

COATING MATERIALS FOR ELECTRONIC APPLICATIONS

Polymers, Processes, Reliability, Testing

by

James J. Licari

AvanTeco
Whittier, California

NOYES PUBLICATIONS

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Major changes have also occurred in government and military procurements of electronic equipment. Numerous military and federal specifications have been canceled or inactivated for new designs and replaced by industry-association specifications. This reliance on industry and commercial specifications resulted from the government's policy of reducing costs by procuring commercial off-the-shelf (COTS) components and equipment, provided they met the performance requirements of a specific program.

Concurrently with changes in the economy and government policies, major advances occurred in microelectronics that dictated new applications for materials in general and coatings in particular. High-purity dielectric coatings were developed and used as interlayer dielectrics and as stress buffers at both the IC and multilayer interconnect substrate levels. Thus, this

book covers low-dielectric-constant coatings for controlled impedance, high-frequency circuits. Included in the coatings that meet these new applications are polyimides, parylenes, benzocyclobutenes, silicones, and fluorinated polymers. Photoimageable coatings have also assumed prominence during this period. From a manufacturing standpoint, photoimageable coatings reduce the number of process steps and, from an engineering standpoint, they permit the design and formation of finer circuit dimensions. Dielectric coatings that are amenable to the formation of microvias by laser ablation or photoimaging have also been developed for chip-scale packages (CSP) and multichip module-D (MCM-D) interconnect substrates.

Processes for cleaning assemblies prior to coating, and processes for dispensing and curing the coatings, have had to be reassessed in view of new local, state, federal, and even global regulations. To minimize material waste, reduce costs, and comply with environmental regulations, methods such as extrusion coating of large flat panels and selective computer-controlled dispensing have been introduced. With the use of “no-lead” solders, higher reflow solder temperatures are required resulting in new cleaning solvents and methods for removing fluxes.

Finally, a major effort has occurred in reformulating coatings to meet federal, state, and county regulations on emissions and toxicity. Coatings having low VOC (volatile chemical compounds) solvents and preferably those having no volatile solvents at all (100% solids coatings) have replaced many solvent-based high-VOC coatings. Conservation of energy was also addressed by the introduction of new uv-curing and microwave-curing formulations to replace heat-curing systems.

Besides a discussion of the functions and requirements for coatings, a significant portion of this book is devoted to the chemistry and properties of coatings as they relate to electronic applications. An understanding of the chemistry and molecular structure of the polymers upon which coatings are based is extremely important in determining the properties desired and predicting the behavior of the coated parts under operating conditions. Manufacturing technology is also treated in detail, covering both traditional processes and new advanced processes for surface preparation, cleaning, dispensing, and curing of coatings. Chapter 4 on “Applications” gives the reader an appreciation of the myriad uses for coatings for electronics from everyday consumer applications to deep-space applications. Lastly, reliability issues are treated and comprehensive lists of test methods and specifications given.

This book is intended for electronics design engineers who are faced daily with decisions on selecting organic coatings, and for materials engineers and chemists who need to know more about electronic applications and their requirements in order to develop new coatings or improve existing ones. This book helps to bridge the gap between these two disciplines. This text should also benefit personnel involved in manufacturing and quality assurance and others directly or indirectly involved in microelectronics such as sales and marketing.

James J. Licari

Whitter, CA
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Because of differences in methods of testing and variations in formulations, the properties of coatings reported throughout this book should not be used in specifications without consulting the manufacturer of each product. Values may differ considerably from those cited throughout the text, depending on the formulation, degree of cure, manner of processing, and test method used.

Acknowledgments

I sincerely hope that the many practitioners, engineers, and suppliers of coating materials and electronic hardware will find this new book even more informative and useful than the two editions of the previous handbook. I am grateful to the hundreds of companies and their personnel who provided information. These companies are referenced and acknowledged throughout the book. Specifically, I thank the following for their contributions: Paul Berry (Dow Corning), Steve Swanson (Dow Corning), Drew Roza (Arch Chemical Co.), Edward Mines (HumiSeal Division of Chase Corp.), Glenn Dickey (FAS Technologies), Sandy Buda (AMI), Vicki Worth (Asymtek), Eric Bagdasarian (Babcock Electronics), Steve Bruner (NuSil Silicones), Sherry Walter (BYK Gardner), Sherri Thompson (Paul N. Gardner Co.), John Kauffman (Phelps Dodge Wire and Cable), Joe Koch (3M Co.), Andrew Brooks and Eugene Schneider (Specialty Coating Systems), Peter Zeigler (DuPont), George Ellis (some illustrations), E. Millas (Methode Electronics), Michael Konrad (Aqueous Technologies), Jackki Morris-Joyner (IMAPS), Philip Trask (Litel Instruments), Dr. Kirk Bonner (JPL), Charles Bodie (JPL), and Andreas Ostman (Fraunhofer IZM).

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Functions and Requirements of Coatings for Electronic Applications

Conformal coatings such as polyurethanes, acrylics, epoxies, and silicones have been used for over 40 years to protect printed wiring assemblies from moisture, handling, ionic contaminants, and particulates. With the advent of integrated circuits and multichip modules, especially in the early years when chip passivation layers could not be relied upon for total protection, a new breed of organic coatings was developed, modified, and purified to render them compatible with the bare chip devices. This resulted in new “semiconductor grade” coatings and materials developed by companies such as Dow Corning, General Electric, and Hysol-Dexter among others. The early epoxies had to be distilled several times to remove fair amounts of chloride and sodium ions^[1] and purify the resins. Epoxy types that do not produce sodium chloride as a by-product of their synthesis were subsequently introduced.

With recent advancements in very high density, high-speed devices and circuits, coatings have been developed and applied as interlayer dielectrics for multichip modules, chip-scale packages, and optoelectronic

packaging. Among these are polyimides, benzocyclobutenes (BCB), fluoropolyethylene, and a host of photoimageable coatings.

Depending on the application, coatings are required to meet a broad range of adhesion, environmental protection, electrical, and thermal functions.

1.1 FUNCTIONS AND REQUIREMENTS

The two key functions of coatings used in electronic circuits are environmental protection, particularly moisture protection, and electrical insulation or isolation. In addition to shielding electronics from moisture, chemicals, and contaminants that result in corrosion and electrical failures, environmental protection includes protection from physical abuse, such as handling and abrasion, temperature extremes, and radiation. Special functions include interlayer dielectrics for high density interconnect packaging, particle immobilization or gettering, Electromagnetic Interference/Radio Frequency Interference (EMI/RFI) shielding, electrostatic discharge (ESD) protection, photoresists, and solder masking. Adhesion of the coatings is critical to fulfilling these functions.

1.1.1 Adhesion—The Basic Requirement

The requirements that a coating must meet depend on the specific application and function that the coating must perform for that application. Moisture and salt spray/fog protection, for example, are important for most unprotected ground-based and ship-borne electronic equipment while low outgassing in a thermal-vacuum environment is critical for space vehicles. However, the one coating requirement that is basic to all functions is good adhesion, both initially and during the operation and lifetime of the hardware. Unless the coating adheres well to all surfaces and maintains its adhesion under storage and duty-cycle conditions it will not perform its intended function and may, ultimately, result in electrical failure of the entire system. Adhesion depends as much on the type of coating and its processing conditions as on the surface condition to which the coating is applied.

Printed circuit assemblies contain a variety of components consisting of different materials and surface conditions. The circuit board itself is

often coated with a solder mask that has been photoetched or chemically patterned. Assembling the components involves fluxing and soldering. If residues from these operations are not thoroughly removed, adhesion will be impaired. Even a single fingerprint left on the part prior to coating, although not visibly detectable, manifests itself as a blister after exposure to moisture. Salt residues from fingerprints, being hygroscopic, absorb and retain moisture subsequently causing lifting of the coating.

