Commercial detectors are designed to minimize temperature fluctuation since RI is strongly dependent upon temperature. Temperature control can be either active (electronic heating devices) or passive (massive metal block surrounding the cell). The mass response of the refractive index detector varies by only a few percent with molecular weight, and it is thus assumed to be a linear concentration detector. It is well to check this assumption if analyses will straddle a broad molecular weight range, particularly at the low end of the range. Caution must be used in the analysis of copolymers since the RI of copolymers varies with composition.

Other detectors are used for special purposes. A UV absorbance detector, usually in series with an RI detector, is suitable for analysis of polymers with strong chromophores, such as those containing styrene, terephthalate, or bisphenol A groups. Infrared absorbance detectors are

used to track particular components of the polymer, but limitations in useful wavelengths and solvents prevent their general application. Another detector is based on "evaporative light scattering." In this instrument the solvent is evaporated as the SEC effluent passes through a gas stream. Any nonvolatile solute is converted to a fine aerosol, which is detected by its ability to scatter a light beam. The evaporative light scattering detector can be surprisingly sensitive, but the calibration curve is usually nonlinear. A detector based on differences in dielectric constant between solvent and solution has many of the advantages of the RI detector, but is not widely available. Caution must be used when applying any detector, since, if the response is not linearly proportional to concentration over a wide molecular weight range, calculation of molecular weight distribution from experimental data may result in serious errors.

Two specialized detectors are worthy of mention: A viscosity detector gives an instantaneous readout of the viscosity of the solution eluting from the chromatograph. It is used in series with an RI detector so that both concentration and viscosity of the eluent are determined, permitting estimation of intrinsic viscosity and hence molecular weight. There are low-angle and multiple-angle laser light scattering instruments designed for use as SEC detectors. Like the viscosity detectors, they are used together with a mass sensitive detector, usually an RI detector. A characteristic shared by both detectors is their intrinsically greater sensitivity as the M_w of the solute increases. Thus a trace of high polymer or undissolved material that might be undetected by refractive index appears as a major component to a light scattering detector. Whether or not this sensitivity is advantageous depends on the application. Viscosity and light-scattering detectors are commercially available, reasonably priced, and reliable. Still, they remain very much the province of the research and development laboratory. This is because the additional information which they provide is not essential for most practical applications. They are not used for routine analysis of paint components nor are they typically used by synthetic chemists.

An *autosampler* is a valuable accessory for GPC, more so than for other forms of HPLC. This is because the long analysis times typical of SEC and the rigorous calibration procedures make it difficult to attain high sample throughput unless the usual 8 h day can be extended. If the column and mobile phase are rarely changed so that calibration is required infrequently, manual injection is practical.

Calibration and Calculations

SEC is a relative technique which requires calibration with standards of known molecular weight. The calibration curve is semilogarithmic, with the SEC columns chosen such that retention volume is linearly proportional to the logarithm of molecular weight over a broad range. Calibration is greatly simplified if specially prepared standard materials of low polydispersity can be used.

The choice of standards is critical since the relationship of retention time to molecular weight varies with different polymers, even those in the same chemical family. Since it is the size of the solvated polymer rather than its molecular weight which determines elution volume, significantly different calibration curves are obtained from branched and linear molecules. The most easily obtainable standards are of polystyrene. Polystyrene has a higher molecular weight for the same chain length than do aliphatic polymers, so a polystyrene calibration curve will give high results for the molecular weight of many common polymers. The method of calibration should always be reported when SEC molecular weight values are given.

A universal calibration system has been devised based on the relationship between viscosity and SEC retention time, since each is a function of the size of the solvated polymer. When using universal calibration, standards and samples may be quite different polymers; it is only necessary that the Mark–Houwink coefficients for standards and samples be known. Of course, the Mark–Houwink coefficients must be known for the polymer in the particular SEC solvent at the temperature used. Obtaining these coefficients is not as demanding a task as preparing narrowly distributed standards of a new polymer, and universal calibration is used in many research laboratories.

Almost all analysts use computerized data systems for evaluation of SEC results. These systems are reasonably priced and aid the operator in all phases of data treatment, from calibration to determination of molecular weight averages to preparation of attractive graphs of molecular weight distribution. Caution must be used in their application; not all systems will give the same results as an intelligent operator performing manual calculations. The greatest difficulty is in mathematical representation of the calibration curve of retention time versus molecular weight. Use of high order polynomials to represent the calibration can introduce large errors compared to simply connecting the experimental data points.

SEC data for narrow molecular weight distributions must be corrected for dispersion contributed by the instrumentation. This correction is not significant for the broad molecular weight distributions typically found in coating raw materials. Band broadening corrections become more important if a molecular weight-sensitive detector is used, such as a viscometer or light-scattering instrument.

SEC procedures and calculations are described in ASTM Test Method for Molecular Weight Averages and Molecular Weight Distribution of Polystyrene by High Performance Size-Exclusion Chromatography (D5296).

Application of SEC

SEC may be performed with either aqueous or organic solvents. Nonaqueous systems are more reliable, but, of course, water-soluble compounds such as polyacrylates are more readily analyzed in aqueous solvents. Nonsize exclusion interactions between the column and sample are more common with aqueous systems. These undesirable interactions include adsorption and ion exclusion/ion retardation and can often be controlled by adding salts or a low percentage of organic solvent.

Elevated temperature is necessary for the analysis of some polymers because of their low solubility or because of the high viscosity of the solvents which they require. In general, this is not a consideration for the relatively low molecular weight polymers used in coatings raw materials.

SEC has long since spread from the specialized central laboratory to the laboratory of the synthetic and formulating chemist. Central analytical laboratories select the SEC column set and mobile phase for optimum resolution of a particular polymer and molecular weight range. Central laboratories also typically perform extensive calibration. Practice in synthesis laboratories is usually different, with a single system used in a comparative fashion for all analyses. Indeed, when SEC is used routinely by resin chemists to follow polymerization reactions, the fine details of calibration are typically ignored and molecular weight is estimated by simple comparison to polystyrene standards, either by visual estimation of "peak" molecular weight or by uncritical acceptance of the default computer-generated report. For most troubleshooting applications, it is enough to overlay the chromatograms of a "good" and a "bad" polymer in order to determine whether differences in molecular weight distribution contribute to a problem. In the case of a product which does not have a single smooth molecular weight distribution but rather consists of two or more discrete distributions, visual comparison of peaks is often more valuable than comparison of numerical values. To monitor a polymerization reaction, it may be enough to watch the gradual disappearance of the peaks due to monomers.

VISCOMETRY

Rheology of paint components is discussed in Chapter 33. We discuss here only viscosity measurement to determine molecular weight.

Solution viscometry is the method of determining molecular weight most suitable for routine quality control. The viscosity/concentration relationship of a polymer solution is a function of the chain length of the polymer, so viscosity can be used as a measure of molecular weight.

As with other methods, determination of true molecular weight by solution viscosity requires purification of the polymer and extrapolation to zero concentration of a series of ratios representing measured values. The zero intercept, representing the limit of the viscosity/concentration relation as zero concentration is approached, is the intrinsic viscosity, [η]. It is related to $\overline{M}_v$ by the relationship expressed in the Mark-Houwink equation

$$[\eta] = K\overline{M}_v^a$$

The constants for the Mark-Houwink equation must be determined experimentally using well-characterized polymer standards of narrow $\overline{M}_w/\overline{M}_n$. ($\overline{M}_w/\overline{M}_n$ must be small for valid calibration since $\overline{M}_v$ is numerically different than $\overline{M}_n$ or $\overline{M}_w$.)

Since viscosity is determined by the hydrodynamic volume of the polymer, the relationship with molecular weight is specific for the polymer, the solvent, the temperature, and, of course, the concentration. A relationship determined for a linear polymer will not be accurate if branched molecules are also present. This means that the constants in the Mark–Houwink equation change with various solvents and with polymers having various degrees of branching. Measurements are made at high dilution to minimize the effect of variables other than molecular size. Capillary viscometers, used to measure the solution flow rate at a specific pressure differential, are most generally suitable. Procedures for determination of solution viscosity are contained in ASTM Standard Practice for Dilute Solution Viscosity of Polymers (D2857), as well as in the other ASTM standards referenced in D2857.

It is unfortunately not possible to discuss this subject without defining a number of viscosity relationships.

Relative viscosity is the parameter which is actually measured when viscosity is determined. It is the ratio of efflux times for the polymer solution versus pure solvent:

$$\eta_{rel} = t/t_0$$

where t and t_0 are the efflux times for polymer solution and pure solvent, respectively. Reduced viscosity takes concentration into account:

$$\eta_{red} = \frac{t - t_0}{t_0 C}$$

where C represents the polymer concentration, usually in grams per 100 mL. Intrinsic viscosity is determined by plotting against concentration several values of reduced viscosity, extrapolating to obtain the intercept at zero concentration:

$$[\eta] = \lim_{C \to 0} \eta_{red}$$

where [η] represents intrinsic viscosity.

Some workers determine Mark-Houwink constants with unfractionated polymers of measured $\overline{M}_w$, thus relating viscosity to $\overline{M}_w$ rather than $\overline{M}_v$. This nonrigorous approach is viable because $\overline{M}_v$ is usually rather close to $\overline{M}_w$.

Solution viscosity is an excellent method for routine QC of relatively uniform polymers. A single analysis at a fixed concentration and temperature will indicate that the product falls into the stated molecular weight range. For example, ASTM Test Method for Determining Inherent Viscosity of Poly(Ethylene Terephthalate) (PET) by Glass Capillary Viscometer (D4603), describes a method for determining inherent viscosity (natural log of relative viscosity, divided by concentration). ASTM Test Method for Intrinsic Viscosity of Cellulose (D1795) describes a one-point procedure for estimating intrinsic viscosity. The results of such measurements can be related to molecular weight and are useful for predicting properties of different batches of well-understood commercial resins. Many polymer chemists routinely make one-point viscosity measurements to monitor synthesis experiments, reserving more sophisticated molecular weight measurements for products chosen for commercialization.

Melt viscosity, the viscosity of the pure polymer, is correlated with $\overline{M}_w$. Equations developed to relate degree of polymerization with melt viscosity use a temperature-dependent function which differs for each polymer system. As a practical matter, polymer melts are nonideal fluids, and their true viscosity can rarely be measured with simple equipment. Thus, melt viscosity is usually determined because of its relation to polymer processability, rather than as an estimate of $\overline{M}_w$. Melt viscosity is a useful tool for rapid comparison of suspect resin batches to controls, especially with resins which are suspected of changing during storage or when there are difficulties in analyzing by SEC. Pour point, the temperature at which the polymer begins to flow, is similarly related to molecular weight, and may be used to estimate it.

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X-Ray Analysis

A. Monroe Snider, Jr.,[1]

X-RAY DIFFRACTION (XRD) AND X-RAY FLUORES-cence spectrometry (XRFS) are powerful, well-established tools used by analytical chemists in many areas of technology. They have great utility in the coatings industry. In areas where they are applicable, they are frequently the quickest and easiest techniques available. XRD is convenient for the identification of diverse crystalline solids encountered in paint research laboratories and production plants. It is particularly well suited for use in the identification and quantitative analysis of crystalline pigments and extenders, either when they are alone or present in paste or paint. XRFS is useful as a stand-alone technique for elemental analysis and as a complementary tool for use with other analytical techniques. X-ray spectrometers typically can analyze all elements with an atomic number of about 11 (sodium) and higher, but some units can reach as low as atomic number 5 (boron). XRFS can span the concentration range from parts per million to high percentages for most elements in liquid or solid samples. Dedicated XRFS units, much lower in cost than scanning spectrometers, can be set up to detect and quantify one or a few specific elements. Portable XRFS units are available for field investigations. The present section summarizes the principles and methodology of XRD and XRFS.

RADIATION SAFETY

Although operation of modern X-ray instruments involves little risk to the operator when proper safety practice is followed, it is imperative that the operator knows and follows proper practice. Exposure to excessive quantities of X-ray radiation is injurious to health. Therefore, users should avoid exposing any part of their bodies, not only to the direct beam, but also to secondary or scattered radiation that occurs when an X-ray beam strikes or passes through any matter. It is strongly recommended that users check the degree of exposure by film badge or dosimeter carried on them. X-ray instruments should not be operated with safety interlocks, shielding, or other protective devices removed or deactivated. Before using the equipment, all persons designated or authorized to operate X-ray instrumentation or supervise its operation should have a full understanding of its nature and should also become familiar with established safe exposure factors by careful study of the American National Standards Institute Standard N43.2-2001, "Radiation Safety for X-ray Diffraction and Fluorescence Analysis Equipment" [1]. Inquiries should be made of state agencies about existing requirements.

X-RAY DIFFRACTION

Application

TYPES OF SAMPLES

XRD is widely used for the analysis of analytes that are crystalline or polycrystalline solids, i.e., solids comprised of atoms or ions arranged in a three-dimensional lattice pattern [2]. The sample may be totally crystalline or may contain one or more crystalline components interspersed with noncrystalline material. Common types of materials analyzed include pigments and extenders (alone, in grind pastes, in liquid and powder paints, or in dried paint chips), miscellaneous crystalline solids, and pretreatment on metal. XRD also has important uses in the study of amorphous materials such as polymers and inorganic glasses [2]. In the case of scanning X-ray diffractometers, a flat surface of the specimen must be presented to the X-ray beam.

Types of Information Provided

X-ray diffraction analysis permits qualitative and quantitative analysis of crystalline components. It can indicate the degree of crystallinity, crystallite orientation, and long-range order in polymers. Long-range order in liquids has also been studied [2].

Range of Concentrations

As a rule, crystalline components can be analyzed by routine methods at concentrations ranging from 100 % down to approximately 1 % or 2 %. However, the limit of detection varies widely with the identity of the analyte of interest, the number and identity of other components, the quality of the instrumentation used for analysis, and the instrument operating conditions. Analysis of components at concentrations as low as 0.01 % has been reported [3].

Physical Principles

XRD experiments are performed by irradiating a specimen of crystalline or polycrystalline material with a beam of X-rays of known wavelength and determining the angle 2θ between the incident beam and each diffracted beam of X-rays and measuring the intensity of each diffracted beam. Diffraction occurs only at discrete angles defined by the Bragg equation [2,4,5]

$$n\lambda = 2d\sin\theta$$

where

n = a positive integer (usually one),
λ = the wavelength of the X-rays used,

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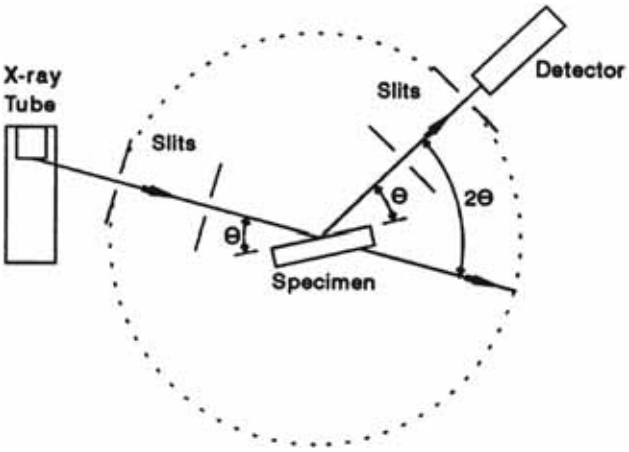

Fig. 1—X-ray diffraction goniometer system.

d = the distance between layers of atoms of a set of lattice planes, and
θ = the angle between the incident X-ray beam and the lattice plane [5].

The wavelength of the X-rays is determined by the choice of the x-ray tube target material, usually copper, and is thus known. The wavelength of copper K_α radiation, the principal component of X-rays from a copper target, is 1.541 84Å. It is common practice to use a crystal monochromator or absorption filter to prevent unwanted wavelengths of X-rays from contributing to the diffraction pattern. Angle θ is half of the diffraction angle 2θ that is determined experimentally. The distance between layers of atoms in a set can be calculated by using the Bragg equation. The distance, d, is determined by the diameter of atoms comprising the crystal, the three-dimensional arrangement of the atoms in the crystal, and the set of lattice planes in the crystal that produced the "reflection" of X-rays. Thus, crystallites of different compounds or different crystal modifications of a single compound will give different sets of d-spacings. Each crystalline phase will produce a unique XRD pattern that can be used as a "fingerprint" for identification. Detailed discussions of the Bragg equation and the physical basis of XRD are available in various treatises on XRD, such as the classic work by Klug and Alexander [2].

Analysis by XRD requires that a specimen be placed in the primary beam of a diffractometer and the diffraction angle and the intensity of each diffracted beam be measured.

Diffractometers use either an electronic detector or photographic film to indicate the position of the diffracted beams of X-rays. Most diffraction units in industrial laboratories today use an electronic detector, usually a proportional counter. Fig. 1 is a simplified diagram of a diffractometer.

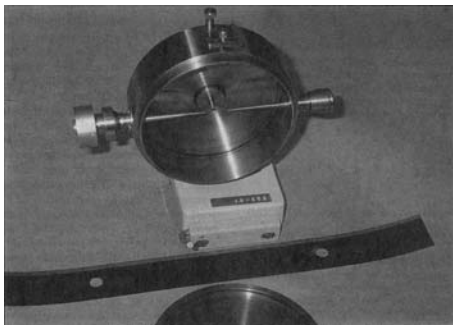

Fig. 3—Debye-Sherrer camera with the front cover removed displayed with a developed X-ray film.

The specimen is placed in a holder at the center of a goniometer system. The goniometer system is a mechanical device that permits accurate measurement of the angle between the primary beam and the surface of the specimen (θ) and the angle between the primary beam and the detector (2θ). A receiving slit and detector slowly sweep around an arc at a fixed distance from the center of the goniometer, facilitating determination of the intensity of X-rays scattered at each angle, 2θ, on the arc. While the detector moves through angle 2θ, the specimen rotates about the same axis through angle θ. A plot of the intensity of scattered radiation as a function of 2θ, a diffractogram or diffraction pattern, is thus produced. Fig. 2 shows the diffraction pattern of the rutile form of titanium dioxide.

A relatively new variation of the electronic detector is the position-sensitive detector (PSD) that uses an arc-shaped solid state detector to sense both the position and intensity of the diffracted radiation [6,7]. The PSD is stationary during data collection, but may be moved to different locations on the goniometer circle, as required, so that its surface can intercept X-rays at all 2θ positions of interest. Compared to a conventional scanning unit, a PSD can markedly shorten the time required to collect data.

The oldest method for collection of diffraction patterns, photographic, is still useful today, with the Debye-Sherrer camera being the most commonly used camera [2]. The Debye-Sherrer camera (Fig. 3) uses a strip of film mounted on the inner surface of a cylindrical holder. The film records XRD over a 2θ range of 360°. The d-spacing of arcs caused by exposure of the film to diffracted X-rays can be calculated from the position of the arcs on the film. Relative intensities of the diffracted x-ray beams can be evaluated by measuring the degree of darkening of the corresponding arcs on the film by an optical density

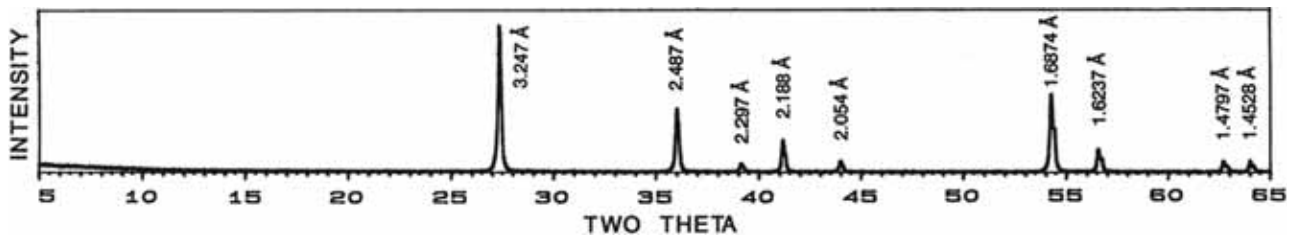

Fig. 2—X-ray diffraction pattern of rutile TiO_2 with the peaks labeled with the d-spacing of the corresponding sets of crystallographic planes.

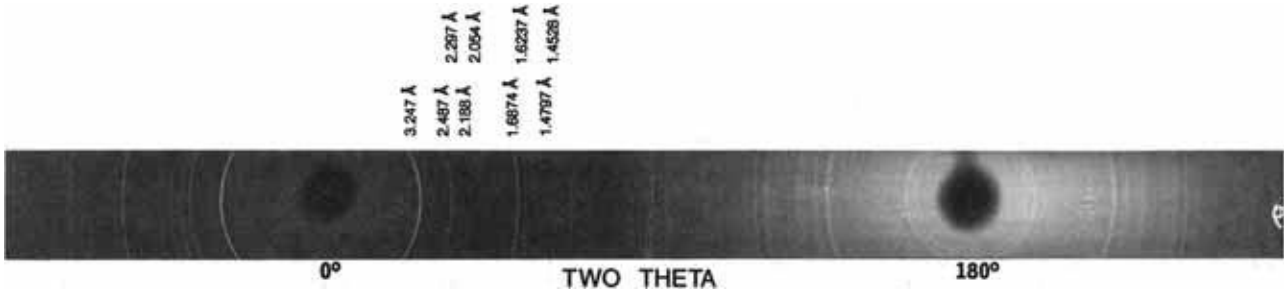

Fig. 4—Debye-Sherrer film with diffraction pattern of rutile TiO_2. The *d*-spacings of selected diffraction arcs are marked for comparison with peaks shown in Fig. 2.

measurement or by visual comparison to standards. Fig. 4 shows the diffraction pattern of rutile TiO_2 recorded with a Debye-Sherrer camera.

Experimental Procedure

SPECIMEN PREPARATION

Specimens for XRD can be any crystalline containing solid that can be mounted to permit collection of a diffraction pattern. For scanning diffraction units, the surface of the specimen should be flat and must be positioned in the focal plane of the instrument's x-ray optical system. The latter requirement can be met by mounting the specimen with its surface flush with the face of the specimen holder designed for the instrument. Failure to do so causes a systematic error in the observed 2θ angle and *d*-spacing of all peaks in the diffraction pattern. Fig. 5 shows a photograph of specimen holders used in some commercial XRDs.

Common types of samples encountered in the coatings industry and the recommended modes for mounting them in a scanning diffractometer are summarized in Table 1.

A Debye-Sherrer camera is useful for analysis in cases where there is too little sample for analysis using a conventional scanning diffraction unit. For small amounts of powder, the specimen is prepared by loading the powder into a thin-walled glass capillary or by mixing the powder with noncrystalline glue and rolling the mixture to form a filament. The capillary or filament after hardening is mounted in the center of the camera on a motor-driven rotating stub. Rotation presents a more nearly random orientation of crystallites to the incident X-ray beam. A single small chip or crystal may be analyzed by attaching it by glue to the end of a glass capillary and exposing it to X-rays in the Debye-Sherrer camera. In Fig. 3, the

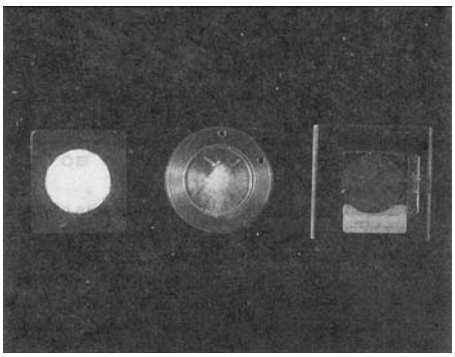

Fig. 5—Specimen holders for three common commercial X-ray diffractometers, each with a different type of specimen: (left) powder in a depression, (center) powder sprinkled on petroleum jelly smeared on a zero background quartz plate, and (right) disk cut from a drawdown of paint.

TABLE 1—Common samples and methods of mounting for XRD analysis

Sample	Method of Mounting
Powder	Put directly in holder or sprinkle on film of petroleum jelly or amorphous glue on zero background plate.
Liquid paint or grind paste	Prepare drawdown film on amorphous plastic sheet. Cut specimen to fit holder. Attach specimen to holder using double stick tape.
Paint chip	(1) Cut specimen to fit holder or (2) scrape off portion of interest, pulverize, and run as powder.
Paint on panel	Cut specimen to fit holder or cut to same dimensions as holder and run without holder.
Pretreatment on metal	Cut specimen to fit holder or cut to same dimensions as holder and run without holder.
Paint with low pigment content	(1) Remove pigment from paint by centrifugation. Dry and grind the pigment plug. Mix the ground material. Run as power.[a] (2) Pour paint into crucible, dry, ash, mix, and run as power.[b]
Suspension in liquid	Isolate solids from liquid by decantation, filtration, or centrifugation. Dry, grind, and mix. Run the resultant powder as described above.[a]
Sludge	(1) Run as drawdown on amorphous plastic sheet or (2) dry, grind, mix, and run as powder.
Gel	(1) Run as smear on plastic sheet, (2) dissolve organic portion with solvent and then handle sample as suspension, or (3) ash and handle as powder.[b]

[a]Caution: The composition of the plug may be heterogeneous because of stratification of the pigments during gravity settling or centrifuging.
[b]Caution: Ashing may change the crystalline composition of a sample by causing decomposition, vaporization, or transformation of phases that are present. Ashing at mild temperature, 450°C, in accordance with ASTM D4451 may prevent or lessen the amount of change of crystalline components [10].

capillary can be seen mounted along the axis at the center of the camera.

Specimens suitable for a Debye-Scherrer camera are equally suitable for XRD units equipped with a PSD and a holder for capillary specimens.

A thin-film XRD, a variation of the scanning diffractometer, can be extremely useful in the analysis of thin films of crystalline coating or contaminant on flat surfaces [8,9]. They also give better results than conventional diffractometers when only a small amount of powder is available. Thin film units operate exactly as conventional scanning diffractometers except the surface of the specimen is irradiated with X-rays at a fixed but selectable grazing angle. In comparison to conventional XRD analysis, this approach reduces the depth of penetration of the X-ray into the specimen and enhances the strength of the signal from crystalline components on the surface [9].

To achieve best results, some types of paint samples require modification before they are mounted in the specimen holder. Procedures such as ashing or centrifuging may be helpful.

Chips or drawdowns of paint that have low pigment-to-binder ratio may yield diffraction patterns with weak intensity and unacceptable signal-to-noise ratio. This problem is common with wood stains and varnishes. The resultant poor quality diffraction patterns may prevent complete and reliable identification of the crystalline constituents and may prevent accurate quantitative analysis. In such cases, the strength and quality of the diffraction pattern can be greatly improved if the organic binder is removed before the diffraction pattern is recorded. Low temperature (450°C) ashing in a muffle furnace can burn away the organic matrix of a sample, with minimum alteration of the chemical composition or crystalline phase of crystalline components. Details of the procedure are provided in ASTM Standard Test Method for Pigment Content of Paints by Low-Temperature Ashing (D4451) [10] and Standard Test Method for Pigment Content of Water-Emulsion Paints by Low-Temperature Ashing (D3723) [11]. Ashing leaves a powdery residue of crystalline material that will yield a much improved diffraction pattern, compared to one obtained directly from the original sample.

The analyst should be aware that the advantages of ashing are accompanied by potential risks. First, ashing, even at low temperature, destroys organic pigments and causes loss of water from hydrated components, if such materials are present. Second, unintended temperature excursions substantially above the intended 450°C may cause chemical changes such as the conversion of metal carbonates to metal oxides, metals to metal oxides, or lower oxides of metals to higher oxides. Analytical results from an overheated sample can be badly misleading.

In the case of liquid samples, high-speed centrifugation can be used to remove crystalline material, generally pigment, from the paint vehicle and concentrate it as a "plug" at the bottom of the centrifuge tube. Details of the procedure are given in ASTM Standard Test Method for Pigment Content of Solvent-Reducible Paints (D2371) [12] and ASTM Standard Method for Determination of the Pigment Content of Solvent-Reducible Paints by High-Speed Centrifuging (D2698) [13]. Noncrystalline particles, if present in the sample, are also incorporated into the plug. If a liquid sample has high viscosity, then pigment separation by centrifugation may be very slow, unless solvent is added to thin the sample. Separation of pigments by centrifugation can be helpful in the case of very low solids paints, such as electrodeposition paints, which tend to give poor quality drawdowns. Centrifugation must be done with sufficient speed and time to remove fine, low-density particles which, if present, tend to settle slowly. The following two cautions should be noted: (1) incompletely precipitated crystalline components will be underreported in the analysis of the resultant plug; (2) centrifugation causes stratification of the various particulate phases in the plug on the basis of density and particle size. The stratified, inhomogeneous plug must be fully retrieved, homogenized, and properly sampled to ensure that subsequent analyses are not biased. Material from the plug may be mounted using one of the methods listed in Table 1.

INSTRUMENT OPERATION CONDITIONS

Operating conditions should be based upon recommendations of the manufacturer of the XRD unit, requirements of the analytical method being used, and practical laboratory considerations. As a general rule, x-ray tubes with copper targets are commonly operated with a potential of about 40 to 45 kV and a filament current of about 35 to 45 mA. If other factors are held constant, then higher power settings can be used to shorten analysis time, lower the limit of detection, and improve signal-to-noise ratio, but at the expense of shortened tube life. For routine, general-purpose analysis by scanning XRD units, the common choice for slits used to define the dimensions of the x-ray beam illuminating the specimen and reaching the detector are as follows: 0.15° for the receiving slit and 1.0° for all other slits. If other factors are held constant, then larger slits can be used to shorten analysis time, lower the limit of detection, and improve signal-to-noise ratio, but at the expense of reduced ability to resolve closely spaced peaks. Conversely, smaller angle slits should be used if higher resolution is required. For analysis of unfamiliar paints, pigments, and other materials, diffraction patterns should be collected over a range scanning at least from 5 to 65° 2θ. Use of a shorter scan range may cause the omission of important diffraction peaks. However, scans spanning a narrow 2θ range may be satisfactory for routine tests based on peaks located within a chosen portion of the diffraction pattern. For routine qualitative and semiquantitative analysis, satisfactory results can be achieved with most step scanning instruments by progressing in steps of 0.02° 2θ, with 1.0 to 1.2 s per step. Longer count time may be required for quantitative analysis. In the case of older diffractometers with analog scanning motors, a scan rate of 1°/min is satisfactory for routine qualitative and semiquantitative analysis.

When analysis of minor components is required, especially in the case of samples that tend to yield weak XRD patterns with poor signal-to-noise ratio, the analyst may find it necessary to resort to the following instrument operating conditions to improve the diffraction pattern: (1) the widest slit set that can be used without producing unacceptable broadening of the diffraction peaks, (2) increased count time per step (slower scan rate), and (3) increased x-ray tube power output (increased filament current and acceleration potential). Of these three factors, wider slits

usually should be tried first, since this option will give the greatest benefit. Signal-to-noise ratio (S/N) will increase with the square root of the count time or scan time (e.g., quadrupling the time to collect a scan will double the S/N). Adding or averaging the signal collected during multiple scans is an alternative to—and generally preferable to—use of a single long scan. Increases in x-ray tube power should be done in accordance with the recommendations of the instrument manufacturer.

Qualitative Analysis

INTERPRETATION OF XRD PATTERNS

Preparation of d-Spacing Intensity Table—after the XRD pattern of a test sample is recorded, the analyst must obtain a list of all diffraction peaks with their *d*-spacing and relative intensity. The peaks should be listed in descending order of *d*-spacing. The intensity is expressed as a percentage of the strongest peak, taken as 100. If the x-ray unit lacks data processing capability, then the analyst must read the 2θ of each peak from the pattern and calculate the *d*-spacings from the 2θ values of the peaks using the Bragg equation. Likewise, the height of each peak must be measured by hand and the relative intensity determined. However, *d*-spacing-intensity tables can be obtained automatically from diffraction units equipped with even the most basic computer capabilities.

General Comments—identification of pigments, extenders, and other crystalline phases by XRD is accomplished by matching the peaks of the diffraction pattern of a sample under analysis with the sets of diffraction peaks exhibited by reference samples of known composition [2,14,15]. XRD provides no chemical information about a test sample other than the identification of each component that is achieved when a full match of its set of peaks is found. Either manual or computer-assisted searches can be done. Manual methods rely on the numerical comparison of *d*-spacings and intensities of diffraction peaks. Computer search methods also begin by matching the *d*-spacings of peaks, but rely in part on the analyst to do visual matching of peaks on a video screen.

Several instrument manufacturers and after-market suppliers offer excellent computerized search-match programs. Operated on personal computers, these programs use diffraction data files stored on compact disk or magnetic medium. The data files are available from the International Centre for Diffraction Data (ICDD), formerly known as the Joint Committee for Powder Diffraction Standards (JCPDS) [16]. Use of these computer programs and data files can greatly speed up qualitative analysis [17].

Manual Search Procedures—diffractionists who are experienced in the analysis of paints, but who do not have computerized search-match capabilities, usually employ a qualitative analysis procedure that has the two following steps. First, the diffraction pattern is inspected for the presence of sets of peaks that are characteristic of commonly used pigments and extenders, or other phases suspected of being present. Sets of peaks found in the pattern that are suspected of resulting from common components are compared to the peaks on reference diffraction patterns. The comparison may be done directly by comparing diffraction patterns or indirectly by comparing the *d*-spacings and relative intensities calculated from reference patterns. Partial or even complete identification of components may be achieved by this procedure. Second, peaks that were not identified by the first approach are subjected to a systematic search using compilations of XRD data, such as the Powder Diffraction File from ICDD. The first approach is most useful when the analyst, because of information available from other sources such as elemental analysis, the appearance, knowledge of the intended use of the paint, or experience, suspects the presence of certain crystalline components.

Fig. 6 shows the XRD patterns of several common paint pigments. For brevity, the term pigment will be used to mean both pigments and extenders. The pigments are readily distinguished from each other and from all other crystalline material by the positions of the peaks on the 2θ scale and by the relative intensities of the peaks. Since the diffraction pattern of each crystalline phase is unique, it may be used as a "fingerprint" for identification. The patterns in Fig. 6 were collected under identical conditions from powder specimens. Although some pigments originally gave patterns with greater peak heights, they are all plotted to about full scale for convenience.

Fig. 7 shows diffraction patterns of dried paint films from two test paints of known composition. Each crystalline component in the paint film contributes its own set of peaks to the pattern, with the position and relative intensity unaltered by the other components. Resin and other noncrystalline components produce only a broad, weak hump in the baseline. Some crystalline components of the two paints represented by Fig. 7 can be identified by comparison with the diffractograms of individual pigments in Fig. 6.

Table 2 lists 37 pigments and extenders commonly used in paint, with the *d*-spacings and relative intensities of their five most intense diffraction peaks. This table, compiled from the Powder Diffraction File of ICDD, may aid the paint analyst in identifying common components. The table may be helpful to analysts regardless of whether they have access to a computerized search-match system. The pigments are listed in order of the d-spacing of the strongest peak. The *d*-spacing of the strongest peak is listed in the first column on the left. The next four strongest peaks of each phase are listed in decreasing order of their *d*-spacings. The subscripts state the relative intensity of each peak rounded off to the nearest integer, with the intensity of the strongest peak taken as 10 and represented by "x."

To use Table 2 in a systematic manner in interpreting a diffraction pattern, the analyst determines the *d*-spacing of the peaks at the high d-spacing end of the pattern of the sample under analysis and then searches the first column of Table 2 for apparent matches. When an apparent match is found for a peak, the pattern of the test sample is inspected for the presence of the remainder of the peaks listed in the same row of Table 2. The absence from the pattern of any one of the listed peaks is usually sufficient reason for rejection of the suspected component. However, in the case of materials consisting of platelet or acicular-shaped particles such as clays, mica, and aluminum flake, preferred orientation may greatly decrease the intensity of some diffraction peaks compared to the intensities listed in Table 2. If the pattern of the test sample has all the peaks listed for the candidate component, then the analysts should note the ICDD file number listed for the phase in the last column. The file number may then be used to

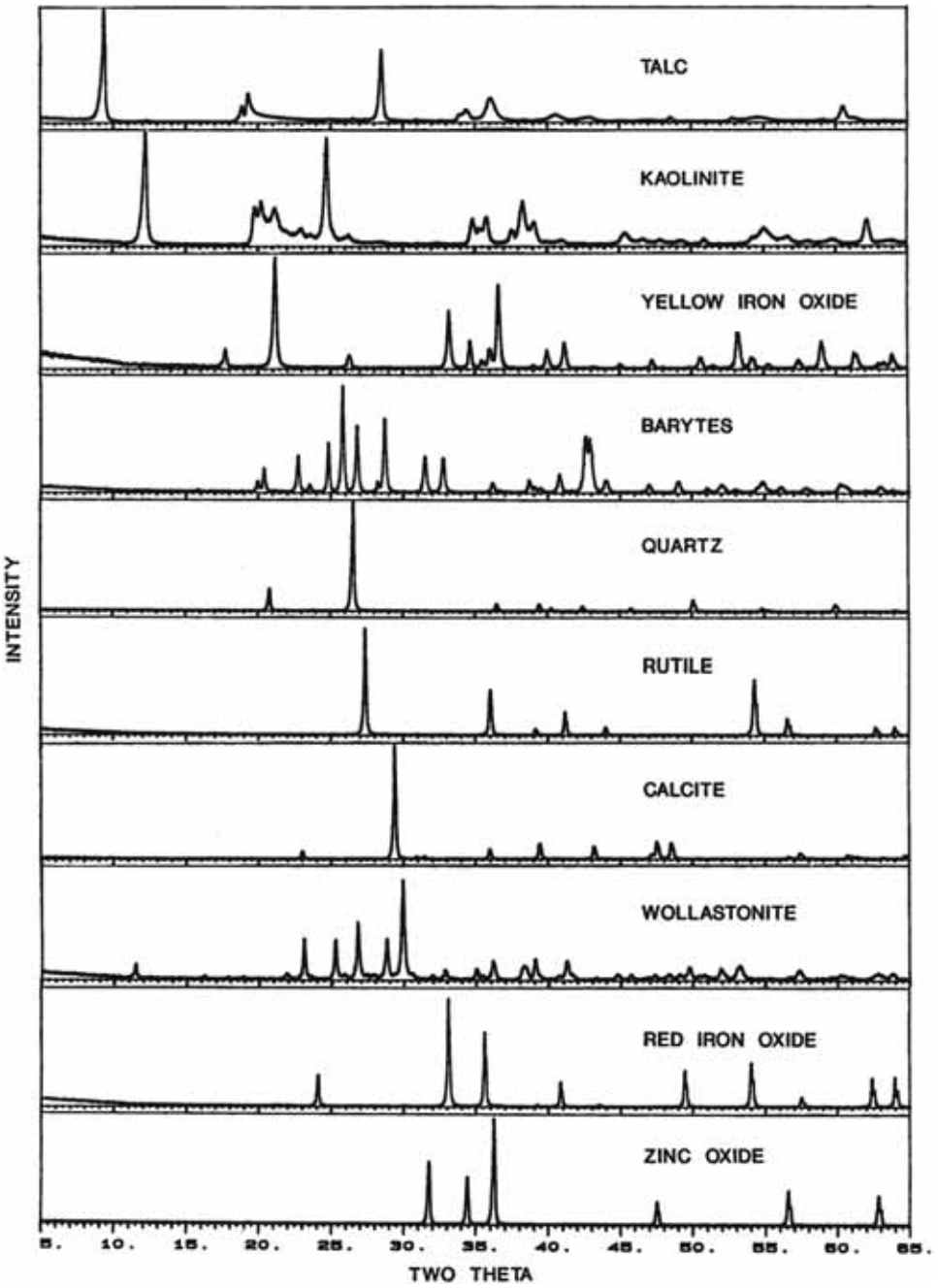

Fig. 6—X-ray diffraction patterns of several common pigments and extenders run as powder.

locate the full set of diffraction data provided by ICDD (and JCPDS) compilations. Using the ICDD data, all peaks attributed to the identified component may be marked on the pattern of the test sample. The identification process is then repeated with unassigned peaks in the pattern, working progressively from the peaks with the highest *d*-spacing, particularly the strongest ones, to the peaks with low *d*-spacing.

In an alternative use of Table 2, the analyst searches the list for crystalline phases that he suspects may be present in the test sample. If the strongest peaks listed in Table 2 for the suspected component are present in the diffraction pattern of the test sample, then the analyst notes the ICDD file number and proceeds as described in the previous paragraph.

Analysis of extraneous deposits may be aided by use of ASTM Standard Practices for Identification of Crystalline Compounds in Water-Formed Deposits by X-ray Diffraction (D934) [18]. Standard D934 contains a table, analogous to Table 2, which lists commonly encountered extraneous materials and their strongest diffraction peaks.