Assuming that the surface is clean of contaminants, adhesion is a function of the ability of the liquid coating to wet the surface and can be measured by the angle that the liquid makes with the solid surface. A drop of liquid on a solid surface forms an angle due to the balancing of three forces comprising the interfacial tensions between solid and liquid, solid and vapor, and liquid and vapor. The angle within the liquid phase is known as the contact angle or wetting angle (θ). It is the angle included between the tangent plane to the surface of the liquid and the tangent plane to the surface of the solid, at any point along their line of contact. At the extremes, a contact angle of zero degrees indicates complete wetting while a contact angle of 180 degrees indicates no wetting. Wettability and contact angle depend on the surface tension of the coating. Generally, the best wettability and adhesion result from surfaces that have high surface energies and coatings that have low surface tensions. As a rule, acceptable bonding adhesion is achieved when the surface energy of a substrate measured in dynes/cm is approximately 10 dynes/cm greater than the surface tension of the liquid. Examples of materials having high surface energies include highly polar solids such as most metals; metals having a natural surface oxide such as aluminum; ceramics such as alumina, silica, and beryllia; and plastic laminates such as epoxy-glass and polyimide-glass. Among materials having poor wettability are those having low surface energies such as gold, Teflon*, fluorocarbon plastics, some silicones, and plastics that have appreciable amounts of plasticizers or mold release agents. It is reported by Ritchie that even the surface texture of a substrate, as of a fully cured solder maskant, affects the wettability and adhesion of the coating.^[2]

Fortunately, both substrates and coatings can be altered and tailored to improve wettability and adhesion. Surfactants, polar solvents, and diluents may be added to coatings to reduce their surface tensions and improve their wetting properties. Solid surfaces can be chemically or physically treated to convert monoatomic or molecular surface layers to polar structures. The inherently poor wettability of polyethylene and polypropylene has been

*Teflon® is a registered tradename of DuPont.

enhanced by a uv/ozone surface treatment while many metals may be treated by anodizing or applying a chemical conversion coating. Adhesion promoters such as primers are also widely used to enhance adhesion. Organo-silanes form the basis for many commercially available primers. They enhance adhesion by forming a molecular bridge between the substrate surface and the coating (see Sec. 1.3 for further discussion of primers).

1.1.2 Other Requirements

Besides adhesion, coatings used on electronic devices and assemblies must meet other engineering and manufacturing requirements. Among the engineering requirements are:

- Low moisture vapor transmission rate (MVTR) and low water absorption.
- No delamination, blistering, flaking, or chemical decomposition on aging, thermal or humidity exposure, or other specific environmental exposures such as ultraviolet or ionizing radiation.
- High purity. Preferably no chloride, sodium, potassium, or ammonium ions.
- Non-nutrient. Must be resistant to microorganisms and prevent growth of fungus and other bioorganisms.
- Low outgassing. No decomposition under the conditions of use or under screen test conditions.
- Low stress, either low modulus of elasticity or coefficients of thermal expansions (CTEs) matching those of the substrate materials.
- Protection of a variety of metals used in electronic circuits from corrosion, specifically thin-film metallizations such as aluminum, nichrome, copper, and solders.
- Excellent electrical properties including insulation resistance, dielectric constant, dissipation factor, dielectric breakdown voltage, and retention of these properties under thermal aging, humidity exposures, and a wide frequency range.

- Resistance to ionizing radiation, atomic oxygen, and other space environments.

Among desirable manufacturing requirements are:

- Low material cost.
- Low loss of material during its application.
- Long shelf life and working life.
- Inexpensive process and process equipment.
- Low organic volatiles and organic solvents; compliance with federal and state regulations.
- Non-toxic, non-flammable.

These and other manufacturing considerations are discussed in Ch. 3 under Manufacturing Technologies.

1.2 ENVIRONMENTAL PROTECTION FUNCTIONS

Besides protection from moisture, coatings are used to protect electronic devices and assemblies from corrosion and from other terrestrial environments such as salt atmosphere, abrasion from particles, dust and blowing sand, handling, ozone, fungus, bioorganisms, cleaning solvents, and chemicals. For space vehicles, protection from exposure to various types and intensities of radiation, high vacuum, atomic oxygen, and meteor debris must also be considered.

1.2.1 Moisture Protection

The main function of coatings in terrestrial applications is to protect parts from moisture-induced corrosion. However, no organic coatings or organic polymeric materials are completely impermeable to moisture, ions, or gases. Varying degrees of moisture protection are possible depending on the molecular structure of the polymer, the degree of cure or polymerization, the amount of impurities, and the degree of adhesion to the surface. Coating or encapsulating with polymeric materials, if required, cannot achieve true hermetic sealing. Yet in most cases, organic materials provide sufficient protection to render the coated part reliable for an application or a specific

environment. Only in the most severe environments and to achieve the highest reliability, as for some military, space, or medical programs, will hermetically sealed circuits be necessary. Even there, a reevaluation of stringent military specifications vis-à-vis recent emphasis on COTS (Commercial Off-the-Shelf) electronics is occurring.^[3]

Selection Criteria. In selecting the optimum coating to protect electronics from moisture, ions, or gases, the coating's permeability to these contaminants must be known or measured. Low moisture permeability and low moisture absorption are two key parameters. Generalizations should be avoided. One cannot unequivocally state that epoxies are better than silicones since there are thousands of epoxy and silicone formulations on the market and many thousands more that are possible. Slight changes in formulation (type of filler, amount of filler, degree of cross-linking and cure, and polarity of the molecule) can create significant differences in moisture or gas permeation rates and water absorptions. Hence, epoxies, depending on the formulation and type, can absorb as little as 0.1% water or as much as 5%. Tables of moisture permeabilities and water absorptions for organic materials are scattered throughout the literature.^{[4]–[6]}

Moisture Absorption. Moisture absorption for a given formulation is reported as the percent of water absorbed at a given temperature in a given period of time. A precisely weighed amount of material is immersed in water at a given temperature, or is exposed to ambients of various relative humidities at given temperatures, and is periodically weighed until moisture saturation has been achieved. This is the point at which no further increase in weight occurs. Precise gravimetric measurements may be made using a microbalance or electrobalance.

Suppliers generally report water absorption data based on ASTM D570-98^[7] where a weighed sample is exposed for 24 hours in water at room temperature or at an elevated temperature and then reweighed. This is a convenient and rapid method to compare coatings, but may not represent the full saturation amount, which may take weeks to develop. Table 1.1 gives some water absorption values for various polymer types.

Moisture Penetration and Permeation. Moisture may seep through a coating by one or both of two mechanisms: passage through microcracks and/or pinholes or permeation through the polymer structure. Permeability or moisture vapor transmission rates (MVTR) are given in grams of water that will pass through a defined area and thickness of a coating material in a specified period of time. The conditions of humidity exposure and temperature must be specified. MVTR is expressed by the following equation:

Eq. (1.1)
$$MVTR = \frac{Ql}{at}$$

where Q = grams of water permeating the coating
l = coating thickness in cm
a = coating area in cm²
t = time in hr

Table 1.1. Water Absorption Values for Some Polymer Types*

Polymer Type	Commercial Product	Manufacturer	% Absorption 24 hrs Immersion
Acetal	various	various	0.25
Acrylic (Polymethylmethacrylate)	various	various	0.3
Benzocyclobutene (BCB)	Cyclotene®	Dow Chemical	0.2; 0.3 (2 hr/boiling water)
Epoxies	various	various	0.5 to 1
Ethylene-tetrafluoroethylene	Tefzel® Teflon® ETFE	DuPont	<0.01
Polyamide	Nylon 6,6	DuPont	0.7 to 1.5 (3.3)**
Polyamide-imide	various	various	0.33
Polyarylsulfone	PAS	various	0.22
Polyethylene	various	various	0.01
Polyimides	various	various	0.5 to 1.7 (2 hr/boiling water)
Polystyrene	various	various	0.01 to 0.03 (0.2)**
Polytetrafluoroethylene	Teflon® PTFE	DuPont	0.001
Polyurethanes	Conathane RN-2000	Cytek	0.25
Polyurethanes	various	various	0.6 to 0.8
Polyvinyl chloride	PVC	various	0.15 to 0.75
Polyvinyl dichloride	PVDC	various	0.11
* Values were obtained from several sources and may vary appreciably from those given because of differences in test conditions, formulations, and processing conditions. More extensive data are given in <i>Modern Plastics Encyclopedia</i> , McGraw-Hill, 1992.			
** Values obtained from Bentec Services Ltd., (www.bentecservices.com)			