The printed Alphabetical Index and Search Manual and its computer compact disk counterparts from ICDD provide an alphabetical listing by name of a large collection of crystalline phases, their formula, the d-spacing and relative intensity of the three strongest peaks, and their ICDD file number. These references are an extremely useful starting point in peak identification when the analyst knows or suspects the presence of certain phases in the test sample. If the three strongest peaks of a candidate are found in the

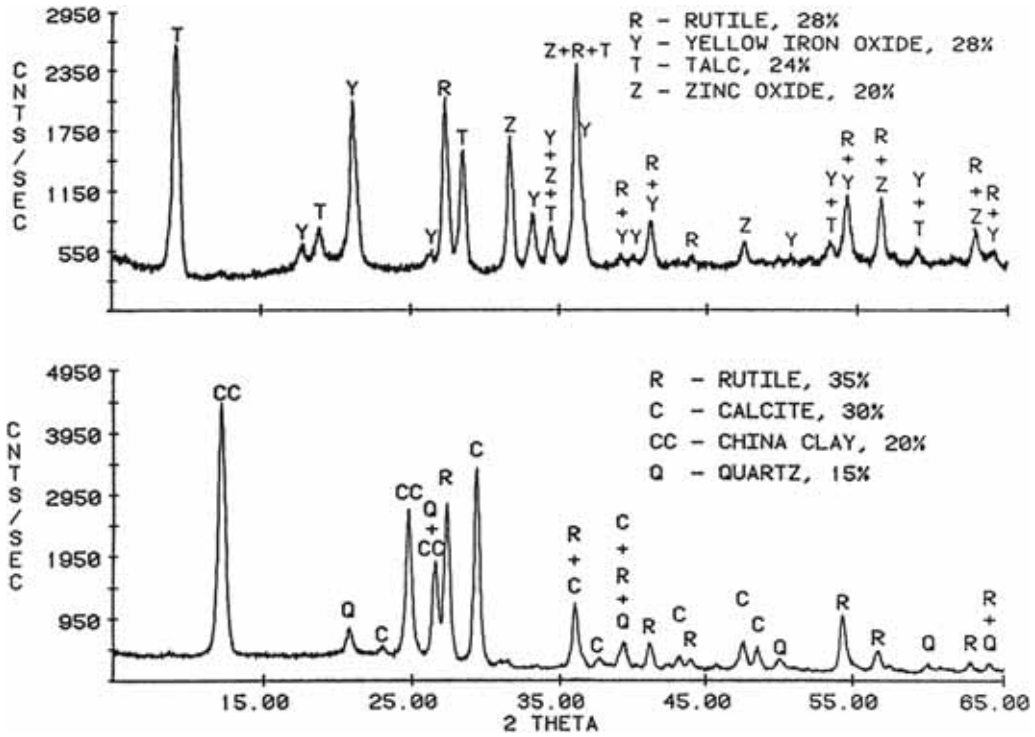

Fig. 7—X-ray diffraction patterns of drawdowns of two paints with the principal peaks of the constituent pigments labeled.

pattern of a test sample, then the analyst should use the ICDD file number to locate the full set of diffraction data on the compact disk or in the equivalent printed volumes. For positive identification, all peaks listed for the candidate in the full data set must be present with appropriate intensity in the test pattern. However, the weaker peaks of low-concentration components may be unobservable.

Peaks that remain unassigned after the information in Table 2 and the alphabetical files has been used must be identified by using the ICDD Powder Diffraction Files and either the Hanawalt or Fink search methods, or other search system. The Hanawalt method is based on the three strongest peaks in the diffraction pattern. The Fink method is based on the eight strongest diffraction peaks of each phase without use of intensity information. The Fink index lists each phase eight times with a cyclic permutation of the eight peaks. Instructions in the Hanawalt and Fink search manuals should be studied carefully before attempting to use either method [16]. Although still used in many laboratories, sale of Fink search manuals has been discontinued.

Computer-Assisted Searches—analysts using computer programs for qualitative analysis must rely on instruction from the program supplier. In general, computer search routines provide a list of crystalline phases that have peaks that match, or approximately match, the 2θ positions of the peaks of the test sample. Unfortunately, since more than one phase, perhaps many, may have peaks at the same 2θ position as the test sample, a search-match program may suggest phases that are not actually present. "False hits" are especially common when the diffraction pattern of the test sample is complex. Computer search routines provide the opportunity for the analyst to include information about elemental content of the sample and a variety of additional physical and chemical data to exclude implausible candidates. They also permit the analyst to adjust the *d*-spacing range spanning each test sample peak to account for possible error in the *d*-spacings of test sample and reference data. The analyst can widen the d-spacing "search window" to reduce the possibility of missing a component of the test sample or narrow the window to reduce the number of false hits. When analyzing "difficult samples," the analyst may benefit from comparing the results of searches run with a variety of search window widths. Some search routines assign a figure of merit to each candidate on the list based on similarity between data for the test sample and the candidate. Most programs permit the analyst to suggest candidates for consideration and exclude specific noncandidates. The analyst may draw on his knowledge of the origin of the sample and use Table 2, when appropriate, to suggest candidates. Visual matching on a video screen of the 2θ positions and intensities of peaks of candidate components, represented by "sticks," with the position and intensity of actual diffraction peaks is a key part of computer-assisted analysis. All candidate components with "extra" peaks not found in the diffraction pattern of the test sample must be rejected unless there is reason to suspect that preferred orientation of the particles can account for the discrepancy. (Preferred orientation exists when platelet or needle shaped crystalline particles are not randomly oriented, but instead have tended to align parallel to one another as may occur when liquid paint film dries, bulk powder is compressed in one direction during specimen preparation, or falling particles settle onto a surface.) Candidates with badly mismatched peak intensities must be considered suspect except when preferred orientation could account for the discrepancy. Relative intensities are especially unreliable for mineral pigments, especially clays, mica, and silica. Complete analysis ideally requires that a set of crystalline components can be identified that can account for all peaks, both their position and intensity, observed in the diffraction pattern of the test

TABLE 2—Strongest XRD peaks of common pigments and extenders for paint

d-Value and Intensity[a]					Name	Formula	ICDD File Numbers
17.6_x	9.5_5	4.49_8	3.58_4	1.504_6	Bentonite[b]	$Na_{0.3}(AlMg)_2Si_4O_{,10}(OH)_2.H_2O$	12-219
10.1_x	4.49_9	3.66_6	3.36_x	2.565_9	Mica[b]	$KAl_2Si_3AlO_{,10}(OH)_2$	7-25
9.34_x	4.66_9	3.116_x	2.476_7	4.870_4	Talc[b]	$Mg_3Si_4O_{,10}(OH)_2$	13-558
7.63_x	4.283_x	3.065_8	2.873_5	2.685_4	Gypsum	$CaSO_4.2H_2O$	33-311
7.36_x	4.56_5	3.66_8	2.451_7	1.531_7	Chrysotile-20rcl	$Mg_3Si_20_5(0H)_4$	25-645
7.31_x	4.57_5	3.65_7	2.27_3	1.535_5	Chrysotile-2Mcl	$Mg_3Si_20_5(0H)_4$	31-808
7.17_x	4.366_6	4.186_5	3.579_8	2.495_5	Kaolinite[b]	$Al_2Si_20_5(0H)_4$	14-164
4.568_x	9.12_6	4.410_2	3.460_3	2.853_7	Zinc phosphate[b]	$Zn_3(PO_4)_2.H_2O$	37-465
4.18_x	2.69_4	2.45_5	2.19_2	1.72_2	Yellow iton oxide	FeO(OH)	29-713
4.04_x	3.136_1	2.841_1	2.487_1	2.486_0	Crystobalite	SiO_2	39-1425
3.52_x	2.370_2	1.892_4	1.700_2	1.667_2	Anatase	TiO_2	21-1272
3.445_x	3.319_7	3.103_x	2.121_8	2.106_8	Barium sulfate	$BaSO_4$	24-1035
3.39_x	6.32_2	2.986_8	2.840_4	2.269_2	Chrome orange	$Pb_2(OH)_2CrO_4$	8-437
3.38_x	2.903_5	2.787_5	2.632_3	1.755_3	Red lead	Pb_3O_4	8-19
3.342_x	4.257_2	2.457_1	1.818_1	1.542_1	Quartz	SiO_2	33-1161
3.31_x	3.129_8	2.926_9	1.903_8	1.7642_5	Zinc sulfide	ZnS	36-1450
3.28_x	4.96_3	4.38_3	3.48_6	3.03_7	Lead chromate	$PbCrO_4$	8-209
3.260_x	9.79_6	5.771_2	4.251_2	3.130_5	Lead oxide sulfate hydrate	$Pb_4O_3SO_4.H_2O$	29-781
3.26_x	3.452_8	3.006_6	2.543_6	2.3085	Strontium chromate	$SrCrO_4$	15-356
3.247_x	2.487_5	2.188_3	1.687_6	1.624_2	Rutile	TiO_2	21-1276
3.22_x	4.89_3	4.72_3	3.12_x	2.668_2	Moly orange	$Pb(Cr_{19}Mo_{11})O_4$	19-685
3.16_x	3.583_8	3.367_6	2.068_6	1.761_5	Cadmium yellow	CdS	6-314
3.142_x	4.571_2	3.494_3	3.174_2	3.188_2	Antomony oxide	Sb_2O_3	11-689
3.03_x	3.852_3	2.284_2	2.094_3	1.8726_3	Calcite	$CaCO_3$	24-27
2.886_x	2.192_3	2.015_2	1.804_2	1.786_3	Dolomite	$CaMg(CO_3)_2$	11-78
2.700_x	3.684_3	2.519_7	1.8406	1.6941	Red iron oxide	Fe_2O_3	33-664
2.666_x	3.663_8	2.480_x	2.176_4	1.672_9	Chrome oxide green	Cr_2O_3	6-504
2.623_x	4.47_6	4.25_6	3.61_9	3.29_9	Lead carbonate	$Pb_3(CO_3)_2(OH)_2$	13-131
2.609_x	7.02_9	3.31_9	3.08_9	2.896_7	Zinc yellow	$K_2Zn_4(CrO_4)_2.3H_2O$	8-202
2.5503_x	2.8766_3	2.3846_7	1.6361_4	1.4376_4	Copper chromium oxide	$CuCr_2O_4$	34-424
2.543_x	2.984_4	2.109_2	1.624_3	1.491_4	Tan iron oxide	$ZnFe_2O_4$	22-1012
2.532_x	2.967_3	2.90993_2	1.6158_3	1.4845_4	Black iron oxide	Fe_3O_4	19-629
2.476_x	2.814_6	2.603_4	1.625_3	1.477_3	Zinc oxide	ZnO	36-1451
2.443_x	2.864_7	2.026_2	1.5602_4	1.424_4	Cobalt aluminum oxide	$CoAl_2O_4$	10-458
2.338_x	2.024_5	1.431_2	1.221_2	0.9289_1	Aluminum metal[b]	Al	4-787
2.091_x	2.473_5	2.308_4	1.687_3	1.342_3	Zinc metal[b]	Zn	4-831

[a]Subscripts represent the relative intensity (rounded to the nearest integer) of the diffraction peaks of a phase, with the most intense peak taken as 10 and represented by "x."
[b]Particles of this material frequently exhibit preferred orientation in paint films, thus causing the observed relative intensities to differ from intensities listed in this table.

sample. In reality, whether the search-match is done manually or with the aid of a computer, it may not be possible to identify all peaks in a diffraction pattern and therefore not all crystalline components in the corresponding sample.

Although computer search-match programs are valuable aides for interpretation of diffraction patterns, common programs that are presently available may suggest the presence of components that are absent and fail to show the presence of phases that are truly present. Therefore, results thus obtained should always be verified and, if necessary, corrected by the analyst.

Limitations—Qualitative analysis by XRD has four principal limitations. First, only crystalline phases can be identified. Noncrystalline components must be identified by other means. Second, different substances can be encountered that have similar diffraction patterns, at least in part. Misidentification can occur when the sample contains several crystalline phases producing a complex pattern and diffraction is the only technique being used for analysis. Examples of potentially confusing coincidences or near coincidences are the strongest peaks of red lead, quartz, and zinc sulfide, with *d*-spacings of 3.38, 3.34, and 3.31 Å, respectively, a secondary peak of barytes at 3.319 Å, and a strong peak of mica at 3.36 Å. The 3.247 Å peak of rutile may conceal the 3.260 Å peak of strontium chromate. The 3.445 Å peak of barytes may conceal the 3.452 Å peak of strontium chromate. Many other similar peaks can be found for common pigments in Table 2. Third, low concentration components may be overlooked, especially if they scatter x-rays weakly or if their strongest peaks are overlapped by peaks of major components. For example, small amounts of zinc oxide may be overlooked if its strongest peak at 2.476 Å is overlapped by a peak of rutile at 2.487 Å or talc at 2.476 Å, particularly when the latter phases are major components. Fourth, the relative intensity of peaks in the pattern of certain phases may differ significantly depending on their history, the degree of preferred orientation of the particles, the specimen preparation techniques, and the instrument used to collect the pattern. Anomalies arise especially from pigments that consist of platelet or acicular particles that exhibit preferred orientation and from clays that have been changed by chemical, thermal, or mechanical processing.

The analyst should not rely upon XRD alone when analyzing unfamiliar samples. Information from all sources should be reconciled before XRD results are reported. The speed and reliability of analyses can be greatly improved if information is available about what elements and functional groups are present in the sample. XRFS and optical emission spectroscopy are convenient techniques for qualitative elemental analysis. Plasma emission, atomic fluorescence, and atomic absorption spectrometry can also be used for elemental analysis. Infrared spectroscopy can provide functional group information and, through spectral matching, may provide independent corroboration of pigment identification. Elemental analysis data are particularly useful in detecting and identifying crystalline components that are present at low concentrations. Elemental analysis and infrared spectroscopy results are useful for identifying noncrystalline pigments. Color, solubility in selected liquids, chemical reactivity, magnetic properties, or response to ashing can sometimes give clues to the presence or absence of suspected components.

Identification of crystalline materials, especially complex mixtures of crystalline materials, is more difficult if the analyte concentrations are low and the XRD pattern is weak and "noisy." In such cases it may be necessary to collect a new diffraction pattern under instrument operation conditions that improve the signal-to-noise ratio (refer to the "Instrument Operation Conditions" section) and then interpret the improved pattern. Complete and reliable analysis may also require that the analyst prepare a fresh test specimen in a manner that increases the amount of crystalline material relative to noncrystalline material (refer to the "Specimen Preparation section").

Quantitative Analysis

THEORY OF QUANTITATION

Quantitative analysis by XRD is based on the principle that the intensity of a diffraction pattern of a crystalline substance is directly proportional to the concentration of that substance in the sample. This relationship and several complicating factors are discussed in detail by Klug and Alexander [2]. The intensity of X-rays diffracted from a given set of crystallographic planes in component *i* in a mixture is given by the equation

$$I_1 = K_i' f_i / \mu$$

where

I_i = the intensity of diffracted X-rays,
K_i' = a constant that depends on both the nature of component *i* and the characteristics of the apparatus,
fi = the volume fraction of component *i*, and
μ = the absorption coefficient of the mixture.

Since the absolute intensity I_i is influenced by the composition of the matrix, the absolute concentration of an analyte cannot be determined unless a calibration curve is established with an internal standard.

However, using the "matrix flushing" method described by Chung, the *relative* concentration of crystalline components in a mixture can be determined without knowledge of the absorption coefficient [19,20]. This approach is based on the fact that all components under analysis are in the same matrix and thus are equally influenced by x-ray absorption. The intensity of x-rays diffracted from a component *i* is given by the equation

$$I_i = k_i X_i$$

where

k_i = a constant that depends on component *i* and the apparatus, and
X_i = the mole fraction of component *i*.

The ratio of the intensity of X-rays diffracted from two components *i* and *R* is given by the equation

$$\frac{I_i}{I_R} = \frac{k_i}{k_R}\frac{X_i}{X_R}$$

where

k_R = a constant that depends on component *R* and the apparatus, and
X_R = the mole fraction of component *R*.

The constants k_i and k_R indicate the relative efficiency of two materials in diffracting X-rays from given sets of

crystallographic planes into the detector of the diffractometer. The relative value of k_i and k_R can be determined from the equation

$$\frac{k_i}{k_R} = \frac{I_i}{I_R}$$

by measuring the intensity of X-rays diffracted from two crystalline components *i* and *R* in a 1:1 binary mixture. Peak area, rather than height, should be used to represent intensity since the former is less influenced by differences in particle-size distribution. Quantitative analysis of a multicomponent mixture requires that the identity of all components be known. One component is arbitrarily chosen as an internal reference, *R*. Binary 1:1 by weight mixtures are prepared with the reference component and each of the other components. The intensity ratio Ii/IR of a peak, usually the strongest, of each component is then measured. The ratio of the intensities of the diffraction peaks defines the k_i/k_R of each pair of components. The ratio k_i/k_R is called a reference intensity ratio RIRs or RIR [21–25]. Corundum, the most commonly used reference material, is the basis of all RIR values given in ICDD Powder Diffraction Files. Davis, Smith, and coworkers published RIR values for some common materials, including several that are used as pigments or extenders in paint [25,26]. Published reference intensity ratios must be used with care since material other than corundum may have been used as the reference and intensity may have been measured as peak height instead of area.

MANUAL CALCULATION OF COMPOSITION

The relative weight percent of each crystalline component in a multicomponent mixture can be determined by the following procedure:

1. Determine the intensity of the diffraction peak chosen for quantitation of each component. (Integrated intensity based on peak area is recommended. Intensity may be expressed in counts per second, relative intensity compared to the most intense peak in the set, or any other consistent system.)
2. Determine the reference intensity ratio (RIR) for every crystalline component in the sample if the information is not already available. (Once a RIR has been determined, it may be saved and used in future analyses conducted under the same experimental conditions.)
3. Divide the intensity of the chosen peak of each component by the corresponding RIR.
4. Normalize the set of quotients so that their sum is 100.
5. The normalized quotients correspond to the relative weight percent of each crystalline component.

EXAMPLE

The diffraction pattern of a sample indicated the presence of three components: rutile, quartz, and tan iron oxide. The analyst determined that the RIRs for these phases are:

3.20 for the 3.247 Å peak of rutile

2.96 for the 3.342 Å peak of quartz

2.32 for the 2.543 Å peak of tan iron oxide

The intensity of the corresponding peak for each component in the diffraction pattern of the test sample is:

Component	Intensity
Rutile	100.0
Quartz	19.1
Tan iron oxide	1.8

The data and calculated values may be organized as follows:

Component	Intensity	RIR	Quotient	Percent
Rutile	100.0	3.20	31.3	81.1
Quartz	19.1	2.96	6.45	16.8
Tan iron oxide	1.8	2.32	0.78	2.1

Two important points about quantitation by XRD analysis should be noted. First, the results do not include noncrystalline components such as carbon black, amorphous silica, or highly processed clays. Second, the results do not represent percent by weight on either a dry film or a liquid paint basis.

The absolute weight percent of crystalline pigments and extenders can be determined by either

1. Using a variation of the above method that includes an internal standard [19,20,27] added in known concentration to the paint.
2. Taking into account the total percent pigment in the paint if no amorphous pigment is present. The percent pigment in dry coating or water-reducible paint can be determined by ASTM Test Method for Pigment Content of Water Emulsion Paints by Low-Temperature Ashing (D3723) [10]. The percent pigment in solvent-reducible paint can be determined by ASTM Method for Determination of Pigment Content of Solvent-Reducible Paints by High Speed Centrifuging (D2698) [13] or ASTM Test Method for Pigment Content of Solvent-Reducible Paints (D2371) [12].

The accuracy and precision of quantitation by XRD are strongly dependent on the number and type of crystalline components present, the accuracy of the RIRs used, the amount of preferred orientation of crystallites, and the instrument-operating conditions. Published studies reported that the "matrix flushing" method described above yielded results that agree with known composition within 4.2 % relative for all components [20]. Standard deviations of about 0.4 % and 5 % have been reported for components comprising 90 % and 5 %, respectively, of three-part mixtures of NiO, μ-Fe_2O_3, and Fe_3O_4 [28]. Smith et al. reported relative error ranging from 0 to 12 % [24]. Dyakonov et al., in a study with seven laboratories, reported relative standard deviations of interlaboratory determinations ranging from 5 to 20 %, but cited relative standard deviations of 60 % for low-concentration components [29]. An approach for dealing with preferred orientation in mica has been suggested by Kamarchik and Ratliff [30].

COMPUTER-ASSISTED CALCULATION OF COMPOSITION

Some computer programs for processing XRD data include a quantitative analysis program that, in principle, can be

used to determine the weight percent of each crystalline component in a mixture of crystalline components. (The results are the percent of total crystalline content, not the percent of total solids.) These programs calculate composition using a computerized version of the manual calculations described and illustrated in the paragraphs above. Because of their simplicity and speed, they can be very helpful if used prudently, but most commercially available quantitation programs have two serious shortcomings. First, they assume that all crystalline materials have a RIR of unity, a markedly inaccurate assumption. Second, they base quantitation on the strongest diffraction peak of each crystalline component, even though the strongest peak may be overlapped by peaks of other components. Consequently, if the strongest peak of a minor component, a peak that would be weak if it stood alone, is overlapped by a strong peak of a major component, then the calculation algorithm gives a much inflated apparent weight percent for the minor component. Thus, careless or uninformed use of these programs may yield results that are wildly inaccurate. Analysts should not rely upon results produced by a quantitative XRD program without investigating and understanding the assumptions and limitations of the program.

Some quantitation programs permit the analyst to replace the default value of unity in the internal RIR table by user-installed RIR values. Ideally, the substituted RIR values have been determined experimentally using the same diffractometer operating under similar conditions, especially with the same slit widths. Less reliable than the foregoing approach, but still far better than using unity, would be entry into the internal RIR table the RIR values obtained from an external source, such as those stated in the ICDD Powder Diffraction Files or in other published literature [16,25,26]. The analyst should consult the user manual to determine the nature of the RIRs used in calculations and the procedure to install alternative RIR values, if changes are desired.

When proper RIR values are used and there is no overlap of the strongest diffraction peak of any component in the sample, computerized quantitation programs give satisfactory results quickly. Under these conditions, the accuracy and precision are similar to those achievable by manual calculations. In the case of samples in which one or more of the components have their strongest peak overlapped by a peak of another component, the analyst probably must resort to manual calculation based either on a weaker, non-overlapped peak or on the strongest peak after overlap contribution has been subtracted.

LIMITATIONS

Quantitation of pigments by XRD is sometimes handicapped by one or more of the following problems. First, the degree of crystalline regularity within particles of some pigments, especially silica and clays, may differ depending on the source and the nature of the processing that they have received. A factor contributing to variability of the apparent crystallinity is the amount of substitution of "foreign" ions in the crystalline lattice. An example is the substitution of magnesium for calcium in calcite and strontium for barium in barytes. Thus, a given amount of pigment in a test sample may diffract X-rays more or less strongly than the supposedly equivalent pigment sample used to establish the RIR. An article by Davis et al. provides a valuable listing of RIRs (versus corundum) for many common pigments and illustrates the variability of reference intensity ratios for pigments from different sources [22]. Second, pigment particles that are platelet or acicular in shape tend to assume preferred orientations in a paint film as the paint dries. If the extent of preferred orientation of the particles in the specimen and the reference specimen used to establish the RIR differs, then quantitation based on the RIR is incorrect. Mica and aluminum flakes commonly exhibit preferred orientation. Third, the strongest peaks normally used for quantitation may be overlapped by peaks of other components, thus requiring the use of weaker and less reliable peaks as the basis of quantitation.

Examples of XRD Analysis

PIGMENT ANALYSIS

XRD analysis is the most direct way to determine the identity and purity of pigments, whether in assessing the quality of pigments from established suppliers or in evaluating pigment from potential new suppliers. Crystalline impurities contribute "extra" peaks to diffraction patterns, differences that may be readily seen in patterns of pigment powders alone or in grind pastes. X-ray analysis has long been established as the method of choice for determination of the amount of anatase in rutile [ASTM Test Method for Ratio of Anatase to Rutile in Titanium Dioxide Pigments by X-ray Diffraction (D3720)] [31]. The widespread use of diffraction in the pigment industry attests to its utility in that field.

Questions concerning the identity or amount of pigments in paint can be more conveniently and definitively answered by XRD than by any other technique. Visual comparison of diffraction patterns or, when necessary, quantitative analysis can be used to determine whether errors in pigment composition account for the difference in performance, color, or gloss of "good" and "bad" paint. Diffraction analysis is a basic tool that may be used to verify whether a paint that exhibits poor performance is the correct paint and comes from the correct supplier. The differences in the two patterns in Fig. 8, one for a good paint and one from a poorly performing suspect paint, coupled with differences in resin and solvent determined by other techniques, proved that the suspect paint was an unauthorized substitute.

METAL PRETREATMENT AND OTHER THIN COATINGS

XRD can be used to determine the identity and amount of pretreatment on metal or, in general, crystalline coatings on substrate. Fig. 9 shows the characteristic part of the diffraction patterns of two common types of pretreatment, hopeite [$Zn_3(PO_4)_2 \cdot 4H_2O$] and scholzite [$CaZn_2(PO_4)_2 \cdot 2H_2O$], on zinc-galvanized steel. Coating thickness or pretreatment weight on test samples can be determined by comparison of the intensity of one or more peaks of the species of interest with the same peaks exhibited by standard samples scanned under identical conditions.

X-RAY FLUORESCENCE SPECTROSCOPY

Application

TYPES OF SAMPLES

XRFS is applicable to any liquid or solid that can be placed at the focal point of the X-ray optics system. Permissible specimen size differs widely with instrument type. Common commercial laboratory units can accept

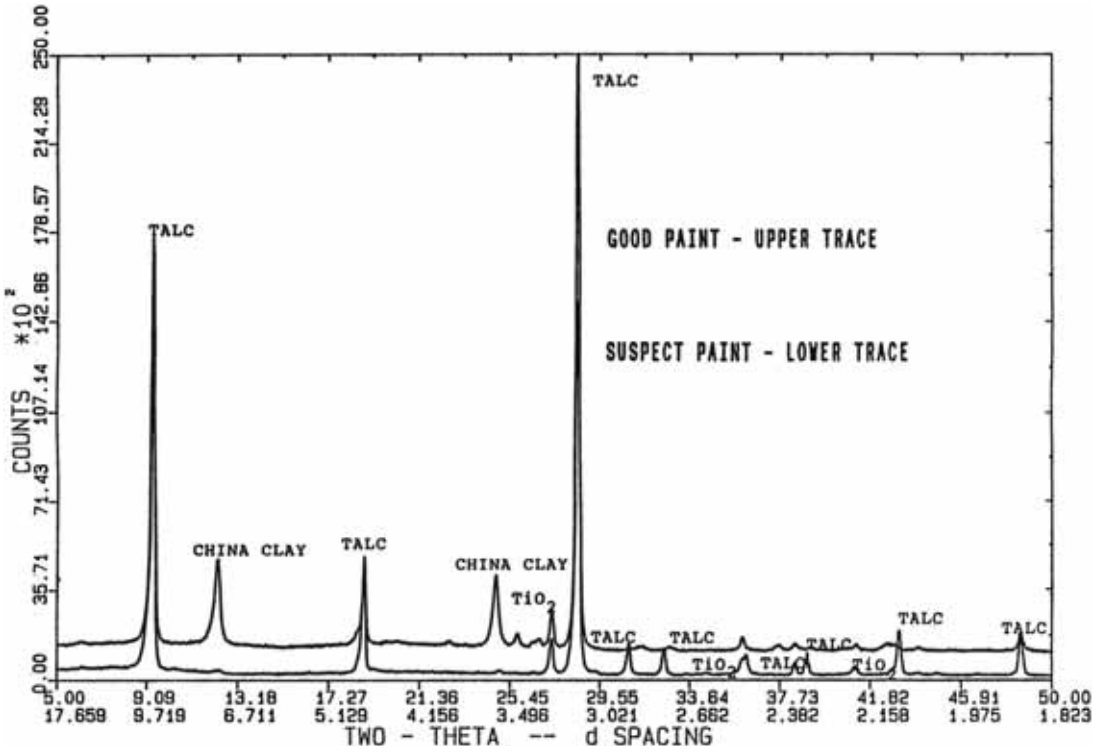

Fig. 8—X-ray diffraction patterns of drawdowns of two paints: one known to be good; one of suspect identity.

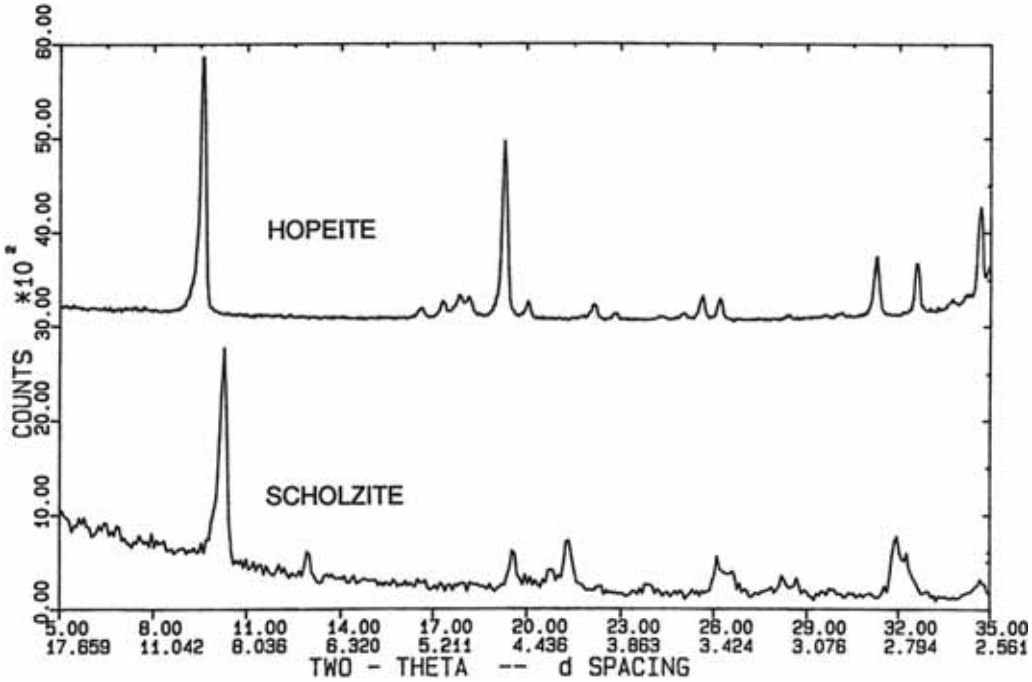

Fig. 9—X-ray diffraction patterns of hopeite and scholzite pretreatment on zinc-galvanized steel. (The principle peaks of zinc metal are beyond the right end of the pattern.)

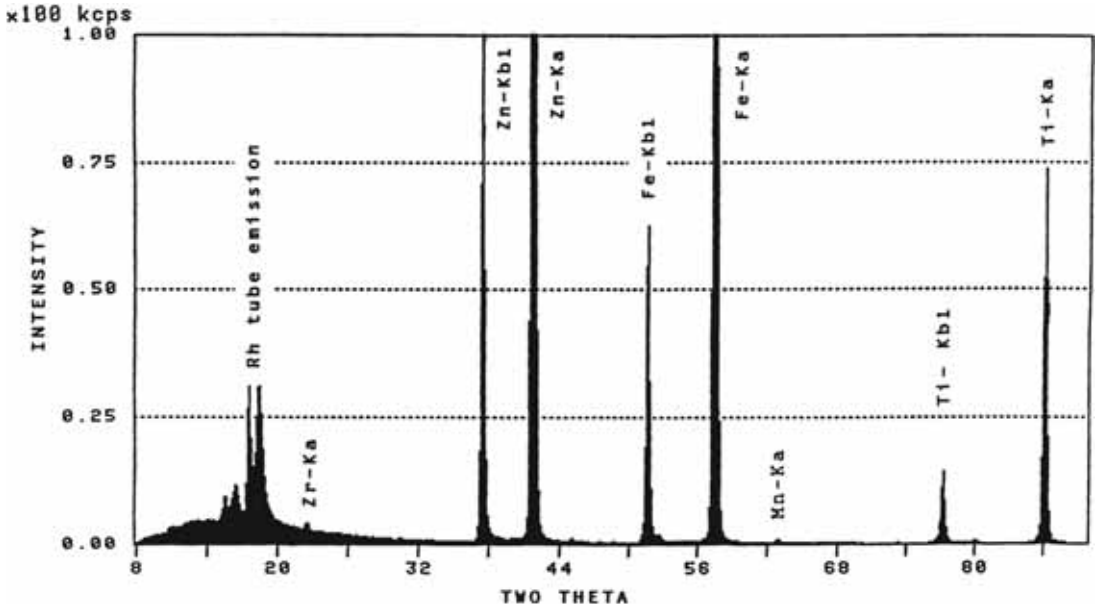

Fig. 10—Part of an X-ray fluorescence spectrum, recorded using a wavelength-dispersive spectrometer, of paint containing rutile, yellow iron oxide, talc, and zinc oxide.

specimens as large as a cylinder about 4.0 cm in diameter and 2.5 cm in height to as small as 1 or 2 mg of powder. Some laboratory models can analyze specimens up to several centimeters in each dimension. There is no maximum size limit for bench top or portable units with hand-held X-ray probes.

TYPES OF INFORMATION PROVIDED

The most sophisticated and costly X-ray spectrometers can be used for qualitative and quantitative analysis of all elements in the atomic number range from 5 (boron) to 92 (uranium). Lower-cost instruments span fewer elements and offer less versatility.

RANGE OF CONCENTRATIONS

Analysis can be performed on elements ranging in concentration from 100 % down to a few parts per million in favorable cases. The limit of detection differs widely with the model of spectrometer, the element of interest, and what other elements are present. The limit of detection rises rapidly with decreases in atomic number, especially below 11 (sodium).

Physical Basis

When X-ray photons of sufficient energy are directed onto a specimen, some photons are absorbed in a process that causes ejection of electrons from core atomic orbitals. The vacancies thus created in the inner orbitals are then filled by electrons from outer orbitals. The transitions of electrons from outer to inner orbitals are accompanied by the release of X-rays in a process called X-ray fluorescence [32,33]. The wavelengths of the fluorescent x-rays are greater than the wavelengths of the incident X-rays. Of key importance in analysis is the fact that every element emits fluorescent x-rays at characteristic wavelengths. The spectra are plotted as intensity as a function of 2θ angle (as in Fig. 10), wavelength, or photon energy (as in Fig. 11). Angle 2θ refers to the position of the X-ray detector that moves at twice the angle of the diffraction crystal used in some instruments to separate different wavelengths to produce a spectrum.

Types of X-Ray Fluorescence Spectrometers

SCANNING

Scanning X-ray fluorescence spectrometers permit the acquisition of spectra spanning a broad wavelength or energy range. These spectrometers, usually floor-standing, are versatile instruments for both qualitative and quantitative analysis. Scanning spectrometers, most using X-rays from Coolidge-type tubes, can be further classified as either wavelength or energy dispersive.

Wavelength-dispersive (WLD) instruments produce a spectrum by using a crystal to diffract the fluorescent X-rays, a single wavelength at a time, onto a detector that measures their intensity. By rotating the crystal through an angle defined as θ as the detector moves around an arc through angle 2θ, only those X-rays that satisfy the Bragg equation reach the detector. The resultant spectrum is usually plotted as intensity as a function of 2θ angle, but could in principle be plotted as intensity as a function of wavelength. By use of several crystals, each effective for a certain span of wavelengths, a broad range of wavelengths can be scanned. Instruments based on energy-dispersive X-ray spectroscopy (EDXS) permit all wavelengths of the fluorescence to reach the detector simultaneously and use a pulse-height discriminator to electronically classify the energy of the X-ray photons that strike the detector.

Descriptions and comparisons of the two types of scanning spectrometers have been provided by Campbell [34]. Compared to EDXS units, the WLD spectrometers generally offer far superior spectral resolution and lower limits of detection. High resolution eases the task of achieving reliable quantitative analysis of elements present at low concentration in the presence of high concentration elements of adjacent atomic numbers. EDXS instruments

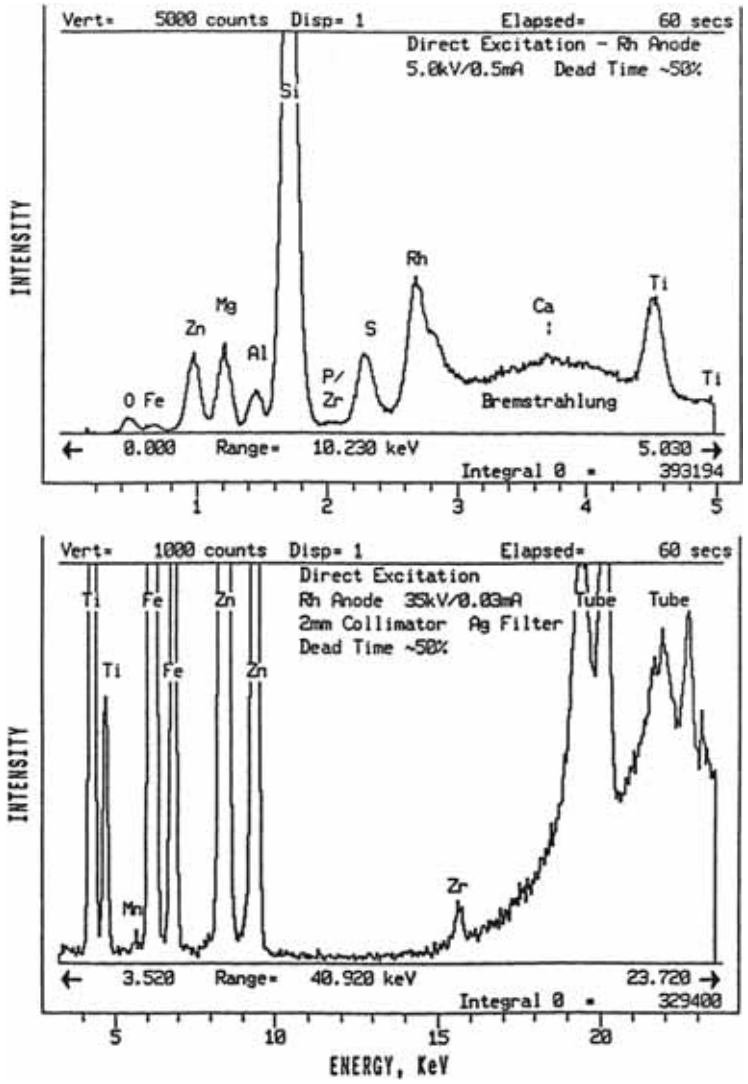

Fig. 11—X-ray fluorescence spectrum, recorded using an energy-dispersive spectrometer, of the paint used for Fig. 10.

provide much faster acquisition of spectra and are usually lower in cost. Scanning spectrometers are convenient for qualitative elemental analysis and are broadly versatile for quantitative analysis [35].

Generally, the large scanning spectrometers offer greater versatility, greater accuracy, greater precision, and lower limits of detection than do less expensive, smaller, dedicated bench-top and portable units. However, recent models of the smaller units have narrowed the performance gap.

DEDICATED (SPECIALIZED APPLICATION)

Dedicated X-ray fluorescence spectrometers, available at much lower cost than the scanning spectrometers, permit quantitative analysis of a single element or a few selected elements. Most of the dedicated units, and all the lowest priced units, use a radioactive isotope instead of an X-ray tube as the source of radiation to excite the specimen [36]. In single element analyzers, the isotope source, detector composition, and operating conditions are chosen to give best performance for analysis of a specific element of interest. Dedicated x-ray spectrometers are typically small bench top units with simple operating procedures. They are well-suited for routine analysis [35].

ON-LINE

Products and process materials may be analyzed on-line by specially adapted dedicated X-ray fluorescence units with remote analyzer heads [37]. The heads house the X-ray source and detector. Flow-through heads can be used for liquids. Fixed or moving heads can be used for moving sheet stock or other solid material. Bulk composition or the composition or thickness of a coating on a substrate can be determined by this method. The apparatus and methodology are custom-designed for each application.

XRFS analysis is well suited for on-line use in production facilities because of its nondestructive nature, high degree of automation and reliability, real-time output of analytical results, ease of interface with computerized data storage systems, and ease of integration with process control systems. On-line XRFS units can function directly in both quality monitoring and process control. These units can be rigged to give an immediate alarm if a process goes out of acceptable operating limits.