Generally, an ambient of 90% relative humidity at 38°C is used. MVTRs are often reported as grams/m²/24 hrs/mil, especially if values are quite small. Many factors affect MVTRs. Besides the polymer type, its formulation ingredients, degree of cure, and molecular structure are determining factors, especially for the epoxies, silicones, and polyurethanes. Other factors that either increase or decrease the MVTRs of polymer coatings are given in Table 1.2. Test methods used are ASTM E96-00^[8] and ASTM D1653-93.^[9] These methods are described in Ch. 6. The MVTRs for some polymers are given in Table 1.3.^[10]

Table 1.2. Factors Affecting Moisture Permeability

Factor	Usual Effect on Permeability
Solvent entrapment	Increase
Plasticizers	Increase
Structure of film	
Polar, hydrophobic	Decrease
Polar, hydrophilic	Increase
Nonpolar	Decrease
Degree of cross-linking	Decrease
Crystallinity	Decrease

Metal Migration. Associated with moisture absorption and permeation is the ability of a coating to prevent or suppress metal migration. Metal migration, especially silver migration, occurs between closely spaced conductor lines in the presence of moisture and an applied voltage. It results in reduction of insulation resistance, an increase in current leakage, and eventual catastrophic shorting. Metal migration has been known and studied for over thirty years because it has been the cause of many microcircuit failures^{[11]–[15]} (see also Ch.5 on Reliability). A rapid test consists of applying a drop of water across closely spaced conductors with an applied bias of several volts. The absence or presence of metal migration can be determined visually. The same test can be used to assess the effectiveness of an overcoating to prevent or minimize metal migration. Figure 1.1 shows the extent of silver migration for an unprotected silver-platinum thick-film conductor test pattern. Figure 1.2 shows the absence of metal migration when gold thick-films were used under similar test conditions. Overcoating of metal conductors that are prone to metal migration can reduce the extent of metal migration.

Table 1.3. Moisture Vapor Transmission Rates for Some Polymers*
(90–95% RH, 40°C)

Polymer	Trade Name (Company)	MVTR, g/m ² /24 hr/25 µm
Benzocyclobutene (BCB)	Cyclotene® (Dow Chemical)	24
Epoxy, anhydride cured		37.2
Epoxy, uv cured		20–23
Epoxy, aromatic amine cured		27.9
Fluorinated ethylene propylene	Teflon® FEP (DuPont)	6.4–7.13
Fluoropolymer film	ACLAR® (Allied Signal)	0.016
Polycarbonate	Lexan® (General Electric)	31
Polyethylene terephthalate	Mylar®	29.45
Polyimide film	Kapton® (DuPont)	54
Polymethylmethacrylate	Acrylic	550
Polystyrene	(Avisun)	133.3
Polysulfide	(Thiokol)	668
Polysulfone		279
Polytetrafluoroethylene	Teflon® PTFE (DuPont)	5
Polyurethane, castor oil cured		66.7
Polyurethane, polyester cured		134.9
Polyurethane	Magna X500	37.2
Polyvinyl fluoride	PT207 (Product Techniques)	46 10.85 (25°C)
Polyvinyl formal	Formvar®	110
Polyvinylidene chloride	Saran®	1.5–7

(cont'd.)

Table 1.3. (cont'd.)

Polymer	Trade Name (Company)	MVTR, g/m ² /24 hr/25 μm
Polyvinylidene fluoride		2.6 (23°C)
Polyxylylene	Parylene C (Specialty Coating Systems)	15.5
Polyxylylene	Parylene N (Specialty Coating Systems)	217
Silicone Gel		1744
Silicone, methyl phenyl		594
Silicone, RTV		1872
Silicone, alkyd		69.8–122.5
* Compiled from Baer ^[10] and various company brochures. Values may vary from those reported depending on the formulation, degree of cure, processing, and test method used. g/(25 μm)(m ²)(24 hr) × 0.0645 = g/(25 μm)(100 in ²)(24 hr)		

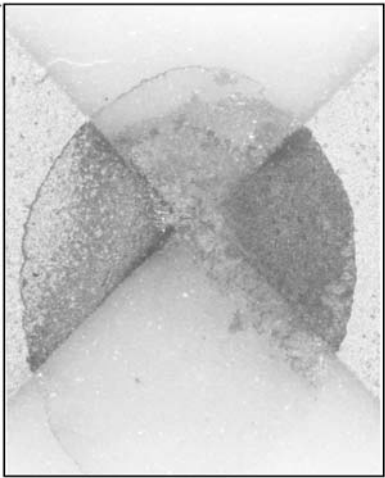


Figure 1.1. Metal migration. Water-drop test for a silver-platinum, thick-film conductor (complete bridging after 25 min, 4 Vdc).

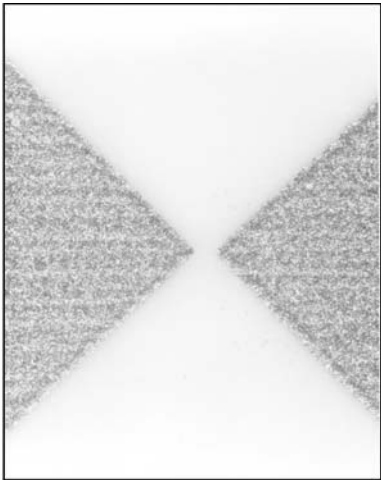


Figure 1.2. Metal migration. Water-drop test for thick-film gold conductor (no evidence of metal migration after 1 hr, 4 Vdc).

1.2.2 Corrosion Protection

Coatings may be applied to metal surfaces or between surfaces of dissimilar metals to protect them from direct chemical corrosion or from galvanic corrosion. A description of other types of corrosion and design criteria to avoid them may be found in Kennedy Space Flight Center’s Document TM-584C.^[16]

Direct Chemical Corrosion. The most commonly encountered corrosive environments are listed in Table 1.4. As a rule, elevated temperatures accelerate the rates of corrosion.

Table 1.4. Environments and their Corrosive Constituents

Environment	Corrosive Constituents
Normal air ambient	Moisture, oxygen, sulfur dioxide, carbon dioxide
Water	Calcium salts and other metal salts, ions
Salt water or salt spray	Sodium and chloride ions, marine organisms
Chemicals and solvents	Numerous acids, bases, oxidizing or reducing agents, solvents, strippers, etc., which may come into contact with the part during processing or operation
Soil	Moisture, fungus, other microorganisms

Metals corrode differently, depending on the nature of the metal and the environment to which they are exposed. Some failure modes for metals and alloys commonly employed in electronic assemblies are given in Table 1.5. Corrosion occurs by either a chemical or electrochemical mechanism and, in almost every case, moisture must be present. Hence, the moisture-barrier and moisture-resistance properties of a coating become key factors in corrosion prevention. With many metals, inorganic metal oxide films form on exposure to air. These oxides may continue to grow until the metal loses much of its strength or is completely consumed, as in the case of iron; or, oxides may form a thin topographical layer that acts as a barrier preventing further deterioration of the bulk of the metal, as with aluminum. Artificially produced, inorganic films may be formed to provide corrosion protection. Called *chemical conversion coatings*, these films are produced by causing the metal surface to react with oxygen, phosphates, chromates, or other chemicals to form a passivation layer. Other passive films, such as anodize, are formed electrochemically. For very harsh environments or long-term exposure, organic coatings are applied over these conversion coatings providing an effective barrier system. Lacquers; baking enamels; and highly resistant epoxies, vinyls, polyurethanes, or silicones are often used.