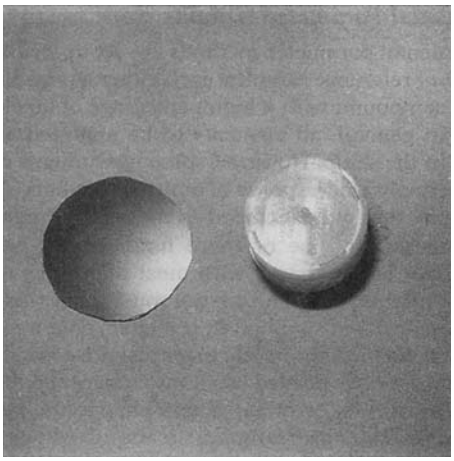

Fig. 12—Two examples of specimens: (left) a disk cut from a painted steel aluminum; (right) a plastic cup covered on the bottom with metal-free plastic film and on the top with a plastic cap. Suitable for liquids and powders.

PORTABLE

Portable X-ray fluorescence units with self-contained power supplies and either single or multiple element capability are available for uses that require mobility. Some of these devices are only a little larger than a cordless telephone handset. They are well suited for rapid analysis in off-line applications, in factory yards, and in field studies [38]. There is growing use of portable units for determining lead content in paint in situ in old residential buildings [39]. However, the operator is cautioned against using calibration curves established with one type of paint on one type of substrate for analysis of other formulations of paint or other substrates.

ELECTRON BEAM EXCITED X-RAY SPECTROSCOPY

Spectroscopic analysis can be performed with X-rays generated by bombardment of a specimen with an electron beam, as in a scanning electron microscope (SEM) or an electron microprobe (EMP) [32]. The spectrum may be produced by either energy-dispersive or wavelength-dispersive means. SEM units, commonly equipped with energy-dispersive X-ray capabilities, are extremely useful tools for the study of surfaces and small features, especially defects such as craters, voids, pinholes, mars, and stains. In addition to providing images, such instruments can perform qualitative and quantitative elemental analysis. EMP units, usually equipped with both energy-dispersive and wavelength-dispersive capabilities, are used when the emphasis is on quantitation rather than imaging. Both SEM and EMP permit elemental analysis as point analysis, line scan, area analysis, or mapping. Present technology permits analysis of all elements with atomic number 4 (beryllium) and higher.

Experimental Procedures

Specimens may be any solid or liquid that can be presented to the X-ray beam. The size of the specimen holder of the spectrometer is the principal practical limitation. Sample preparation methods have been discussed by Bertin and Leyden [32,40]. Fig. 12 shows two types of specimens.

Many of the recommendations given in Table 1 for XDR also can be used to prepare specimens for qualitative analysis by X-ray fluoresence spectroscopy. However, the analyst is cautioned that the X-rays used for X-ray fluorescence spectroscopy are commonly more penetrating than those used for diffraction analysis. Unless care is taken, the fluorescence spectrum may show elements in the backing material used to support the intended specimen material. The analyst must either use a specimen that is sufficiently thick to prevent X-ray fluorescence from the backing from reaching the detector or use a backing (such as a metal-free polymer) that is free of conflicting elements. It is common practice to place liquid or powder in a disposable plastic cup, the bottom of which is covered with a thin plastic film that transmits X-rays. (Liquids and powder are most conveniently analyzed in spectrometers that irradiate the specimen from below. For instruments of the opposite configuration, the specimen cup must be filled so that there is no bubble when the cup is inverted in the analysis chamber.) Paint chips may be placed directly in the specimen cup, and drawdowns of paint on metal-free plastic sheets such as Mylar may be cut to fit the specimen holder.

For quantitation, powders may be pressed into disks in a binding agent such as orthoboric acid, granular cellulose, or graphite or cast as pellets after dissolution in molten flux such as lithium tetraborate or lithium metaborate. Ashing or extraction with acid or organic solvent is sometimes useful to remove analytes from bulky matrices, thus lowering the limit of detection and perhaps increasing analytical accuracy. Dissolution with acid or other solvent may make the sample more amenable to quantitation methods described under "Quantitative Analysis." Detailed procedures for briquetting, fluxing, and ashing are available in the *Spex Handbook of Sample Preparation and Handling* [41]. Powders and liquids can be analyzed in disposable cups, as mentioned above. Disk-shaped specimens cut from solid samples may be handled in a similar manner. Bertin provides valuable information about specimen preparation [32].

Specimens are analyzed under vacuum whenever possible to minimize absorption of X-rays by the atmosphere in the analysis chamber. However, liquids and powders must be run under helium or air to prevent spatter. Portable analyzers and certain models of bench top units can operate without the specimen in vacuum or purge gas because of the short distance between the specimen and critical instrument parts.

Operating procedures differ widely with the make and model of X-ray spectrometer. Manufacturer instructions on safety and operation should be consulted.

Qualitative Analysis

Qualitative elemental analysis can be conveniently done using a scanning X-ray fluorescence unit. Elements in a specimen can be identified by the position of the peaks on the spectrum expressed as photon energy (kilovolts), 2θ angle, or wavelength. Peak identification tables can be found in manuals provided by manufacturers of the spectrometers or in treatises on X-ray spectrometry [32]. Modern X-ray spectrometers have computer programs that can indicate what elements are present in a specimen. For instruction in use of these programs, the analyst should refer to the instrument operation manual.

Fig. 10 shows part of an X-ray fluorescence survey spectrum (collected using a WLD instrument) of a drawdown of a tan paint, the same one used to produce the diffraction pattern in Fig. 7(*a*). Note the corroborative nature of element content indicated in Fig. 10 and the identity of

the pigments determined from the diffraction pattern in Fig. 7(*a*). For comparison, Fig. 11 is an X-ray fluorescence survey spectrum, recorded by an energy-dispersive instrument, of the same sample.

Quantitative Analysis

GENERAL PRINCIPLES

The principles of quantitative analysis by XRFS have been discussed in detail by many workers including Bertin [32,33]. The basic equations show that the intensity of the fluorescent X-rays is proportional to the amount of element that produced the X-rays, but is influenced by other factors such as the density and absorption coefficient of the specimen. Nevertheless, the linear proportionality between analyte concentration and fluorescence intensity shows that common analytical methods such as standard addition can be readily employed in X-ray spectrometry. Direct comparisons of concentration can also be made between samples that differ only in the amount of analyte of interest. Analyses by these simple methods can be done with small, low-cost, bench-top analyzers. Analysis of more than one element, especially in a matrix of variable composition, is best done with more sophisticated scanning spectrometers with suitable computers and software. Yet, some bench-top analyzers equipped with computers can determine the concentration of more than one element in matrices of variable composition. X-ray spectrometers must be programmed and calibrated by the analyst or the manufacturer for each analytical application before reliable quantitative analysis can be done. Recalibration must be done periodically.

DIRECT COMPARISON METHOD

Quantitation by direct comparison is done as follows. The analyst prepares or collects a set of three or more reference specimens that contain an element of interest at a range of known concentrations, but are otherwise essentially identical. Equal amounts of each specimen are placed in specimen cups or otherwise prepared for analysis. The analyst collects fluorescence intensity data for the element of interest from the set of samples and establishes a calibration plot of intensity versus concentration. Modern X-ray spectrometers with integrated computer capabilities can store the calibration plot for convenient use. When the spectrometer lacks computer capabilities, the analyst can construct the plot manually or use an external computer. Test samples of unknown composition are then run on the spectrometer under conditions identical with those used when the calibration samples were run. Intensity data from each test sample can be converted to concentration through use of either a manual or computer-stored calibration plot. To avoid extrapolation error because of unexpected plot curvature or other reasons, the range of concentration of the reference specimens should span the concentration of the specimens being analyzed. If the test specimen lies outside the range, then either the specimen should be diluted by a known amount to bring it "on scale" or the calibration plot should be extended with additional reference specimens. Operating instructions from the supplier of the spectrometer should be followed.

When applicable, direct comparison is usually the simplest, most convenient element quantitation method available. It can be done with even the simplest X-ray spectrometers. Most modern X-ray spectrometers can store several, perhaps many, calibration plots suitable for different applications.

Note the following three cautions. (1) If a test specimen differs in matrix composition or physical state from the reference specimens used to establish the calibration plot, then the analytical results may be incorrect. Error can be large if the matrices of the test sample and the reference samples differ widely in absorptivity of X-rays. Thus, in general, a calibration plot established with one type of sample should not be used to analyze other types of samples. (2) The calibration curve may show a significant amount of curvature if the analyte and the matrix differ widely in absorptivity (e.g., tin in resin) and a wide range of concentrations is spanned. If the intensity versus concentration plots shows curvature, then either a polynomial fit must be used or another method of analysis must be employed. (3) Calibration plots tend to lose accuracy with time and must be replaced or corrected following manufacturer instructions. As a consequence of aging, progressive changes in the output of the x-ray source and in the sensitivity of the detector contribute to calibration "drift."

STANDARD ADDITION METHOD

The method of standard addition can be used when no suitable reference samples are available to permit analysis by direct comparison. In this method, the analyst divides the test sample into at least three equal portions of known volume or weight. One of the divided specimens is retained for analysis with no further change. Each remaining specimen is "spiked" with the element of interest in a series of different known amounts. This method has convenient application only to liquids, and perhaps to powders, because of the need to mix uniformly the added component with the original material. The concentration of *added* analyte in each specimen is then calculated. The intensity of x-ray fluorescence of the analyte in each specimen is measured under identical conditions. The intensity of the analyte fluorescence signal is plotted as a function of added analyte concentration, as in Fig. 13. The data line of the graph is extrapolated to the point of interception (a negative number) on the concentration axis. The absolute value of the concentration intercept corresponds to the concentration of the original unspiked sample. Many modern X-ray spectrometers have computer programs that do the calculation.

EMPIRICAL METHODS

The empirical methods require the use of a set of reference samples that span the concentration range of all elements of interest. All modern high-priced and most mid-price X-ray spectrometers can perform analyses using one or more variations of this approach when equipped with suitable software. The analyst must follow the instructions from the instrument supplier. Empirical methods are well suited for routine multielement analysis of large numbers of samples of the same type. A different program, with its own set of reference samples, must be established for each class of samples and choice of elements. High accuracy and precision are achievable when the reference samples properly represent the test samples.

FUNDAMENTAL PARAMETER METHODS

Fundamental parameter methods are set up by the analyst with a set of reference samples, each either a pure element

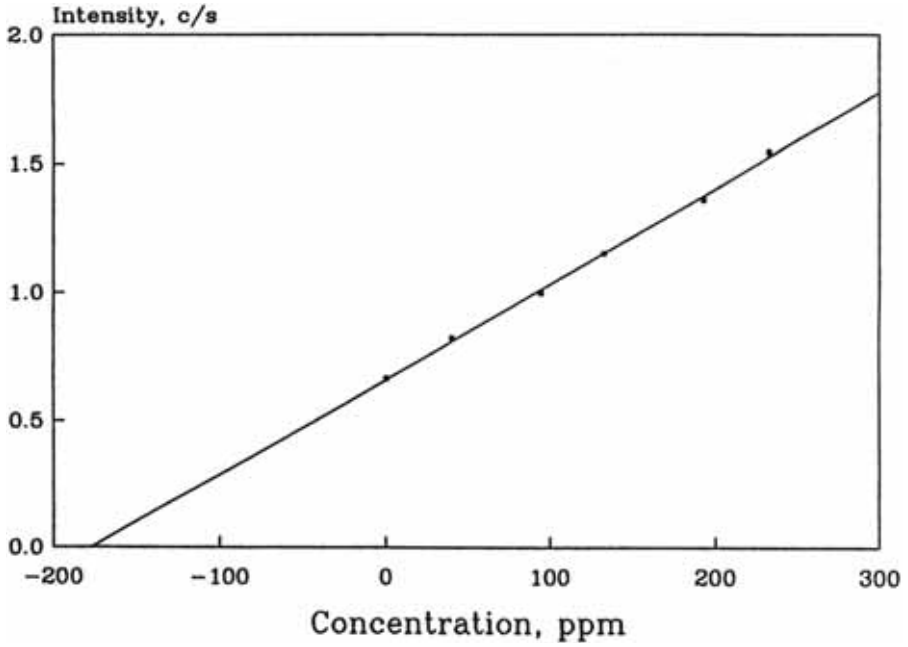

Fig. 13—A plot of the intensity of the sulfur, K_α, peak as a function of the concentration of sulfate in the analysis of an aqueous solution by a standard addition method.

or a simple compound with a high percentage of an element of interest. In general, all elements to be analyzed should be included in the setup. However, some instruments can interpolate the analytical response of omitted elements from similar elements that were included in the setup. Programs that permit analysis by one or more fundamental parameters methods can be purchased with all high-price and some mid-price instruments. The analyst must follow instructions from the instrument supplier. In principle, once a program is established, no further reference samples are needed. In practice, recalibration is needed when instrument repair, maintenance adjustments, or other factors change the instrument response. No standard samples, in the usual sense of the word, are needed for calibration. Fundamental parameters programs can be used to perform multielement quantitative or semiquantitative analysis of test samples of widely varied composition and unfamiliar nature. If an analyst must perform a quick semiquantitative analysis of an unfamiliar sample, then the fundamental parameter program is the method of choice. Accuracy varies with the task and the sophistication of the instrumentation and software.

COMPARISON TO OTHER TECHNIQUES

In quantitative analysis of liquid samples, XRFS, compared to atomic absorption or plasma emission spectrometry, offers the advantage of being able to handle samples with (1) higher concentrations of analyte without use of large dilution factors and attendant inaccuracy, (2) matrices that are ill-suited for aspiration into nebulizers, and (3) elements that are not easily detected by flame or plasma photometric techniques.

Applications of X-Ray Fluorescence Spectroscopy

ANALYSIS OF ELEMENTS IN SOLUTION

Fig. 13 shows a plot of data used in the quantitation of sulfur in an acidic aqueous solution by a standard addition method. The sample resulted from flushing a steel panel retrieved from outdoor exposure with citric acid and then concentrating the solution by evaporation. This example illustrates a general-purpose method. ASTM Standard Test Method for Sulfur in Petroleum Products by Wavelength Dispersive X-ray Fluorescence Spectrometry (D2622) could be adapted for analysis of sulfur in other organic liquids or solutions [42]. ASTM Standard Test Method for Determination of Elemental Content in Polyolefins by Wavelength Dispersive X-Ray Fluorescence Spectrometry (D6247) is applicable to a variety of elements and could be adapted for use with other types of organic samples [43].

SURFACE ANALYSIS

Foreign substances may sometimes be detected on surfaces by X-ray fluorescence spectroscopy, eliminating the need to resort to X-ray photoelectron spectroscopy and other "surface analysis" techniques. To be detectable, the contaminant must contain an element that is not present in significant amounts in the surface itself. Fig. 14 shows a silicon peak in the high-resolution X-ray fluorescence scan of the surface of a piece of aluminum extrusion from which poorly adhering paint was peeled. Comparison of Figs. 14(*a*) and 14(*b*), respectively, prove that washing the peeled surface with hexane significantly reduced the amount of silicon present. The elevated silicon signal on a substrate to which paint adhered poorly and the ready removal of the silicon material by hexane suggested the presence of silicone oil. This suspicion was confirmed using analysis by micro-infrared spectroscopy of residue left by evaporation of the hexane washings.

METAL PRETREATMENT

XRFS provides a quick and convenient way to determine the amount of pretreatment on metal surfaces. Once reference samples have been used to establish a calibration plot

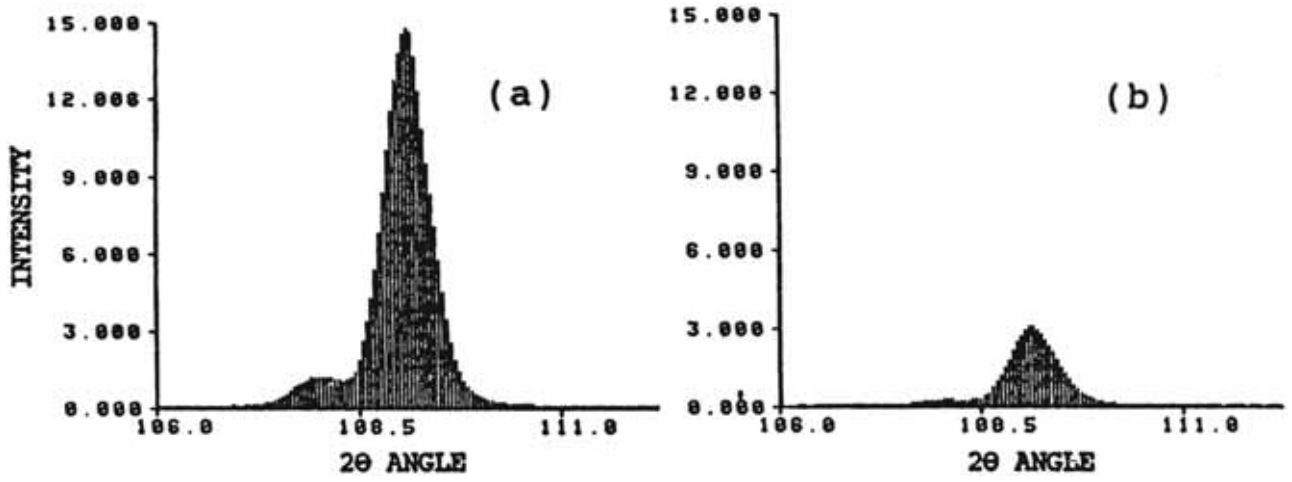

Fig. 14—The K_α peak of silicon on extruded aluminum from which poorly adhering paint has been peeled: (a) peeled only; (b) peeled and washed with hexane.

that relates fluorescence intensity, expressed in convenient units such as counts per unit time, to coating weight, which was determined by an independent method, the instrument can be used to determine pretreatment weight on test samples. Fig. 15 shows a calibration plot for the weight of chromium conversion coating on aluminum sheet [44]. Even low cost bench-top or portable units can give quick direct readout of pretreatment weight using internally stored calibration plots. ASTM Standard Practice for Determination of Chromium Treatment Weight on Metal Substrates by X-Ray Fluorescence (D5723) details the procedure for chromium-containing pretreatment [45]. With suitable instrumentation, the method can be adapted for phosphorus of phosphate or for other types of thin surface coatings.

DETECTION OF BULK CONTAMINANT

The low limit of detection of X-ray fluorescence spectroscopy makes it well suited for the detection of trace impurities, some of which may not be detectable by any other means. There is the tacit requirement that the contaminant contain an element that is not a normal component of the sample. Although small amounts of impurity may have no perceptible impact on the performance of a material, knowledge of the presence and amount of an impurity may be crucial in determining the cause of substandard performance. Table 3 summarizes data collected by XRFS in the investigation of a case in which silicone contamination was suspected as the cause of cratering exhibited by certain batches of waterborne paint. Quantitation was by a standard addition method. Although XRFS cannot distinguish between different silicon-bearing species, the higher level of silicon in batches of resin used in the crater-prone paint supports the suspicion that silicone caused the cratering. The data also suggest that a threshold concentration between 7 and 13 parts per million silicone in the resin, based on the silicon signal, is needed to produce cratering in the paint produced from it.

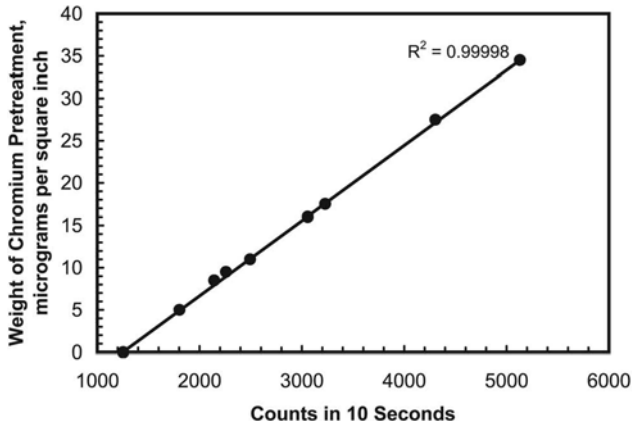

Fig. 15—Plot of weight of chromate conversion coating on aluminum sheet as a function of fluorescent signal intensity. Each point is an average of three 10-s measurements.

QUALITY CONTROL

Dedicated X-ray fluorescence units that can determine the concentration of a single element have great utility in production plants for monitoring the composition of raw materials, intermediates, and products. Fig. 16 shows a calibration "curve" that was established to permit monitoring the percent cobalt in a cobalt drier solution used in the manufacturer of paint [46]. Similar results have been demonstrated for calcium, zinc, and zirconium driers [47]. Driers are metallic salts of carboxylic acids used to catalyze the curing of paint films.

TABLE 3—Concentration of silicone, determined by XRFS, in batches of resin used in batches of paint of known extent of cratering

Extent of Cratering	Concentration of Silicone, ppm
None	3
None	4
None	7
Bad	13
Bad	13
Worst	40

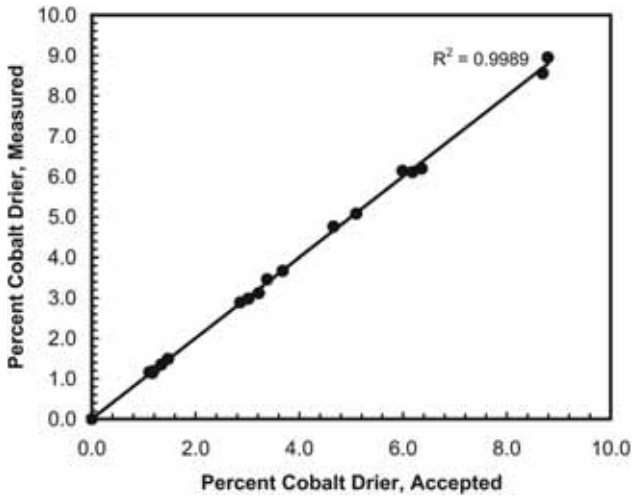

Fig. 16—Plot of the amount of cobalt in a drier solution as measured by a benchtop XRFS unit versus the accepted amount.

Dedicated x-ray analyzers have also been used to monitor the amount of rutile in batches of paint in production plants [48]. Caution: A different calibration plot must be established for each paint formulation to be monitored, unless the compositions of the dried paints films are essentially identical in all respects other than rutile content.

Guidance on the use of X-ray analyzers to determine the coating thickness is given in ASTM Standard Test Methods A754/A754M, Coating Weight (Mass) of Metallic Coatings on Steel by X-Ray Fluorescence [49], and B568, Measurement of Coating Thickness by X-Ray Spectrometry [50].

ANALYSIS IN THE FIELD

Concern over the potential adverse health effects of lead in paint in residential buildings has prompted an interest in convenient, nondestructive methods of testing for lead. Fully portable X-ray analyzers that can detect lead in paint on walls and other surfaces are commercially available. The analyzers can detect lead-containing paint beneath layers of lead-free paint, and some can provide direct readout of the amount of lead per unit area of paint surface [51]. The accuracy and precision are not well documented. The Department of Housing and Urban Development established a limit of 1.0 mg of lead per cm^2 of painted surface, a level detectable by portable analyzers [52]. Caution: In accordance with the constraints of all X-ray fluorescence spectrometers, matrix differences between test samples being analyzed and reference samples used to establish instrument calibration curves may compromise the accuracy of the apparent lead concentrations reported by portable units.

Other uses of portable analyzers include determination of the weight of pretreatment on metal, the thickness of paint, and the concentration of key elements in samples at environmental cleanup sites.

SUMMARY

XRD and XRFS, used alone or in combination, can provide valuable information about coatings, coating ingredients, impurities, and substrates. Sample preparation effort is minimal for both techniques. XRD offers easy qualitative and quantitative analysis of crystalline materials in general and pigments in particular. XRFS is widely useful for qualitative analysis and, when suitable standards are used, for quantitative analysis. Attractive features of XRFS for quantitative analysis include its suitability for all elements except a few with lowest atomic number, applicability over a broad concentration range, tolerance of chemically reactive specimens, and applicability to samples of diverse physical states. Both XRD and x-ray spectrometry are suitable for applications including basic research, product and process development, quality control, and practical problem solving. The area of greatest potential growth is the use of dedicated x-ray fluorescence spectrometers in production plants for quality control, particularly for on-line monitoring.

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Part 16: Specifications

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Paint and Coating Specifications and Standards

Joseph V. Koleske[1]

INTRODUCTION

COATING AND PAINT SPECIFICATIONS ARE A COM-monality established between a customer and a supplier. They define what a customer can expect from a supplier and what the supplier is required to do to meet the customer's expectations. Often such agreements are between organizations that purchase the products in large volume for construction and maintenance projects, for resale to distributors, or to end-use consumers. Details of how to carry out the testing required to meet such specifications is left to the devices or procedures (often termed standards or test methods) of a third, uninterested party such as ASTM International or similar groups that are listed elsewhere in this chapter. Purchasing organizations may be federal, state, and local governmental agencies and departments, large industries as for example the automotive, petroleum, and pipe industries, public utilities, railroads, retail companies such as Sears and Wal-Mart, universities and other educational institutions, as well as others. However, in certain instances, the standards used to meet the specifications can carry down to the final consumer as sometimes evidenced on certain products, for example the listing of volatile organic compounds on a can of paint.

Simplistically, a specification is a precise, though detailed, statement of requirements that must be satisfied by a material, product, system, or service that indicates the procedures—standards or test methods—to be followed when determining whether each of the requirements is satisfied [1]. Paints and coatings used in industrial new construction may be specified in construction documents, while such materials used in maintenance finishes or sold through retail outlets may be described in the particular specifications of the purchasing organization. Engineering departments often specify finishes applied by large manufacturing industries, as, for example, the automotive industry, the appliance industry, and the packaging industry. Those who develop the specifications for large quantities of original equipment, maintenance or other finishes, such as public utilities, transportation organizations, and government agencies, purchase on a specification basis and most often by competitive bidding.

Coating specifications set by, for example, the United States Navy and other government agencies will sometimes specify that a coating or paint be manufactured according to a specific formula or recipe that passes the requirements stated in particular, delineated test methods (www.nstcenter.com). If one goes to the "Technical Resources" tab at this site and clicks on "Standards and Specs," items that are used to specify many products can be found.

Federal Test Method Standard 141D, "Paint, Varnish, Lacquer, and Related Materials: Methods of Inspection, Sampling and Testing" is a document[2] that describes a number of coating test methods used by various Federal agencies in their specifications for a number of products. The test methods include coating material characterization tests, volume solids, nonvolatile content, density/weight per gallon, drying time, spectroscopic analyses, chemical resistance, corrosion resistance, as well as other coating performance characteristics such as adhesion, abrasion resistance, accelerated weathering, hardness, impact resistance, and the like.

An example of a detailed specification used by the United States Navy that specifies a paint formula is MIL-DTL-15090D, November 6, 1996, *Enamel, Equipment, Light Gray* (*Navy Formula 111*). To illustrate the complexity of the requirements, within this specification, two particular Federal and two particular Department of Defense specifications as well as two Federal Standards are included along with two Environmental Protection Agency documents and a reference to the Federal Register. The requirements do not stop with these inclusions. Also included in the specification are 28 ASTM standard test methods and standard practices and one Steel Structures Painting Council specification. The actual formula for this paint specifies 16 specific ingredients by weight and weight percentage and a variety of quantitative requirements for the liquid paint and the final paint film. Military specifications such as this one may be altered and may be superseded, as was the case with the above-cited MIL-DTL, which superseded MIL-E-15090C, March 30, 1982. Those interested in supplying or bidding on contracts for the various products should maintain an awareness of such changes.

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[2]Federal specifications and standards discussed in this chapter refer to documents of the United States of America government and are available through the U. S. General Services Administration, Federal Supply Service, FSS Product Acquisition Center, Supply Standards Division, Arlington, VA 22202. Downloadable versions of the documents are available on the Internet. When international or specific country documents are discussed, they will be noted by country designation (see Table 1 for some examples).

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The United States General Services Administration has a "Numeric List of Federal Standards" available on the Internet (www.fss.gsa.gov/pub/fedspecs/). This site has both numeric and alphabetical listings of Federal Standards, Federal Qualified Products, and other publications. Also included are ways to download the publications, costs, addresses, and other useful information.

SPECIFICATION CONSIDERATIONS

The Construction Specifications Institute (CSI) [2] indicates that the following items should be considered in a project construction specification: scope, related sections, referenced documents, definitions, performance requirements or properties, submittals, quality assurance, delivery-storage-handling project considerations, and sequence scheduling. Submittals also cover paint and coating product data as well as color samples.

Material specifications in the ASTM format [3] usually include terminology, ordering information, chemical composition, physical and mechanical properties, performance requirements, sampling, physical and analytical test methods, inspection, packaging and marking, and, if needed, quality assurance.

Donlin [4] has an excellent description of the complex military standards system. His study summarizes information from government manuals, standards, specifications as well as other documents. It represents an effective way to become familiar with the government's documentation system that was in place when the study was developed and make its complexity easier to understand. It is pointed out that the federal documents were developed with government funds, and, if unclassified, are readily available for public use. The article also contains listing of many "milspecs" as they are often termed.

Some paint and coating specifications (for example, those for military use) require prequalification of the products described. Such a requirement exists when the time to conduct tests will exceed 30 days, when quality conformance inspection would require special equipment not commonly available, or when the specification deals with life survival or emergency life-saving equipment. The specifications for such products include the requirements for qualification, the qualification tests, and the name of the activity responsible for qualification. Products that are so qualified are listed on Qualified Products Lists.

SOURCES OF SPECIFICATIONS AND STANDARDS

International Sources

International specifications and standards for paints and coatings are of interest in these days of international or global commerce. For example, Canadian standard 1-GP-71, *Methods of Testing Paints and Pigments,* is available from the Canadian General Standards Board (CGSB). This particular standard contains about 80 methods of analysis in the category termed "Paints and Related Products." In Germany, the German Institute of Standardization (DIN) develops standards. The International Organization for Standardization[3] (ISO) is a nongovernmental network of the national standards institutes of 146 countries who contribute to the development, manufacturing, and supply of products and services in an efficient, clean, safe manner. ISO standards may be obtained from the American National Standards Institute (ANSI). Table 1 is a listing of the address and other pertinent information about these organizations and about several other organizations that deal in specifications and standards.

The Asian Forum for the Standardization of Information Technology (AFSIT) is an organization that has 16 Asian country members. It deals in the promotion of the active information exchange of technology and its standardization. It can be accessed on the Internet at www.cicc.or.jp/ where one can find routes to the standards department of their member countries, such as India, Republic of Korea, Sri Lanka, Vietnam, and several others.

In the summer of 2004, ASTM International (www.astm.org) announced that they had signed a Memorandum of Understanding (MOU) with the national standards body of China, the Standardization Administration of the People's Republic of China (SAC). This is expected to accelerate development of product and testing standards in China, encourage greater access to ASTM standards in China, and give a greater voice to Chinese experts in the content of ASTM standards. This interaction furthers a history of ASTM involvement with Asian standards organizations such as the Chinese National Institute of Standardization (CNIS) and the Shanghai Institute of Standardization (SIS). A similar MOU was completed in June 2001 between ASTM Committee D01 on Paints and Related Coatings, Materials, and Applications and ISO TC 35 on Paints and Varnishes [5]. The purpose was to reduce the duplication of standards activities.

Automobile manufacturers have developed their own standards, which may incorporate many standards and methods of organizations such as ASTM International. Such private industry standards can and often do differ from one manufacturer to another and are known by their own in-house designations. Usually these standards are available to the public or to vendors so they can develop products that meet the requirements of the industry. Other, usually large scale, manufacturers also have their own standards.

Although the list given in Table 1 is not complete, it should provide guidance to interested parties. Wide varieties of standards can be obtained (purchased) from SAI Global (www.sai-global.com), Beuth Verlag (www.beuth.de), British Standards (www.StandardsUK.com), and many others at international and national sites.

Non-Government Sources

TECHNICAL SOCIETIES

Committee D-1 on Paint and Related Coatings, Materials, and Application of ASTM (See Table 1) has developed an extensive number, more than 670 standards, test methods, practices, and procedures that are concerned with paints and coatings. These standards are published as Vols. 6.01 to 6.04 of the *Annual Book of ASTM Standards.* They are also available as separate standards. Standards that relate to the ASTM test methods, procedures, and guides related to the radiation curing of coatings have been published and are

[3]ISO is a nongovernmental organization. This is a network of the national standards of 157 countries with one member per country. The organization is coordinated by a Central Secretariat in Geneva, Switzerland, and it acts as a bridging network that can obtain consensus on solutions that meet both the requirements of business and needs of society.

TABLE 1—Selected organizations/sources that are concerned with specifications and standards

Organization	Abbreviation	Mailing Address	Telephone	FAX	E-mail Address	Web Address, http://www.
ASTM International	ASTM	100 Barr Harbor Drive West Conshohocken, PA 19428-2959	610-832-9500	610-832-9555	service@local.astm.org	astm.org
American Architectural Manufacturers Association	AAMA	1827 Walden Office Square, Suite 550 Schaumburg, IL 60173	847-303-5664	847-303-5774	See Website for Various	aamanet.org
American Association of State Highway & Transportation Officials	AASHTO	444 No. Capitol St. NW Suite 249 Washington, DC 20001	202-624-5800	202-624-5806	info@aashto.org	transportation.org
American Institute of Architects	AIA	1735 New York Ave., NW Washington, DC 20006	800-AIA-3837 202-626-7300	202-626-7547	infocentral@aia.org	aia.org
American National Standards Institute	ANSI	25 West 43rd Street 4th Floor New York, NY 10036	212-642-4900	…	info@ansi.org	ansi.org
British Standards Institution	BSI	Good Relations Holborn Gate 26 Southampton Bldgs. London WC2A 1PQ UK	+44 (0) 20 7861 3188	+44 (0) 20 7861 3131	cservices@bsiglobal.com	bsi-global.com or StandardsUK.com
Canadian General Standards Board	CGSB	Place du Portage 11/6B1 11 Laurier Street Gatineau, Quebec	819-956-0425 800-665-2472	819-956-5644	See Website for Various	Ncr.cgsb-ongc@pwgsc.gc.ca
China Association for Standardization	CAS	. . .	010-68033227/ 68048948	. . .	cas@china-cas.com	china-cas.com
Construction Specifications Institute	CSI	99 Canal Center Plaza, Suite 300 Alexandria, VA 22314	800-689-2900	703-684-8436	csi@csinet.org	csinet.org
French Standards Organization	AFNOR	11, Avenue Francis de Pressensé 93571 Saint-Denis La Plaine CEDEX (France)	+33 01 41 62 80 00	+33 01 49 17 90 00	webmaster@email.afnor.fr	afnor.org
German Institute for Standardization	DIN	DIN Deutsches Institut für Normung e.V. Burggrafenstrasse 6 19787 Berlin, Germany	+49 30 2601-0	+49 30 26011231	See Website for Various	din.de
Global Engineering Documents	GED	14 Inverness Way East Englewood, CO 80112	303-397-7956 800-854-7179	303-397-2740	global@iha.com	global.ihs.com

(Continued)

TABLE 1—Selected organizations/sources that are concerned with specifications and standards (Continued)

Organization	Abbreviation	Mailing Address	Telephone	FAX	E-mail Address	Web Address, http://www.
IHS Group	IHS	15 Inverness Way East Englewood, CO 80112	800-716-3447 + 1-303-397-2896	800-716-6447 + 1-303-3972410	info@his.com	ihs.com
International Organization for Standardization	ISO	1 Rue de Varembé Case Postale 56 CH-1211 Geneva 20 Switzerland	+41 22 749 0111	+41 22 733 3430	See Website for Various	iso.org
Japanese Industrial Standards	JIS	1-3-1 Kasumigaseki Chiyoda-ku Tokyo 100-8901 Japan	. . .	. . .	jisc@meti.go.jp	jisc.go.jp/eng
Maple Flooring Manufacturers Association	MFMA	60 Revere Drive, Suite 500 Northbrook, IL 60062	847-480-9138	847-480-9282	mma@maplefloororg	maplefloor.org
National Association of Corrosion Engineers	NACE	1440 South Creek Drive Houston, TX 77218	713-492-0535	. . .	msd@mail.nace.org	nace.org
National Association of Pipe Coating Applicators	NAPCA	AmSouth Bank Building 333 Texas St., Suite 717 Shreveport, LA 71101	318-227-2769	318-222-0482	. . .	napca.com
National Institute of Building Sciences	NIBS	1090 Vermoint Avenue, NW, Suite 700 Washington, DC 20005	202-289-7800	202-289-1092	nibs@nibs.org	nibs.org
Society of Automotive Engineers	SAE	SAE World Hqtrs. 400 Commonwealth Dr Warrendale, PA 15096	877-606-7323 724-776-4970	724-776-0790	customerservice@sae.org	sae.org
Standardization Admin.of the People's Republic of China	SAC	Zhichun Road, No. 4 Haidian District Beijing, China 100088	+86-10-62000675	+86-10 -62033737	webmaster@sac.gov.cn	sac.gov.cn
Standards Australia	SA	286 Sussex Street Sydney, NSW, 2000 Australia	+61 2 8206 6000	. . .	mail@standards.org.au	standards.org.au
Steel Structures Painting Council	SSPC	40 24th Street, 6th Floor Pittsburgh, PA 15222	412-281-2331 877-281-7772	412-281-9992	See Website for Various	sspc.org
Swedish Standards Institute	SIS	SE 118 80 Stockholm, Sweden	+46 8 555 520 00	+46 8 555 520 01	info@sis.se	sis.se
Underwriters Laboratories, Inc.	UL	333 Pfingsten Road Northbrook, IL 60062	847-272-8800	847-272-8129	See Website for Various	ul.com
United States General Services Administration	GSA	Federal Supply Service, Supply Stds. Division Arlington, VA 22202	703-605-2567	703-605-9856 or -9855 or -9852	See Website for Various	fss.gsa.gov/pub/fedspecs/

available in soft-cover book or CD-ROM format [6]. Other ASTM committees have developed a myriad of tests, some of which are related to or have an impact on the paint and coatings industry and are available in other volumes of the *Annual Book of ASTM Standards*. Many specifications and standards of other national and international organizations list ASTM documents as the necessary requirement for approval.

The American Architectural Manufacturers Association (AAMA) publishes standards for architectural products including organic coatings for aluminum. The American Association of State Highway and Transportation Officials (AASHTO) has developed standards that deal with highway-marking materials, highway materials of construction, bridge construction and maintenance, and other related products. The Maple Furniture Manufacturers Association (MFMA) publishes specifications and standards for wood flooring and a list of conforming floor-finish products.

The National Association of Corrosion Engineers (NACE) has developed standards that deal with corrosion testing, selection of corrosion-resistant materials, and the use of coatings to reduce corrosion. Their documents include standards for surface preparation, corrosion control, coating materials, and selection, application, and testing of coatings and paints. They also develop standards in cooperation with the Steel Structures Painting Council (SSPC). This latter group deals in the same type tests as NACE and includes quality control and contractor qualification standards and specifications.

The Construction Specifications Institute (CSI) has developed several "SpecGuides" that are used as part of construction documentation that deals with the preparation of technical specials for paints, coatings, and application [2]. The National Institute of Building Sciences (NIBS) has developed a powerful electronic database termed the *Construction Criteria Base* that includes the complete construction guide specification of most federal government departments and agencies as well as those of many nongovernment organizations. Model building codes are also accessible in this database, which is available in CD-ROM format from NIBS (Table 1). This consolidated system includes full copies of supporting documentation and the software needed to develop contract specifications for projects including:

Applicable codes and regulations.

Construction guide specifications of major military departments and civil agencies.

Design and estimating guidance documents.

Materials, testing, and processing documents.

Product data, available in full-color graphics.

Built-in software for search and processing functions. Military and federal specifications and standards, commercial item descriptions, and referenced nongovernment specifications and standards are accessible in the *Construction Criteria Base*.

AUTOMOTIVE INDUSTRY

The automotive specifications and testing area is complex, and numerous standards have been either adopted from standards developed by private, technical, or governmental organizations or developed within their own companies. Snowwhite [7] has given an overview of the performance requirements for automotive coatings and presents a general specification for interior and exterior automotive coatings in North America. The general requirements include physical properties, general film and coatings properties, durability, and chemical resistance and these are specified by 60 tests or test methods to meet these requirements. The listing is of documents by ASTM International, Society of Automotive Engineers, Chrysler, Ford, and General Motors.

TESTING LABORATORIES

Although it is left to individuals to decide on which laboratory to use and what standards to measure them by, one method is to determine if a given laboratory has a quality assurance program and the management to meet international standards is to ascertain their accreditation. There are two accrediting agencies for testing laboratories, and these are:

- NVLAP, National Voluntary Laboratory Accreditation Program, that is carried out under the auspices of the United States Department of Commerce
- A2LA, American Association of Laboratory Accreditation

It is beyond the scope of this chapter to describe the many testing laboratories that exist nationally and internationally. Readers can find many such organizations by sourcing the Internet or the open literature.