The effectiveness of conversion coatings may vary widely, depending on differences in surface preparation, cleanliness of the surfaces, and thickness of the coating. Thicker coatings reduce the probability of imperfections in the coating, increase protection from abrasion and mechanical damage during use, and increase the moisture resistance of the film. In general, the thicker the coating, the better its anticorrosive properties.

Galvanic Corrosion. *Galvanic* or electrochemical corrosion occurs when dissimilar metals are in contact with each other or are electrically connected in a conductive solution so as to generate an electric current. Accelerated corrosion occurs in the more active metal (anodic) and decreased corrosion in the less active metal (the cathode). The extent of galvanic corrosion can be predicted from the electromotive series in which metals are listed in the order of their individual electrical potentials.^[17] The greater the differences in potential between two metals, the greater the propensity for corrosion. Thus in some ambients, magnesium, zinc, steel, and aluminum in contact with copper, stainless steel, and nickel result in appreciable corrosion. An essential condition for galvanic corrosion is the presence of an electrolyte between the metals such as moisture and some ionic residues. Thus, theoretically, two dissimilar metals that are super clean in an ultra-dry environment should not corrode. But these conditions are rarely achieved in practice and, if so, are difficult to maintain. Thus, dissimilar

Table 1.5. Corrosion Modes for Metals and Alloys Commonly Used in Electronic Assemblies

Metal or Alloy	Type of Corrosion
Copper	Thermal-air exposure results in black oxidation product; forms green copper carbonate (verdigris) which inhibits further corrosion except as accelerated by galvanic coupling; exposure to salt environment produces high electrical resistance due to formation of copper salts; tarnishes in sulfur containing ambients.
Copper-nickel alloys and copper-beryllium alloys	Tarnishes in sulfur containing ambients and in moist air.
Aluminum, pure or 5052, 6061, 1100, 3003	Forms white oxide, which is usually superficial and entails no structural damage.
Aluminum high-strength alloys 2024, 2014	Susceptible to tunneling, exfoliation, and stress corrosion.
Aluminum high-strength alloys 7075, 7079	Susceptible to stress corrosion.
Aluminum alloys, general	Galvanic corrosion from dissimilar metal couples.
Magnesium AZ31B	Rapid local dissolving at breaks in metallic coatings or at points of coupling with nobler metals; oxidizes slowly in moist air.
Magnesium-lithium alloy	Interaction of moisture with the lithium portion of the alloy results in rapid evolution of hydrogen and formation of white lithium hydroxide; organic protective coatings used are permeable to moisture and blister and lift due to hydrogen generation; also reacts with carbon dioxide from the ambient to give white lithium carbonate.
Magnesium-thorium alloy	Very susceptible to moist ambient
Beryllium	Stable in air; forms a metal-oxide protective layer on heating in air; will react rapidly with methyl alcohol; attacked by alkalis with evolution of hydrogen.
Nickel	Little corrosion problem except for galvanic couples; very stable in air and water owing to presence of nickel oxide layer.
Silver	Black silver sulfide “tarnish” on exposure to ambient owing to interaction with SO ₂ and H ₂ S contaminants in air.
Gold	Extremely inert, no corrosion products.

metals should be avoided or, if used, an organic coating, inorganic coating, or insulative film should be applied to separate the two metals to prevent the electrochemical cell from generating. Other precautions consist of thorough cleaning of the mating surfaces, thorough drying, and maintaining a moisture-free ambient. Guidelines for the prevention of galvanic corrosion are defined in MIL-STD-889.^[17]

Filiform Corrosion. *Filiform corrosion* is a unique type of corrosion that forms beneath a painted or coated metal surface. Its name derives from the appearance of thread-like projections of the corrosion products. The corrosion starts at small, often microscopic, defects in the coating through which moisture can penetrate. It occurs primarily on carbon-steel or aluminum surfaces that have been coated with lacquers or other quick-drying coatings. Filiform corrosion can be avoided by surface pretreatments, such as anodizing, chemical conversion coating, or priming, followed by a topcoat. The use of heat-cured epoxies as the topcoat has been found to be especially effective in preventing this type of corrosion.

Filiform corrosion is not a problem with electronic assemblies, subassemblies, and components since established pretreatments and high-performance coatings are used to protect metal parts.

1.2.3 Salt Spray Resistance

In addition to protection from moisture and high humidity/temperature environments, organic coatings are extensively used to protect electronic hardware exposed to marine environments where salt spray/fog dominate. Salt spray testing is commonly used to evaluate and compare different coatings on the same substrate for their relative resistance to salt spray and their ability to protect electronic circuits and components from the corrosive effects of salt exposure. The test defined in MIL-STD-883, Method 1009, consists of subjecting the parts to a fine mist of 0.5 to 3% salt solution at 35°C for various periods of time ranging from Condition A (24 hrs) to Condition D (240 hrs) and inspecting at 10–20 times magnification for corrosion or other defects in the coating or substrate. The salt spray test, however, is not considered an accelerated test to predict service life.

1.2.4 Permeation of Gases

Like moisture vapor, other gases permeate through polymer films to varying degrees depending on the molecular structure of the film, the nature

of the gas, the temperature, and pressure. Though not as detrimental as moisture, the penetration of oxygen, carbon dioxide, hydrogen sulfide, and sulfur dioxide to active semiconductor surfaces and thin-film metallization can chemically alter the surfaces. Oxygen can oxidize thin metal films while hydrogen sulfide causes silver surfaces to tarnish. Both carbon dioxide and sulfur dioxide form acids in the presence of moisture. The formation of sulfuric acid from sulfur dioxide is probably the most serious situation, but not very common. In general, sulfur gases in the ambient are quite low and electronics are well packaged and stored.

Several methods are used to measure the gas permeabilities of polymer films. According to ASTM D1434^[18] either a manometric (M) or a volumetric (V) test method may be used. In either case, the sample film is mounted in a gas transmission cell so as to form a sealed semibarrier between the two chambers. One chamber contains the test gas at a specific elevated pressure. The second chamber is either evacuated, into which the permeation of gas is measured by an increase in pressure (Method M), or contains the gas at a lower pressure to record a change in volume (Method V).

1.2.5 Handling and Abrasion Resistance

Coatings provide handling protection from both physical abuse and from ionic residues from fingerprints. Coatings will increase the ruggedness of solder joints, wire bonds, and fragile components. As an example, 1-mil-diameter aluminum or gold wire bonds that inherently may have a pull strength of 7 to 10 grams, if overcoated with parylene, are strengthened and require 20–30 grams to pull them to destruction. Coatings can strengthen other marginal wire bonds. There are some situations, however, where a coating has been known to stress interconnections due to its thickness and high expansion coefficient. Some soft silicones, though protecting devices from moisture, have been known to transfer stresses and break wire bonds simply through pressure applied to and transferred by the silicone in aggressive handling.

Applications subjected to excessive handling, rubbing, or contact with other objects require coatings that have a high degree of abrasion resistance. Abrasion resistance may be determined qualitatively by periodic examination while the coating is in actual use. However, excessive time would be required to obtain meaningful data this way and the results would be more or less qualitative. Fortunately, several accelerated quantitative methods are available that may be correlated with actual service perfor-

mance or used to compare the relative abrasion resistances of coatings. These include projecting a controlled stream of abrasive material, such as carborundum (silicon carbide) or sand (ASTM D968), against the sample, use of an abrasive tape, controlled scraping with a metal tool until the coating is penetrated,^[19] or the use of rotating abrasive wheels. The last method, referred to as the *Taber abrasion test*, has become the industry standard and is the most widely used method for testing polymer coatings and plastics in general. A description of this test method is given in Ch. 6. Taber abrasion resistance values for some polymer coatings are given in Table 1.6.