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Part 17: New Coating Technology

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Radiation Curing of Coatings

Joseph V. Koleske[1]

INTRODUCTION

RADIATION CHEMISTRY AND ITS RELATIONSHIP TO the coating and paint technology industry involves the application of a low viscosity mixture principally comprised of reactive monomers and oligomers but containing, as well, conventional coating additives such as fillers, colorants in the form of dyes or pigments, surfactants, and so on to a substrate and exposing them to a radiation source—particularly ultraviolet (UV) or electron beam (EB) radiation—for very short periods of time. When required, as in UV radiation curing, a small amount of photoinitiator is included in the formulation. When exposed to the radiation source, the mixture of materials is almost instantaneously converted into an effectively cross-linked, high quality coating or other product [1].

Radiation technology, as applied to coatings, had its infancy in the late 1960s and early 1970s when governmental regulation began requiring that solvent emissions from paint and coatings be decreased and regulated. At that time, most coatings were formulated with high molecular weight polymers and large amounts (often 80 % or more) of inexpensive solvents and cosolvents that for the most part were emitted to the atmosphere. Regulation increasingly forced companies to decrease these emitted solvents, and it was in this environment that new technologies such as high solids, powder, and radiation-cured coatings were born. Changes were slow to come into being in the stodgy (at that time) paint and coatings business, but today each of these methods of formulation and curing has become an important part of the coating and paint business.

RADTECH International[2] is an association for ultraviolet and electron beam technology as related to radiation-cured products for the adhesive, coating, ink, paint, and related industries. This group publishes a report (RadTech Report) five times a year, conducts UV/EB technology expositions and conferences and publishes the conference proceedings, has various publication and information available, and maintains a link between the various facets of the UV/EB industry (see www.radtech.org).

CURING EQUIPMENT

Electron Beam Systems

An electron beam is a stream of electrons that is emitted from an electron beam gun and in which the electrons are moving at essentially the same speed and in the same direction. Almost all substances absorb electrons, which are small atomic sized, high energy, negatively charged particles. Such radiation is known as ionizing radiation. The electrons are capable of penetrating into and through a substrate and/or a coating to reach, for example, an adhesive, a pigmented paint, or other opaque liquid and thus effect polymerization and cure of the appropriate chemical formulation [2,3].

Basically, the sequence of events in the cure process is as follows. While the stream of electrons is passing through the material to be cured, individual electrons are able to collide with an electron that is in a molecule of the uncured compounds. This collision can result in removal of an electron from the molecule and thereby generate a free radical. Such free radicals are able to react with ethylenic unsaturation in the formulation, as is found in acrylates, and initiate the sequence of polymerization, propagation, and termination with the result a cured, cross-linked material. A photoinitiator, which is required in ultraviolet radiation polymerization systems, is not required to initiate polymerization when electron beam technology is used.

In a general sense, there are two types of electron beam processors used in curing systems [4]. The swept or scanned beam type processors involve generation of a relatively narrow beam of electrons that are accelerated in a vacuum that is maintained in the high voltage section of the device. The beam of electrons is then moved, swept or scanned, across a metal foil window by means of an electric or magnetic field. From the window, the beam is sent to the process area where it contacts the reactive, liquid coating and polymerization is induced. The curtain or filament beam processors are single or multiple linear filament emitters with the filament(s) located parallel to the direction of "to-be cured" product movement. A broadband or curtain of electrons is sent to the process area where polymerization is initiated and polymerization, as well as termination, takes place. Since oxygen can inhibit polymerization of free radical systems, it is important to inert the process area with a compound such as nitrogen to obtain good surface and through cure [5].

Ultraviolet Radiation Systems

One of the distinctions between electron beam curing and ultraviolet radiation curing is the requirement for a photoinitiator to be used in the later curing method. Photoinitiators are compounds that are stable until exposed to ultraviolet radiation of one or more wavelengths. When

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TABLE 1—Examples of homolytic fragmentation type photoinitiators

Compound	Appearance	Absorption, (nm)
2,2-Diethoxyacetophenone	White solid	242–325
1,Hydroxycyclohexylphenyl ketone	White solid	208, 245
n-Butylbenzoin ethers (mixture)	Light yellow liquid	246–325
2,2-Dimethyl-2-hydroxyacetophenone	Clear liquid	265–280, 320–335
Benzil dimethyl ketal	White solid	220, 254–335

exposed the compounds absorb the radiation and degrade to form a species that is capable of initiating polymerization—usually free radicals or cations, the type depending on the nature of the system employed. Recently, Lapin [6] developed a comparison of UV and EB for printing and packaging applications and described in detail the fundamental differences in the two technologies.

If coatings are to be cured on flat stock, the curing equipment is relatively simple in nature. An ultraviolet radiation source and a means of cooling the lamp or lamps that serve as the source. The system is comprised of a power supply, radiation source, reflectors, and a conveyor [7]. The power supply is the control device within the system and either stepped or variable ballast systems are used for energy and intensity comparisons [8]. If three-dimensional objects are to be coated, special configurations of the radiation source and reflectors and/or a means of rotating the object when in contact with the radiation are used [9].

There are two general types of ultraviolet radiation sources [10], namely mercury vapor lamps and xenon lamps. Mercury and mercury-doped vapor lamps are widely used because when mercury is vaporized and ionized, it is one of the richest sources of ultraviolet radiation. Doping the mercury alters the transmission spectrum produced by the lamp or bulb, and it is used to efficiently interact with particular photoinitiators. Compounds such as the halides of antimony, cobalt, iron, silver, and others are used alone or in combination as the materials for doping mercury. The lamps are sealed, transparent quartz bulbs that are of three general types—low pressure, medium pressure, and high pressure. Medium pressure electrode and electrodeless lamps are the most widely used industrial ultraviolet radiation sources in the paint and coating industry.

The reflectors [11] have a variety of geometries such as elliptical, diverging, converging, parabolic, and others. The reflectors may be interfocused wherein the radiation is spread over a relatively large area or they may be focused wherein the radiation is concentrated into areas of high intensity. The large area systems are often used when three-dimensional objects are cured.

CHEMISTRY

Photoinitiators

Compounds that absorb ultraviolet radiation and are raised to an excited level from which they photolyze or degrade directly or indirectly into free radicals or cations are termed photoinitiators. The free radicals or cations become the polymerization initiating species and cause very rapid polymerization of photocurable formulations based on a variety of chemistries such as acrylates and methacrylates, polyenes/thiols, and styrene/unsaturated polyesters, all of which are cured by a free radical mechanism and cycloaliphatic epoxide/polyol and vinyl ether systems which are cured by a cationic mechanism. Vinyl ethers can be polymerized with either free radicals or cations and thus are ingredients that can be used in combination-cure systems.

TABLE 2—Examples of hydrogen abstraction type photoinitiators

Compound	Appearance	Absorption, (nm)
Benzophenone	White solid	250–350
Isopropylthioxanthone	Pale cream solid	~320–340
2-Chlorothioxanthone	Pale yellow solid	360
4-Methylbenzophenone	White solid	—
Thioxanthone	Solid	—

Free Radical Photoinitiators

The two main types of photoinitiators that form a species capable of initiating polymerization of ethylenically unsaturated compounds are the homolytic fragmentation process type (Norrish Type I) and the hydrogen abstraction process type (Norrish Type II). The homolytic fragmentation or α-cleavage compounds directly form free radicals capable of initiating polymerization [12]. The absorbed radiation causes bond breakage to take place between a carbon atom and an adjacent carbonyl group and a free radical is formed. Hydrogen abstraction type compounds function through a bimolecular reaction process [13]. They are activated with radiation and form free radicals by electron extraction or hydrogen abstraction from a second compound that is termed a synergist. After this process, the second compound becomes the actual initiating species. Examples of the homolytic fragmentation type compounds are given in Table 1 and of the hydrogen abstraction type are given in Table 2.

Synergists are compounds that have a carbon atom with at least one hydrogen atom in the alpha position to a nitrogen atom. For example, dimethylethanolamine has an alpha carbon atom in the methylene group next to the nitrogen group. Triethylamine has three alpha carbon atoms located on the three methylene groups next to the nitrogen group. Synergists are usually tertiary amines, but ureas and amides have been used as well as particular alcohols and

TABLE 3—Some common low molecular weight synergists

Specific Compounds
2-Ethylhexyl-p-dimethylaminobenzoate
Dimethylethanolamine
N,N-Dimethyl-p-toluidine
Triethanolamine
Triethylamine

ethers. As mentioned earlier, after the bimolecular reaction, the synergist becomes the initiating species. Examples of synergists are given in Table 3.

Oxygen Inhibition

Radiation excited or activated molecules are quenched and markedly decreased in activity or made inactive by oxygen which, of course, is present in all air environments [14]. Such quenching results in inhibition of polymerization in formulations that involve fragmentation-type photoinitiators. Free radicals will react with propagating molecules and termination with accompanying low molecular weight and poor properties result. Oxygen inhibition can be circumvented by curing in an inert atmosphere, addition of oxygen scavengers or waxes, use of shielding films, dye sensitizers, surface active initiators, or high photoinitiator concentrations, and increasing ultraviolet radiation intensity [1].

Cationic Photoinitiators

Cationic photoinitiators are onium compounds that are excited by ultraviolet radiation and then photolyze to form Lewis or Bronsted acids that will rapidly polymerize cycloaliphatic epoxides. In the photolysis process of these compounds, free radicals are also formed and therefore, both epoxides and ethylenically unsaturated compounds can be polymerized in a dual-cure process. Watt [15] has published a detailed study of the cationic curing of epoxides, particularly cycloaliphatic epoxides, over the period of 1965 to 1981.

Diazonium Salts—Lewis Acids

Although presently cationic photoinitiators are used to generate Bronsted or protonic acids from sulfonium or iodonium salts, cationic curing of coatings began with the use of diazonium-type photoinitiators that generated Lewis acids. A variety of anions were used including PF_6^-, $SbCl_6^-$, SbF_6^-, BF_4^-, and AsF_6^- [16]. In a general sense, when radiated with ultraviolet radiation sensitive compounds such as aryl hexafluorodiazonium phosphorous, will photolyze and form gaseous nitrogen, an aryl fluoride, and phosphorous pentafluoride. The latter compound is a Lewis acid and it will initiate the polymerization of epoxides, particularly cycloaliphatic epoxides, into a highly crosslinked network.

Diazonium salt-based radiation cure was developed by American Can Corporation and was known as "Americure." At the time, the early 1970s, this technology was considered a major breakthrough in high solids coatings development. However, the technology had two major deficiencies that inhibited large-scale commercial development. As noted above, during photolysis nitrogen gas was generated. If the coating films formed were greater than about 5 to 10 μm in thickness, nitrogen bubbles were trapped in the "instantaneously" cured film and they were readily visible to the naked eye. The second deficiency involved an instability of the diazonium salts in formulated systems that comprised cycloaliphatic epoxides, other epoxides, and optional additives such as polyols, surfactants, etc. These two factors were serious deterrents to commercial development, and when this was coupled with the onium salt introductions the demise of Americure was assured.

Iodonium and Sulfonium Salts—Bronsted Acids

Compounds that contain an element with an unshared pair of electrons, such as sulfur and phosphorous, can form onium salts. For example, a sulfide, R_2S, can react with an alkyl halide, CH_3I, to form a sulfonium salt, $R_2CH_3S^+I^-$. The commercial onium salts are known as aryl sulfonium and aryl iodonium salts and have the counter ion MF_6^-, where M is antimony or phosphorous [17,18]. Usually, the sulfonium salts were known as triarylsulfonium salts which was a misnomer, since these compounds are complex mixtures of sulfonium salts with the prominent species and have the following generalized structures:

$$Ar - S - (Ar_3)S^+(MF_6)^- \text{ and } (MF_6)^-S^+(Ar_3) - S - (Ar_3)S^+(MF_6)^-$$

The iodonium salts are diaryl compounds with the same counterions and the generalized structure of $I^+(Ar_2)^-$ and $I^+(MF_6)^-$. When these compounds are radiated with ultraviolet radiation, they photolyze and form Bronsted or protonic acids, $(PF_6)^-$ or $(SbF_6)^-$. The protonic acids cause rapid polymerization of cycloaliphatic epoxides alone or in combination with hydroxyl bearing compounds such as polyols, glycols, and alcohols. Although both protonic acids cause very rapid polymerizations, the antimony compound causes the most rapid polymerization and iodonium salts are more rapid in their cure ability than sulfonium salts.

The onium salt photoinitiators are available in the United States, Europe, and Asia under a variety of trade names from both manufacturers and distributors. Various physical and chemical characteristics, as well as ultraviolet radiation absorption maxima for these compounds and other cationic photoinitiators, has been published by Gaube [19]. While free radical systems can be inhibited by atmospheric oxygen, the cationic systems are not inhibited in this manner and thus do not require an inert atmosphere to cure well.

Acrylates—Monomers and Oligomers

Although other free radical-based formulations involved with ethylenically unsaturated molecules can be used for radiation curing of coatings, this brief chapter will be concerned with radiation curing of molecules such as acrylates and methacrylates—preferably acrylates. Other chemistries that are in use or that have been used in free radical initiated systems [1] include unsaturated polyester/styrene systems [20,21], polyenes/thiol systems [22–24], and vinyl ethers [25].

Acrylates are ethylenically unsaturated compounds of the general form

$$CH_2 = C(R)COOR'$$

where R is hydrogen for an acrylate and methyl for a methacrylate and R′ can be any one of a number of groups such as linear and branched alkyl, 2-phenoxyethyl, isonorbornyl, hydroxyalkyl acrylate, and many more. The term acrylate is often taken to mean both acrylates and methacrylates, but since acrylates cure more rapidly than methacrylates, in radiation cure it should be stated as one or the other. There are many types of acrylates and related compounds than can be used in radiation-cure formulations and these include:

- Monofunctional acrylates as described above.
- Difunctional and higher functionality acrylates.

- Oligomeric acrylates of varying molecular weights and viscosities.
- Reactive diluents such as N-vinyl-2-pyrrolidone and vinyl ethers.

Each type has a particular function [1] in the formulation. Monofunctional acrylates are used to decrease viscosity; di- and higher functionality acrylates are used to provide crosslinking and to give rapid molecular weight build; oligomeric acrylates provide flexibility and toughness to the final cured films; and the reactive diluents provide a way of decreasing viscosity with reactive compounds that co-cure into the final product.

Difunctional acrylates include products such as 1,4-butanediol diacrylate, diethyleneglycol diacrylate, neopentyl glycol diacrylate, tripropylene glycol diacrylate, and many others. Higher functionality acrylates include compounds such as ethoxylated trimethylolpropane triacrylate, pentaerythritol triacrylate, trimethylolpropane triacrylate, pentaerythritol tetraacrylate, and so on.

Oligomeric acrylates are of two types, epoxy acrylates or urethane acrylates. These compounds are of quite high molecular weight and viscosity and for this reason are often modified with low molecular weight mono or difunctional acrylates to reduce viscosity and thus improved handling characteristics during formulation and application to a substrate. Urethane acrylates are of two basic types that depend on whether an aliphatic or an aromatic isocyanate is used in preparation. These can be subclassified by the type of polyol that is used to make the oligomeric compounds—polyester or polylactone polyols are more weatherable than poly(propylene oxide) polyols. Poly(tetramethylene oxide) polyols can offer other specific and useful characteristics.

Other oligomeric and/or polyfunctional acrylates include the acrylated oils that can be prepared from what are known in the coating industry as drying oils (see Chapter 4 of this Manual). The oils are epoxidized triglycerides as are found in linseed oil, palm oil, soybean oil, sunflower seed oil, palm oil, and others. Some of these oils and their epoxidized versions have uses other than in radiation curing as in plasticization of poly(vinyl chloride) and other polymers.

Acrylates can be eye and skin irritants, toxic, and, in certain instances, human sensitizers. These factors vary with the particular acrylate and with molecular weight and it is important that Material Safety Data Sheets and other information be consulted regarding specific hazards and precautions about these and any other chemicals that are used in coating, paint, adhesive, ink, and other formulations. Suppliers should have, or can obtain, any desired information about their products and usually represent an important, up-to-date source of safety and handling data.

Cycloaliphatic Epoxides

Cycloaliphatic epoxides form the basis of almost all cationic curing formulations. They are used in combination with the above described onium salt photoinitiators, polyols of various molecular weights, and other typical formulation ingredients. Such systems offer certain advantages over free radical curing acrylate systems. They have improved adhesion because there is low shrinkage of about 2 to 4 % during the photopolymerization reaction that takes place during cure. Also, the systems are all relatively low viscosity liquids that are miscible—factors that lead to easy handling characteristics. There is no oxygen inhibition exhibited with cationic systems.

The main cycloaliphatic epoxide used is 3,4-epoxycyclohexylmethyl-3,4-epoxycyclohexanecarboxylate. A moderately higher viscosity diepoxide that is also used is bis(3,4-epoxycyclohexylmethyl)adipate. This latter epoxide can add a degree of flexibility to a final product. Epoxidized oils such as soybean oil epoxides, Vernonia oil (a naturally occurring epoxidized oil), and others can be used. Monoepoxides are also useful as viscosity reducers, and they do not act as chain-growth terminators because after the epoxide reacts into a growing chain, it leaves a hydroxyl group on the residue and this group is capable of reacting with other epoxide groups to maintain the integrity of the growing chain. There are other available and developmental products that can be found in the literature.

The polyols are added to formulations to provide flexibility and toughness. Most, if not all, polyols can be used and these include polyester polyols, polyether polyols, poly(tetramethylene oxide), glycols, and so on. By balancing end-use requirements and the amount of polyol used, a wide variety of physical properties can be achieved.

Vinyl Ethers

Vinyl ethers are interesting in that they can be cured by either free radical [25] or cationic means [26]. These compounds have the general structure

$$CH_2 = C(H)ORX$$

wherein R can be alkyl, ethylene glycols, cyclohexanedimethanol, and similar compounds and X can be another vinyl ether, hydroxyl, propylene carbonate, etc. Examples are butanediol divinyl ether, diethylene glycol divinyl ether, hydroxybutylvinylether, dodecylvinylether, etc. One very useful attribute of vinyl ethers in cationic systems was its function as an effective reactive viscosity reducer. Other advantages include good miscibility with other compounds, high conversion rates of the vinyl functionality, high cure speeds, low odor for many of the vinyl ethers, usually low toxicity, and no oxygen inhibition [27].

Vinyl ethers have also been investigated in donor/ acceptor or charge-transfer polymerizations [28], been developed into oligomeric urethane vinyl ethers [29] and ester vinyl ethers [30], and used in silicone-vinyl ether blends [31].

Radiation-Curable Powder Coatings

This topic is dealt with in another chapter of this manual (see Chapter 80). Also, generalized information can be found in Ref. [1].

Testing

A broad variety of tests that are useful in testing radiation-cured coatings, adhesives, and inks have been consolidated into one publication by ASTM International [32]. Specific ASTM documents that have been developed for the radiation-cure area include topics such as package stability, cure times, and volatile content along with standard terminology related to radiation measurement and dosimetry and a practice for exposing adhesive specimens to ionizing radiation. These documents are listed in Table 4.

There is a ten-day test requirement for a moisture resistance test in Military Specification-I-46058C (Method

TABLE 4—Methods for examining and testing radiation-cured coatings, adhesives, and inks

ASTM	Standard
E170	Terminology Relating to Radiation Measurements and Dosimetry
D1879	Practice for Exposure of Adhesive Specimens to Ionizing Radiation
D3732	Practice for Reporting Cure Times of Ultraviolet-Cured Coatings
D4144	Test Method for Estimating Package Stability of Coatings for Ultraviolet Curing
D5403	Test Methods for Volatile Content of Radiation Curable Materials

106 of Mil Std 202F). This long time period is tedious and time consuming when a number of potential candidates are screened. An in-house screening test was developed to examine and ascertain strong, potential candidates that could be examined with the long test period of the Mil Spec [33]. In the test, a Soxhlet extraction apparatus is modified and a raised glass platform is placed inside a Soxhlet extraction chamber. The test specimen is placed in a vertical position on the glass platform. Test specimens used were radiation-cured "Y" pattern boards as specified in the Mil Spec for conformal coatings, but other types of specimens could be used for other end uses. Water and a few boiling chips are placed in the flask portion of the device and heated. When the water boils, the exposed test specimen is subjected to a condensing humidity at a temperature of about 95 to 98°C. The test can be carried out for as long as desired and successfully screened candidates can be tested according to the military specification. The test is harsh, but useful in eliminating many unsatisfactory candidates. Details of the test and test equipment are explained in the cited reference.

End Uses

Some of the early successes of radiation curing of coatings were in the printing and packaging areas. That area remains of great importance to the radiation curing because it is a high volume end use, and the technology is easily adaptable to the packaging and printing area. End use industries served by ultraviolet and electron beam radiation curing include adhesives, aerospace and defense; automotive OEM, collision repair, refinishing and components; building products, composites; electronics including conformal coatings, printed circuit board coatings, component adhesives; metal finishing, medical devices, plastics, packaging including food packaging, UV inkjet inks, UV powders, and wood finishing. Today, a listing of many particular end uses can be found on the Internet and specifically at RADTECH's website (www.radtech.org).

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Powder Coating

Joseph V. Koleske[1]

INTRODUCTION

ALTHOUGH THE FIRST POWDER COATING WAS developed in the late 1950s, it was not until the early 1970s that governmental regulations and the "80 % solids rule" brought about what was termed the "powder explosion." Requirements indicated that liquid coatings were to have markedly decreased volatile organic content, and this provided the impetus for companies to look into new coating technologies—powder coating, radiation cure, and high solids. It was a difficult task for entrenched companies to change and product manufacturing, equipment costs, and lethargy slowed progress. Solvents were inexpensive and it was easy to apply low-solids, solvent-based coatings. But, a number of old and newly established companies continued with development of the new systems, and today these three new technologies have a strong position in the coatings industry. Numerous industrial, consumer, and automotive finishes, for a broad range of products, are applied with powder coating technology. Powder coating has grown over the past few decades, and today it is a widely used technology that has captured about 12–15 % of the finishing market.

Powder coatings are dry, effectively 100 % solids materials that are supplied as free-flowing powders. The final coatings are either thermoplastic or thermoset in character. They differ from conventional coating systems in that a solvent is not needed to keep the polymeric binder, pigment and/or filler, and additives in a combined state for application and film formation. They are mainly applied by a thermal (fluid bed) method, an electrostatic (spray) method, or a combination of thermal and electrostatic methods. After application, the powder is heated and the particles melt and flow to form a hard protective and/or decorative coating for a wide variety of consumer and industrial end uses.

Although powder coatings provide very high quality finishes for metal, plastic, and wood substrates, they have other important advantages in today's marketplace. These advantages are often described within the industry as the Five E's, and they should be kept in mind when contemplating the use of powder coatings:

- Economy
- Efficiency
- Energy savings
- Environmental compliance
- Excellence of finish.

POWDER PREPARATION

Powder coatings in a general sense are prepared by a melt-mix, grind, and sort operation. The appropriate polymer, pigments, and additives along with cross-linking agents, if thermoset coatings are involved, are weighed into a premixer that ensures a homogeneous dry blend. At this point in the process, adjustments for color matching or other properties can be made. The premix is sent to an extruder wherein component dispersion and melt mixing take place. The extruder barrel can be heated and additional thermal energy is supplied to the mass through viscous heat generated from the mechanical screw system that drives the extruder.

The melt blended extrudates are usually discharged from the extruder in the form of a thin sheet, rapidly cooled, and then crushed or kibbled into small chips that are suitable for grinding. The chips, and usually a dry-flow additive, are then ground in a pin-disk mill, for example, to form a fine powder. This powder may be sieved to remove large-size particles or classified to remove particles below a selected size. Powders are usually processed into specified particle size distributions or ranges for specific applications and then packaged.

Although not practiced commercially, powders have been prepared by spray drying a solution of the premix into an inert atmosphere and, optionally, into a nonsolvent [1]. Such a process requires particular safety considerations including carrying out the operation in an inert atmosphere, properly grounding, etc. The powder produced by this process was micronized in a fluid energy mill to reduce particle size and yields a free flowing powder—again a process that currently has only limited usage. Recently, a "minisuspension" polymerization process that directly forms particles with spherical morphology and narrow particle size distributions has been described [2]. Such a direct process eliminates the numerous energy intensive steps involved in conventional powder preparation. This process quite probably is not widely used.

POWDER APPLICATION

Fluid Bed Technology

Fluidized-bed powder coating technology involves dipping preheated objects into a vat or tank that has a porous bottom plate. Low pressure air is supplied by means of a plenum located below the plate. The rising air suspends the powder in a liquid-like state. The fluidized powder adheres to the heated part and begins to flow and coalesce. After a predetermined immersion time, the part is removed and the melt–flow process continues. Usually the coated part is placed in an oven and the melt–flow process is completed resulting in a smooth, continuous, durable coating.

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TABLE 1—ASTM test methods, practices and specifications documents applicable to powder coating

Reference	Title
ASTM A882	Standard Specification for Filled Epoxy-Coated Seven-Wire Prestressing Steel Strand
ASTM A934	Standard Specification for Epoxy-Coated Prefabricated Steel Reinforcing Bars
ASTM A950	Standard Specification for Fusion-Bonded Epoxy Coated Structural Steel H-Piles and Steel Piling
ASTM A972	Standard Specification for Fusion Bonded Epoxy-Coated Pipe Piles
ASTM B117	Standard Practice for Operating Salt Spray (Fog) Apparatus
ASTM B368	Standard Method for Copper-Accelerated Acetic Acid-Salt Spray (Fog) Testing (CASS Test)
ASTM D2967	Standard Test Method for Corner Coverage of Powder Coatings
ASTM D3415	Standard Practice for Identification of Waterborne Oils
ASTM D4217	Standard Test Method for Gel Time of Thermosetting Coating Powder
ASTM D4242	Standard Test Method for Inclined Plate Flow for Thermosetting Coating Powders
ASTM D522	Standard Test Methods for Mandrel Bend Test of Attached Organic Coatings
ASTM D523	Standard Test Method for Specular Gloss
ASTM D3415	Standard Practice for Identification of Waterborne Oils
ASTM D714	Standard Test Method for Evaluating Degree of Blistering of Paints
ASTM D870	Standard Practice for Testing Water Resistance of Coatings Using Water Immersion
ASTM D1308	Standard Test Method for Effect of Household Chemicals on Clear and Pigmented Organic Finishes
ASTM D1654	Standard Test Method for Evaluation of Painted or Coated Specimens Subjected to Corrosive Environments
ASTM D1725	Standard Test Method for Viscosity of Resin Solutions
ASTM D2247	Standard Practice for Testing Water Resistance of Coatings in 100 % Relative Humidity
ASTM D2794	Standard Test Method for Resistance of Organic Coatings to the Effects of Rapid Deformation (Impact)
ASTM D3170	Standard Test Method for Chipping Resistance of Coatings
ASTM D3359	Standard Test Method for Measuring Adhesion by Tape Test
ASTM D3363	Standard Test Method for Film Hardness by Pencil Test
ASTM D4060	Standard Test Method for Abrasion Resistance of Organic Coatings by the Taber Abraser
ASTM D5965	Standard Test Methods for Specific Gravity of Coating Powders
ASTM D6441	Standard Test Methods for Measuring the Hiding Power of Powder Coatings
ASTM D7378	Standard Practice for Measurement of Thickness of Applied Coating Powders to Predict Cured Thickness
ASTM F2408	Standard Specification for Ornamental Fences Employing Galvanized Steel Tubular Pickets
ASTM G154	Standard Practice for Operating Fluorescent Light Apparatus for UV Exposure of Non-metallic Materials
ASTM G155	Standard Practice for Operating Xenon Arc Light Apparatus for Exposure of Non-metallic Materials.
ISO 8130-2	Coating Powders—Part 2: Determination of Density by Gas Comparison Pyknometer
ISO 8130-3	Coating Powders—Part 3: Determination of Density by Liquid Displacement Pyknometer
ISO 8130-6	Coating Powders—Part 6: Determination of Gel Time of Thermosetting Coating Powders at a Given Temperature
ISO 8130-11	Coating Powders—Part 11: Inclined-plane Flow Test

Coatings applied by this process are thicker than those from other powder application processes. Part complexity plays a role in coating quality, since areas that trap excess powder or entrap air can lead to excessive build-up or uncoated/thin regions. Often dedicated fluid beds are used for each color, since color changes involving clean up may be time consuming. Thermoset or thermoplastic coatings can be used with the fluid bed process.

Electrostatic Fluidized Bed

This process involves dipping a grounded part into a vat of air-fluidized powder [3–5]. The fluidized bed in this case has a high voltage, direct current grid installed within the plenum. A cloud of electrostatically charged powder particles is generated in the tank [3]. These particles are attracted to and wrap around a part that is at ground potential. Thinner coatings than those obtained with conventional fluid bed technology are obtained with the electrostatic fluidized bed, and they are similar in thickness to those obtained with the electrostatic spray process. The parts to be coated can be un-heated or preheated, but usually preheating is not required. Small parts can be coated with this process.

Electrostatic Spray

Electrostatic spray powder coating involves air fluidization of the powder in a small bed, transporting the fluidized powder by means of a hose to a spray gun, and imparting an electrostatic charge to the powder by means of a high voltage, direct current or by frictional forces in the gun. The charged powder is directed at the part to be coated, which is at ground potential. Such guns can be manually or automatically controlled and can be fixed or reciprocating in nature. The part may be at ambient temperature or heated prior to coating, though it usually is not necessary to preheat the part. The charged powder will wrap around the part and thus coat the entire object. The coated part is then sent to an oven and heated to a melt flow temperature to develop the final coating. If the coating is thermoset in nature, the heating step is conducted in such a manner that melt flow takes place before substantial cross-linking to ensure a smooth coating results. Overspray powder is collected, filtered, and reused. As a result, high material usage of greater than 95 % can result. Electrostatic spray applied coatings are thinner than fluid bed coatings because the charged particles are self-limiting in thickness build-up.

Basically, there are three types of electrostatic spray guns. Corona charging guns are the most widely used. These guns use either internal or external charging to generate a negative charge on the powder. "Tribo" guns charge the powder particles by friction or more specifically by acquiring a triboelectric charge. The positive charge is acquired when the powder rubs along a fluoropolymer tube located in the barrel of the gun. Electrostatic disk or "Bell" guns apply the charge to the particles in the nozzle area as they are fired from the gun toward the grounded part.

CHEMISTRY

A wide variety of polymers can be used to prepare powder coatings. Both thermoplastic and thermoset powders are used. Thermoplastic powders, as well as the films formed from them, can be remelted and reformed, if desired. They are subject to attack by solubilization in the presence of certain solvents. Thermoset powder coatings are formulated with a cross-linking agent, often termed a hardener, that will react with functional groups present on the polymer and an insoluble coating results. Although they are insoluble, thermoset coatings may be swellable in the presence of certain solvents. Once reacted, thermoset powder coatings cannot be remelted and reformed.

A variety of additives can be used in powder coatings, and these usually are dependent on the particular polymer involved. Additives include accelerators, plasticizers, colorants, fillers, extenders, flow control agents, thermal and ultraviolet radiation stabilizers, and the like. Flow control additives are used to facilitate dry powder handling as well as others for melt flow improvement. Melt flow control agents include polyacrylates, silicones, surfactants, and fluorinated alkyl esters.

Thermoplastic Coatings

Thermoplastic polymers include poly(vinyl chloride), vinyl chloride copolymers (see Chapter 15), polyamides, polyesters, poly(vinylidene fluoride), fluoropolymers [2], and polyolefins. Many thermoplastics require base coating with a primer to achieve good adhesion to metal substrates.

Vinyl Powder Coatings

Coatings prepared from poly(vinyl chloride) have excellent chemical and corrosion resistance, hardness, and tensile and dielectric strength. Plasticizers are added to the mix to improve flexibility and toughness and to allow flow-out for smooth films. End uses include dishwasher baskets, lawn furniture, fence posts, shelving, and various wire items such as chain-link fencing. Fluoropolymers include fluorinated ethylene-propylene copolymers, ethylene–tetrafluoroethylene copolymers, poly(vinylidene fluoride) and vinylidene fluoride/hexafluoroproplene copolymers. These polymers can impart good weatherability as well as chemical, dielectric, and heat resistance to a substrate. Some of these polymers can provide coatings that may be cost-effective alternatives to stainless steel and glass linings [6].

Nylon Powder Coatings

Nylon powder coatings have very good abrasion, chemical, and solvent resistance, impact resistance, low coefficient of friction (good lubricity), low toxicity, good thermal resistance, and toughness. Such coatings have relatively poor acid resistance. Nylon coated metal parts are used in rotating and sliding bearing systems and other bearing systems that are used in appliances, farm and textile machinery, relay plungers, and similar items. Other end uses include coatings on meat and other types of hooks, baskets used for degreasing and meat smoking, surgical equipment, and valves. Because of nylon's ability to withstand sterilizing temperatures, hospital equipment coated with nylon can be sterilized numerous times without destructive effects. In the United States, Nylons 11 and 12 are commonly used in these coatings.

Polyolefins

Powder coatings formed from polyethylene and polypropylene have excellent chemical and corrosion resistance to most acids, bases, alcohols, and salts up to temperatures of about 95°C, however, this type of chemistry can be softened by certain greases and oils. Moisture absorption is effectively nil. Properties of polyolefin coatings are dependent on polymer density/degree of crystallinity with properties, in general, improving as density increases. End uses include coatings for a variety of holding racks, glass bottles, pipe hangers, tank lids for containers holding chemicals, certain laboratory tools, and covers for a variety of items.

Thermoset Powder Coatings

Thermoset powder coatings contain a polymer with functional groups such as oxirane, hydroxyl, or similar reactive sites. The cross-linking agent that is to react with these groups must be sufficiently stable to withstand the thermal rigors of compounding and not be reactive until the melt–flow process has taken place during the curing cycle. The compounded powder must also be storage/shipping stable.

Polymers used for thermoset coatings include epoxides such as the diglycidyl ethers of Bisphenol-A, epoxy-polyester hybrids, functionalized acrylics, urethane polyesters, polyester triglycidyl isocyanurate (polyester TGIC), functionalized vinyl chloride copolymers, methacrylate terminated polyesters, vinyl ether capped polyurethanes, and the like. Curing agents include dicyandiamide, solid di- and polyanhydrides, phosphonium compounds, blocked isocyanates,

adipic and succinic acid dihydrazides, as well as many others.

Epoxy powder coatings are often termed "fusion bonded epoxy coatings" (FBE). These are used to coat products such as concrete reinforcement bars (rebars), steel pipe and connections, valves and similar items and thus provide corrosion protection and chemical resistance. Typically, these coatings cure at temperatures of about 150 to 230°C (300 to 450°F).

Radiation-Cured Powder Coatings

In 2001, a publication indicated that a new line of radiation-curable powder coatings was available [7]. The coatings would cure by oven baking at low temperatures of about 100°C for 2 min to melt-flow the coating followed by a five-second ultraviolet radiation exposure to cross-link the coating. These coatings were considered as hybrids of two new technologies—powder coating and radiation curing—since they combine features of both [8–12]. The coatings formed are thermoset in nature. They allow powder coatings to be used on heat sensitive substrates such as plastics and wood. Smooth, adherent, hard, functional and decorative coatings result through two independent processes with flow being promoted by moderate heating and cure by means of cross-linking through ultraviolet radiation.

Chemistries used include unsaturated polyesters based on fumaric or maleic acid and vinyl ether functional polyurethanes, methacrylated urethanes, methacrylated polyesters and epoxy acrylates. Both cationic and free radical ultraviolet radiation cures have been investigated [13]. Benefits, advantages, and chemistry have been detailed in various literature articles [14]. The technology is relatively new, but has current and future promise especially for temperature sensitive substrates such as wood and plastic.

CURING

Thermoplastic powder coatings only require a single heating to melt and flow or "cure" the coating. Thermoset coatings require thermal treatment to effect the cross-linking reaction that insolublizes the final coating.

Four methods are used to cure powder coatings. Gas or electric powered convection ovens that operate at about 140 to 220°C are used to cure coatings on metal substrates. Curing times vary from 30 to 45 min. Infrared ovens operate at higher temperatures of about 160 to 250°C for coated metal substrates and cure times vary from about 1 to 15 min. Combinations of infrared and convection ovens operate at about 140 to 220°C and cure times can vary from about 10 to 25 min. In such curing lines, convection heating follows infrared heating.

The fourth method is used for ultraviolet radiation-curable powder coatings and involves heating in an infrared/ convention oven for about 1 to 3 min at a temperature of about 90 to 120°C to cause melting and flowing. This is followed by ultraviolet radiation for a second or two. The process is used for metal, plastic, and wood substrates.

TESTING

ASTM D3451, Standard Guide for Testing Coating Powders and Powder Coatings, is a summary of numerous ASTM, ISO (International Organization for Standards), and PCI (Powder Coating Institute) documents that are of interest to the powder coating community. The guide does not address test methods developed specifically for the powder coating market, but it does provide guidance to over 100 test methods of general interest.

Specific ASTM documents devoted to powder coating and others that are used by some laboratories are listed in Table 1. Certain of these documents offer options to an investigator. For example, ASTM D5965, Standard Test Methods for Specific Gravity of Coating Powders, has three methods:

- A—for testing coating powders excluding metallic powders. This is a less expensive and less precise determination than that of Method B.
- B—for testing that requires greater precision than test method A, including metallic powders and using helium pycnometry.
- C—for theoretical calculations based on raw material specific gravity. This is a method often used to estimate powder coating coverage at a given thickness.

ASTM D7378, Standard Practice for Measurement of Thickness of Applied Coating Powders to Predict Cured Thickness, has three procedures for measuring dry coating powder thickness:

- A—a procedure that uses rigid metal notched (comb) gages.
- B—a procedure that uses magnetic or eddy current coating thickness gages.
- C—a procedure that uses non-contact ultrasonic powder thickness instruments.

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MAX. Cs	38	168	588	784	1401	78	228	804	869	1827	14	48	128	278	441	1418	278	441	1418	48	138	320	1125	42	148	804	546	14	48	128	278	441	1418	82	168	823	2911	546	48	138	320	1125	185	882	2297	15408	MAX. Cs
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Cs/SEC.**	1.3	3.3	10.5	13.9	24.2	2.0	4.5	11.0	16.5	27.0	0.4	1.0	2.0	6.0	7.5	25.0	2.5	3.8	12.5	0.9	2.5	10.3	19.0	1.0	2.8	14.2	8.4	0.2	0.5	1.0	2.5	3.8	12.5	0.5	1.4	7.1	22	4.7	0.9	2.5	10.3	18.0	1.0	4.8	20.6	138.9	Cs/SEC.**
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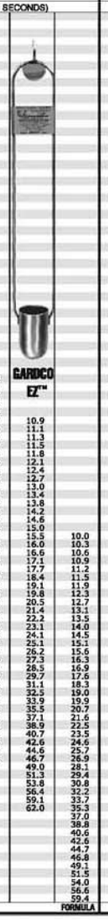

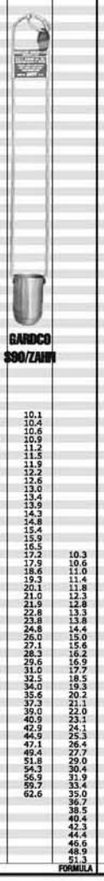

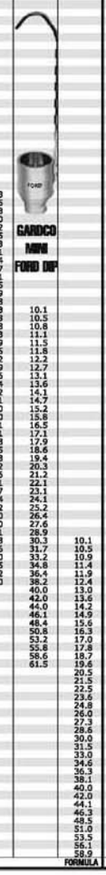

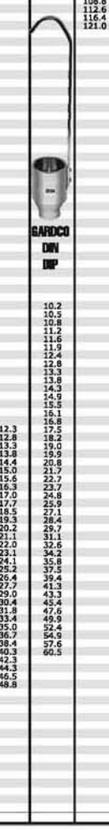

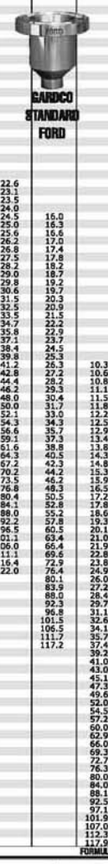

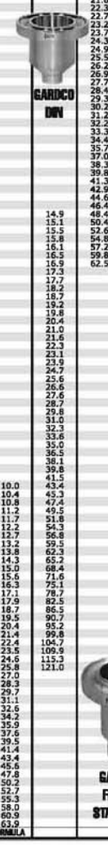

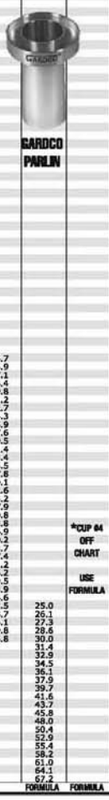

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