Table 1.6. Taber Abrasion Resistance Values for Some Polymer Coatings

Coating Type	Taber Wear Index (mg/1000 cycles)
Polyurethane Type 1*	43–155
Polyurethane Type 2*	28–33
Polyurethane Type 5*	60
Alkyd	147
Vinyl	85–106
Amine-catalyzed epoxy varnish	38
Epoxy polyamide	95
Phenolic varnish	91–172
Epoxy-polyester	116–121
Chlorinated rubber	220
* Types are defined in Ch. 2	

1.2.6 Resistance to Friction

With the repeated sliding or insertions that can take place in electronic drawers, consoles, and other metal or ceramic parts, surfaces having moderate-to-high coefficients of friction will abrade and wear out quickly. In such cases, some organic coatings having very low coefficients of friction are used to facilitate the sliding action and reduce or prevent abrasion and wear out. The *coefficient of friction* (CoF) is a non-dimensional term defined as the ratio of tangential force to a normal load during a sliding process. CoF is a measure of the ease with which two surfaces

slide against each other or, conversely, the resistance to sliding. Plastics and polymer coatings are generally tested against polished steel according to equipment and methods defined in ASTM D3702 or ASTM D1894.

Among the best low-CoF materials are the fluorocarbons, notably Teflon, and the polyamides such as nylon. Because Teflon is inherently mechanically weak, it is used as a filler in the more abrasion resistant, harder coatings such as epoxies or polyurethanes. Other low-CoF fillers for coatings include graphite and molybdenum disulfide. Table 1.7 provides comparative coefficients of friction for some coatings and other materials. These values should be used only as a guide since values vary depending on many factors including the surface cleanliness, dryness, and roughness. Theoretical treatments for both friction and abrasion are given elsewhere.^[20–21]

Table 1.7. Coefficients of Friction for Typical Coatings and Materials

Material	Coefficient of Friction
Polymer Coatings	
Epoxy coatings with Teflon filler, air dried	0.15
Polyamide (Nylon)	0.3
Polyethylene	0.6–0.8
Polyimide (Pyre ML)	0.17
Polymethylmethacrylate (acrylic)	0.4–0.5
Polystyrene	0.4–0.5
Polytetrafluoroethylene (Teflon TFE)	0.02–0.05
Polyvinyl chloride	0.4–0.5
Parylene N	0.25
Parylene C	0.29
Parylene D	0.31–0.33
Polysulfone (against steel)	0.40
Other Materials	
Graphite	0.1
Molybdenum disulfide	0.12
Steel	0.74
Aluminum	1.1–1.7
Diamond	1.0

1.2.7 Hardness

Besides abrasion and friction, the hardness of a coating is also a measure of its wear resistance. A soft coating is more susceptible to abrasion, scratching, and other mechanical abuse than a hard coating. A popular method for determining hardness is the *Sward hardness test*. This test is based on the principle that the amplitude of oscillation of a rocking device decreases more rapidly the softer the surface of a coating on which the test is performed (see Ch. 6). The tester automatically records the number of swings made by a standard rocker in contact with the test surface before it comes to a stop. The coating is normally applied to a rigid, thin substrate, such as aluminum. The test is reported to be sensitive to ± 1 or 2 units.^[22] Values are related to the value for polished glass, which is taken as 100. Although the Sward hardness test is nondestructive, it often cannot be used on an actual part because of the limited size and shape of samples that the tester can accommodate.

Note that hardness values can be used to establish the approximate degree of cure of a coating, because the coating hardens progressively as it cures or dries. Hardness values change rapidly at first, but eventually level off to a constant value. Thus, Sward hardness measurements are useful in determining optimum cure schedules (time and temperature) or optimum catalyst concentrations. Figure 1.3 shows a plot of Sward hardness versus the percentage of amine catalyst used to cure a polyurethane coating. It is evident from the curve that hardness values have stabilized between one and three percent of the catalyst concentration and that a higher percent of catalyst would provide no further benefit under the time and temperature conditions used.^[23]

If the catalyst concentration is kept constant at 0.5 percent for the same resin system, the Sward hardness values may be used to establish the optimum cure time, as shown in Fig. 1.4.^[23] The use of hardness values to establish cure endpoints applies more to slow room-temperature-curing or air-drying formulations than to the bake or heat curing types. Hardness values are not sensitive enough to detect the small changes in cure that occur on post-baking a coating after it has had an initial high-temperature cure.

A second hardness test (ASTM D3363) employs the use of a series of pencils of varying hardnesses to scratch through the coating to the substrate. The method, called the *pencil hardness test*, is relatively simple, but somewhat subjective and also destructive in nature. Numerous other hardness and scratch tests have been developed and occasionally used.^[24]

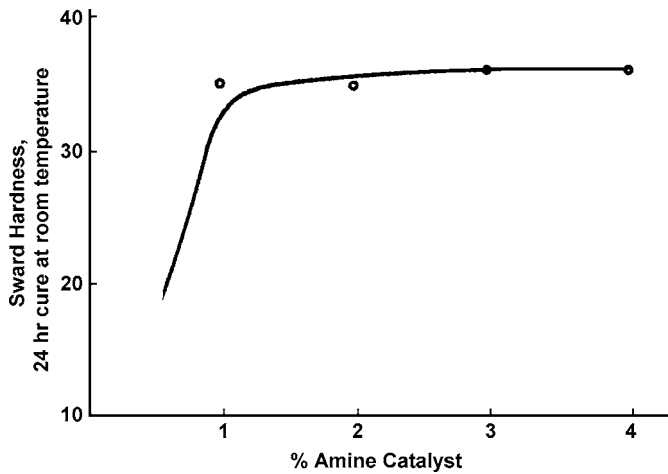


Figure 1.3. Sward hardness vs catalyst concentration for polyurethane coating.

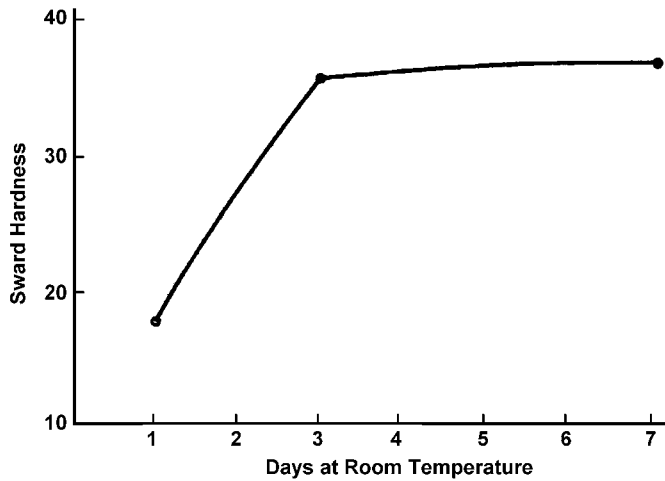


Figure 1.4. Sward hardness vs cure time for polyurethane coating.

1.2.8 Particle Shielding

Although organic coatings are not generally used in hermetically sealed circuits, some NASA and military programs have required their use to assure that any particles that remain on the circuit after cleaning or that may slough off after sealing do not migrate and cause electrical failures. Under vibration, impact, or acceleration, particles trapped within a hermetic seal, especially metallic electrically conductive particles, can cause shorting between conductor traces. Larger particles such as solder balls, solder splatter, or pieces of detached ceramic can physically damage fragile components and interconnections. Particles may result from fabrication processes, such as wire bonding or soldering. They may subsequently be generated, as from silver-filled epoxy used for die attachment. A *particle immobilizing coating* serves to freeze loose particles in place so that they cannot subsequently move. This prevents particles that may detach later from affecting the circuit. Parylene and silicones have received the greatest attention as particle immobilizing coatings because of their high purity, low-temperature processing, low outgassing, and compatibility with semiconductor devices. Both materials are used in high-reliability hybrid microcircuits and multichip modules (see also Ch. 4).

Particle Getters. Plastic resins that cure to a tacky state may be used as alternates to coatings in immobilizing particles. Soft, high-purity silicone gels are generally used by applying a small quantity to the inside of the lid prior to hermetically sealing a device or circuit. The effectiveness of silicone getters has been demonstrated by several companies through controlled experiments in which known amounts of metal particles of various sizes were purposely introduced (seeded) on a circuit containing the getter, then vibrated, and evaluated for loose particles by the Particle Impact Noise Detection (PIND) test, radiographic inspection, and electrical testing.^{[25]–[26]} The types of particles used were representative of those that might be found in a hybrid microcircuit package. They included pieces of gold and aluminum wire, solder balls, and pieces of eutectic alloys. It is important to apply the getter to the center of the lid to avoid contaminating the seal area with organic “bleed out” from the silicone. Another consideration in using silicones as getters is the amount of outgassing. As with other organic materials, the extent of outgassing is a function of the material used, its degree of cure, and the vacuum bake schedule. Silicone gels are available from both General Electric and Dow Corning.

1.2.9 Radiation Protection

Protection from radiation and resistance to its damage are major concerns for spacecraft and space probes. The natural space radiation environment consists of ionizing particles that cause transient or permanent changes in electronic parameters and in materials. A high concentration of electrons, protons, and heavy ions occurs in the Van Allen belts through which spacecraft must pass. Other heavy ions originate outside the solar system and are generally impervious to shielding. In view of this, both electrical components and materials must be selected that are “rad-hard”; that is, they must be selected or designed to be resistant to the expected radiation doses and intensities.

Organic coatings as well as potting compounds or encapsulants do little to protect electronics from radiation exposure, and may themselves be degraded. Thus, their vulnerability to radiation damage and decomposition must be known. Polymers differ in their susceptibilities to radiation damage based on their molecular structures, degree of cross-linking, formulation ingredients, and the type and duration of the radiation. As a general rule, the more aromatic and the more cross-linked the polymer structure the more resistant it will be to radiation. Among the most stable polymers are the polyimides, benzocyclobutenes, and polystyrenes because of their highly aromatic heterocyclic structures (see Ch. 4). Preventative measures, such as shielding with various thicknesses of aluminum, can protect both the coatings and the electronics from radiation damage.

1.2.10 Resistance to Solvents and Processing Chemicals

Electronic modules and assemblies are often subjected to cleaning solutions, organic solvents, chemicals, or greases and lubricants after they have been conformally coated. The nature of these materials must be known and coatings selected that will withstand them or alternate benign solvents must be used. Silicones, for example, are known to soften, swell, and even dissolve in halogenated solvents. Other coatings such as acrylics have been reported to craze or dissolve when exposed to some organic solvents. However, the solubility of some acrylic and silicone coatings in chlorofluorocarbon solvents can be a benefit in completely removing the coating so that printed circuit boards can be reworked. On the other hand, epoxies, polyimides, and parylenes are among the most solvent- and chemical-resistant coatings, rendering rework difficult.

1.2.11 Resistance to Microorganisms

Microorganisms (fungi, molds, and bacteria) are the cause of many millions of dollars of annual economic losses because of material degradation. Microbial growth can decompose polymers, degrading both their physical and electrical properties, can induce corrosion of metals and bimetallic combinations, and can alter surface properties of plastics increasing roughness and friction. The resistance of coatings to attack by microorganisms is particularly important for electronic hardware that is stored or operated in humid, tropical, or semitropical environments or in contact with the soil. Contact of materials with moist soil provides an ideal condition for microbial growth, since it is estimated that one cubic centimeter of soil contains as many as 50,000 fungi, 500 million bacteria, and 250 million actinomyciles (filamentous bacteria that resemble fungi).^[27]

Table 1.8. Commonly Used Biocides

Salicylanilide
Brominated salicylanilides
Organotin compounds
Bis(8-quinolinolato)-copper or zinc
Phenylmercuric oleate, -salicylate, stearate or phthalate
Di(phenylmercuric)dodecenylsuccinate
<i>N</i> -(trichloromethylthio) phthalimide
Phenylmercuric- <i>o</i> -benzoic sulfimide
Zinc dimethyldithiocarbamate
2-Mercaptobenzothiazole
Zinc pentachlorophenoxide
Pentachlorophenol
Quaternary ammonium carboxylates
Bis(tri- <i>n</i> -butyltin)-oxide
Sodium or zinc pyridinethione- <i>N</i> oxide
<i>p</i> -Toluenesulfonamide

Most microorganisms thrive in an environment of only 50% relative humidity and temperatures of 20° to 45°C. Some microorganisms may even adapt and grow under extreme conditions such as very cold (0° to -10°C) or very hot (50° to over 100°C) conditions.^{[28]–[30]} Fortunately, most synthetic polymers are non-nutrients and inherently resistant to microorganisms. Others may be rendered non-nutrients by adding antimicrobial chemicals to their formulations. These chemicals either kill the organisms (fungicides or

bactericides) or suppress their growth (fungistats or bacteristats). Salicylanilide and bis(8-quinolinolato)-copper are examples of two widely used biocides. Others, such as the organotin compound bis(tri-n-butyltin)-oxide, have been reported to control a wide variety of bacteria, fungi, algae, and even barnacles.^[31] Examples of biocides and biostats are listed in Table 1.8.

Because of their fungus resistant properties, organic coatings have been used to protect otherwise nutrient substrates. Coatings conforming to MIL-V-173, a fungus resistant varnish, may be used over nutrient materials. Such protection, however, is only as good as the integrity of the overcoating; should the coating be scratched, abraded, or in any way detached from the surface, microbial growth will occur in the exposed areas.^[32]

As a rule, the newer synthetic coatings, such as epoxies, silicones, and polyurethanes, are inherently fungus and bacteria resistant. Ether linkages in a polymer structure, as in epoxies, tend to reduce fungal growth. Much of the success of epoxy resins as replacements for naturally occurring resins and varnishes has been due to their fungus-resistant properties. Some formulations, however, may not be as resistant as others due to the presence of plasticizers or other nutrient additives. Some formulations may deteriorate with age or on exposure to humidity, producing nutrient decomposition products. The use of naturally occurring nutrient materials in synthesizing or polymerizing the coating does not necessarily render the final coating as a fungus nutrient material. The important factor is the form in which the nutrient material exists in the final formulation. If it is co-reacted completely with the base resin and becomes an integral part of the polymer structure, it is unlikely to be a nutrient. A clear example is the use of castor oil (a vegetable oil) in curing isocyanate resins. The resulting polyurethane polymers are generally fungus inert because the castor oil becomes chemically bound and integrated in the final molecular structure. However, if the nutrient is unreacted or if an excess amount has been used so that there remains some unreacted amount in the final polymer, then the coating will support microbial growth. Knowledge of the composition and chemistry of a coating formulation is, therefore, helpful in predicting its fungus resistant properties.

Plasticizers are probably the greatest source of fungal or bacterial growth. On the basis of available information, nutrient plasticizers include the diesters of saturated aliphatic dibasic acids containing 12 or more carbon atoms. Other nutrient plasticizers are di-n-hexyladipate, di-2-ethyl-hexylazelate, epoxidized soybean oil, triethyleneglycol, derivatives of soybean or tall oil fatty acids, methyl acetylricinoleate, dioctylsebacate, and tetrahydrofurfuryloleate. However, the maleates are somewhat fungus

resistant, as are the alkyl derivatives of phosphoric and phthalic acids. It has been observed that under suitable environmental conditions the enzymatic action of microorganisms converts the plasticizers in vinyl resins to water-soluble salts that can then be easily extracted. Stiffening, weight loss, and dimensional changes may follow. Air and water entering the tunnels left by extraction cause further erosion. This process continues until the tunnels penetrate the entire material and destroy its physical integrity. Further, the electrolytic solutions that may collect in the crevices and tunnels degrade the electrical insulation properties of the coating. Stains and odors also develop from the waste products of microbial growth. Attention has focused mainly on the effects of fungi on vinyl polymers. Polyvinyl chlorides, polyolefins, and polyesters are inherently resistant to fungus attack, but some of the formulation additive ingredients such as plasticizers, fillers, pigments, stabilizers, and processing aids, support mildew formation and other microbial growth. Surface greases and other contaminants also can act as nutrients for microorganisms, including bacteria such as *pseudomonas*, *salmonella*, and *bacillus*.

Considerable work has been performed on the effects of microorganisms on plastics and numerous ASTM and military test procedures are available (see Ch. 7 under Specifications). One method for determining the microbial resistance involves coating a steel panel, exposing it to humidity or other environmental conditions, then placing the panel in a petri dish containing a nutrient and inoculating it with the microbes. A microbe-resistant coating will prevent the growth of the spores on its surface. A list of acceptable and preferred materials taken from Guideline 4 of MIL-HDBK-454 is given in Table 1.9.

1.3 SPECIAL METAL PROTECTION

Certain metals and alloys such as magnesium, tin-lead solder, aluminum, and magnesium-lithium alloy require special pretreatments and primer coatings to provide adequate protection from corrosive environments. Effective and established pretreatments consist of anodize, chemical conversion coatings, or primers prior to topcoating with an organic coating. The pretreatments and primers provide enhanced adhesion and performance of the top coating. In some benign environments, the pretreatment alone may provide sufficient protection.

Table 1.9. Susceptibility of Materials to Fungi (MIL-HDBK-454)

Group I - Fungus-inert Materials (Fungus-inert in all modified states and grades)	Group II - Fungus Nutrient Materials (May require treatment to attain fungus resistance)
Acrylics	ABS (acrylonitrile-butadiene-styrene)
Acrylonitrile-styrene	Acetal resins
Acrylonitrile-vinyl-chloride copolymer	Cellulose acetate
Asbestos	Cellulose acetate butyrate
Ceramics	Epoxy-glass fiber laminates
Chlorinated polyester	Epoxy resins
Fluorinated ethylenepropylene copolymer (FEP)	Lubricants
Glass	Melamine-formaldehyde
Metals	Organic polysulfides
Mica	Phenol-formaldehyde
Plastic laminates: Silicone-glass fiber Phenolic-nylon fiber	Polydichlorostyrene
Diallyl phthalate	Polyethylene, low and medium density (0.940 and below)
Polyacrylonitrile	Polymethylmethacrylate
Polyamide*	Polyurethane (the ester types are particularly susceptible)
Polycarbonate	Polyricinoleates
Polyester-glass fiber laminates	Polyvinyl chloride
Polyethylene, high density (above 0.940)	Polyvinyl chloride-acetate
Polyethylene terephthalate	Polyvinyl fluoride
Polyimide	Rubbers, natural and synthetic
Polymonochlorotrifluoroethylene	Urea-formaldehyde
Polypropylene	
Polystyrene	
Polysulfone	
Polytetrafluoroethylene	
Polyvinylidene chloride	
Silicone resin	
Siloxane-polyolefin polymer	
Siloxane polystyrene	
* Literature shows that under certain conditions polyamides may be attacked by selective microorganisms. However, for military applications, they are considered Group I.	

1.3.1 Magnesium

Because of its high strength-to-weight ratio, good fatigue strength, and dimensional stability, magnesium is widely used for electronic applications, especially those intended for flight and space hardware. Heat sinks, housings, coolant tubes, and frames are a few examples of the use of magnesium. In a benign ambient such as indoor exposure, in a controlled environment such as a clean room, or in an enclosure sealed with inert gas, a protective finish for magnesium is not normally required. Even for normal weathering or short-term outdoor exposure, an electrochemical conversion coating alone or a single coating of a clear lacquer may provide sufficient protection.

However for military uses, magnesium is usually treated with a chromate conversion coating or an anodize finish prior to applying an organic finish. Some commonly used anodizing treatments are galvanic anodize (Dow 9 and Dow 17), fluoride anodizing plus post-treatment (usually dichromate), and stannate immersion (Dow 23).^[33]

Other chemical treatments that are useful as protective coatings, either alone or as bases for primers and topcoats, include Dow 1 (chrome pickle), Dow 19 (dilute chromic acid), and Dow 21 (ferric nitrate bright pickle).^[34]

The treatments most widely used for electronic hardware are:

- Dow 17, an excellent paint base for long-term exposure to humid and salt environments
- Dow 9, used for optical and electronic components where non-reflective coatings are required or as a paint base
- Dow 19, applied as a touch-up by brush, spray, or swab for rework on Dow 9 or Dow 17 surfaces

The various treatments are compared in Table 1.10.

These surface treatments are all acid types that either neutralize or acidify the normally alkaline magnesium surface. Neutralizing the inherent alkalinity of magnesium is essential to improving adhesion and durability of subsequently applied paints and coatings. To be effective, primers for magnesium should be based on alkali-resistant vehicles such as polyvinyl butyral (contained in wash primers), acrylic, polyurethane, vinyl epoxy, or baked phenolic. Zinc chromate or titanium dioxide pigments are often employed as further corrosion inhibitors.^[34] Because of their low solubilities, strontium chromate and basic zinc chromates are reported to provide sufficient corrosion inhibition together with longer service life.^[35]

For severe or extensive exposure, as might be encountered in ground or marine equipment, a durable finish system may consist of a conversion coating, a primer, and an organic topcoat. Vinyl, acrylic, epoxy, or polyurethane topcoats have been proven to give excellent protection. Another example consists of a Dow treatment, an epoxy primer, and an epoxy-polyamide topcoat such as MIL-M-45202 surface treatment, MIL-P-23377 epoxy primer, and MIL-C-27251 epoxy topcoat.

1.3.2 Tin-Lead Solder

For maximum protection of solder joints and solder-plated surfaces, conformal coatings should be used. As with other metals, corrosion can be prevented or minimized by following certain design guidelines. For example, bimetallic combinations of tin-lead solder with either copper or aluminum should be avoided in high humidity or salt water environments. Coating such bimetallic combinations provides only temporary protection unless the two dissimilar metals are isolated from each other. Primer-coating combinations, anodize, conversion coatings, and even tapes can be used to isolate the bimetallic members. Other difficulties associated with the corrosion protection of solder joints or solder plating are caused by the incomplete removal of corrosive fluxes during cleaning. Conformal coatings will not provide protection unless these contaminants are completely removed. Some cleaning procedures for flux residues are discussed in Ch. 3 under Manufacturing Technology.

The current intense industry research efforts to eliminate lead from solders by substituting other metals does not alleviate the risk of corrosion. This is because the potential substitute metals are also prone to corrosion unless properly protected.^[36]

1.3.3 Aluminum

Like magnesium, aluminum is widely used in electronics because of its high strength-to-weight ratio, high thermal conductivity, and current carrying properties. Although less susceptible to corrosion than magnesium, it too must be protected. This regardless of the fact that the normal oxide film that forms on its surface upon exposure to air is highly protective and prevents further deterioration of the bulk of the metal. Several oxide coatings (anodize) may be purposely formed as surface protective treatments and to

Table 1.10. Dow Finish Treatments for Magnesium and Magnesium Alloys

Name/Type	MIL spec	AMS spec	Appearance	Uses	Comments
Dow 1/Chrome pickle	MIL-M-3171 Type 1	2475	Matte gray to yellow-red	Protection during shipment and storage	Simple dip process, slight dimensional loss, good base for paint
Dow 7/Dichromate	MIL-M-3171 Type 3	2475	Brass to dark brown	Good combination of paint base and protective qualities	Does not materially affect dimensions
Dow 9/Galvanic anodize	MIL-M-3171 Type 4	2475	Dark brown to black	On alloys that will not take Dow 7 or where a black coat is needed	Requires galvanic couple between the part and steel cathode, no external current required
Dow 17/Anodize thin	MIL-M-45202	2478; 2479	Light gray to light green	Excellent protective and decorative finish	Thin 0.1 to 0.3 mil, coating is stable above melting point of metal, best abrasion resistance, best paint base, most consistent of all Dow treatments for magnesium
Dow 17/Anodize thick	MIL-M-45202	2478; 2479	Dark green	Excellent protective and decorative finish	Same as Dow 17 thin except 1 to 1.5 mils thick

(cont'd.)

Table 1.10. *(cont'd.)*

Name/Type	MIL spec	AMS spec	Appearance	Uses	Comments
Dow 19/Dilute chromic acid	MIL-M-3171 Type 6	2475	Brass to brown	Touch up treatment; used as paint base when refinishing	Less critical than Dow 1 by brushing, solution not harmful if trapped in joints
Dow 23/Stannate immersion	-	-	Medium to dark gray	Good paint base and protective finish; used with dissimilar metal inserts (except A1 or in assemblies)	Must be neutralized if painted, retards galvanic corrosion

improve the adhesion of subsequently applied organic coatings (MIL-A-8625). Primers such as wash primer, phenolic, and epoxy are useful in serving as a bridge between the anodized surface and the topcoat. As with magnesium, epoxy primers and epoxy or acrylic topcoats offer outstanding long-term corrosion protection.

1.3.4 Magnesium-Lithium Alloys

Magnesium-lithium alloys are attractive to designers of airborne electronic equipment because of their stiffness and high strength-to-weight ratios. They afford a 20 to 25% weight savings over magnesium alone or other magnesium alloys. However, the high reactivity of magnesium-lithium with moisture and carbon dioxide limits its use to hermetically-sealed enclosures containing dry inert gas. Even in an enclosed sealed box, an incompatible situation can arise when moisture evolves from plastic or from other components within the enclosure. Moisture reacts with the lithium portion of the alloy, forming hydrogen gas and lithium hydroxide. In the presence of carbon dioxide, white lithium carbonate powder forms on the surface of the alloy. These corrosive products result in the deterioration of the alloy. Additionally, an even more harmful secondary effect results from the reaction of the evolved hydrogen gas with some devices, especially with some chemically sensitive metal-oxide thick-film resistors. Hydrogen reduction of the oxides to metal in early resistor formulations resulted in wide changes and instabilities in resistance values.

Although several coatings are claimed to protect magnesium-lithium in normal environments, no organic coating and/or primer combination is known to provide sufficient protection to pass military accelerated humidity/temperature and salt spray tests.

1.3.5 Wash Primers

Wash primers improve the adhesion of subsequently applied coatings and provide effective corrosion protection for metals such as aluminum, magnesium, steel, zinc, and tin. They may be used alone or, where superior protection against salt spray and moisture is required, in conjunction with a topcoat such as epoxy, vinyl, or alkyd. In some cases, a three-step process, wash primer, primer, and topcoat is used. A wash primer-epoxy topcoat system was shown to protect either magnesium or aluminum for over 800 hours of salt spray exposure performed according to MIL-STD-881. Over

2000 hours of salt spray exposure, without deterioration, was reported for a vinyl (VAGH) coating applied over either a wash primer or a red-lead primer.

Wash primers consist of rust-inhibiting pigments, chiefly basic zinc chromate or lead chromate in an alcohol solution of polyvinyl butyral resin as one part of a two-part system.^[37] The second part consists of phosphoric acid-water-isopropyl alcohol solution. The first part is acidified with the second occurring just prior to use. This primer is commonly referred to as WP-1^[33] and its precise composition is given in Table 1.11.

Wash primers are applied in thicknesses of 0.3 to 0.5 mil by spraying, brushing, or swabbing. They may be purchased from paint manufacturers by specifying military specifications such as MIL-C-8514 or commercial specifications.

Because of the chromate constituent of wash primers and the high VOC (Volatile Organic Compounds) of the solvents used, studies are in progress to find alternate environmentally benign treatments. For example, the Army has found that abrasive blasting of steel can be used as a substitute for wash primers. However, abrasive blasting is not suitable for most electronic hardware.

Table 1.11. Composition of Wash Primer WP-1

Ingredients	Percent by Weight
Pigment Base	
Polyvinyl butyral resin	9.2
Basic zinc chromate	8.8
Magnesium silicate	1.3
Lampblack	0.1
n-Butyl alcohol	20.5
Isopropyl alcohol	57.7
Water	2.4
Total	100
Acid Diluent	
85% Phosphoric acid	18.5
Water (maximum)	16.5
Isopropyl alcohol	65.0
Total	100

1.3.6 Other Primers

Other types of primers are also employed to improve adhesion of topcoats and provide better corrosion resistance for metals. The performance of vinyl coatings, for instance, is greatly improved by priming the metal surfaces. Primers may consist of other specially formulated vinyls, phenolics, epoxies, or butadiene acrylonitriles.^[38]

Epoxy primers are very effective in improving the adhesion of polyurethanes. In protecting either aluminum or steel, an epoxy primer followed by two topcoats of a moisture-curing polyurethane resulted in panels that passed 800 hours of 20% salt spray exposure when tested according to ASTM B117.^[39] Epoxy primers may consist of the normal coating formulations that have been thinned further and sprayed on very thin (flash primers) or of coatings formulated to contain many ingredients, such as the formula in Table 1.12.

Table 1.12. Primer Formulation MP

Ingredient	Amount, pbw
Red iron oxide (R.K. Williams R-4800)	7.5
Basic lead silicochromate (National Lead M-50)	23.6
Talc (Whitaker, Clark & Daniels No. 399)	7.8
Lecithin (soya 50% in xylene)	0.4
Epoxy (Shell Epon 1004)	15.5
Cellosolve acetate:toluene:xylene (2:1:1)	39.2
Mondur CB-75 (Bayer Corp.)	3.3

1.4 ELECTRICAL FUNCTIONS

Coatings may be electrically insulative, electrically conductive, or semiconductive depending on their molecular structures and the ingredients with which they are formulated. One of the most important functions is providing electrical insulation and dielectric isolation for active and passive devices. The effectiveness of a coating is expressed in terms of its insulation resistance: volume resistivity, surface resistivity, and dielectric strength. Other electrical functions include storage of electrical current expressed as

capacitance and conductance of current expressed in terms of conductance, dielectric constant, and dissipation factor. Knowledge of exact electrical values and how these are affected by composition, purity, structure, and environment is important in selecting the most reliable coatings for a specific application. In the following sections, these electrical parameters and their dependence on temperature, humidity, frequency, and other variables will be discussed. More theoretical discussions of electrical parameters may be found in the literature.^{[10][40]}

1.4.1 Resistance and Resistivity

Insulation resistance (IR) is the ohmic relationship of the ratio of applied voltage to the total current between two electrodes in contact with a specific material. Insulation resistance is directly proportional to the length and inversely proportional to the area of the specimen as follows:

$$\text{Eq. (1.2)} \quad IR = \rho l/A$$

where IR = insulation resistance, ohms

l = length, cm

A = area, cm^2

ρ = a proportionality constant called the specific resistance or resistivity, ohm-cm.

It is convenient to compare materials in terms of their resistivities, because these values reduce resistance measurements to a common denominator. For example, the frequently used *volume resistivity* is the ohmic resistance of a cube of bulk dielectric material one centimeter per side expressed as ohm-cm. *Surface resistivity* is the resistance between two electrodes on the surface of an insulating material expressed in ohms per square unit. ASTM D257 describes the test method for measuring dc resistance of insulating materials.

Materials may be classified according to their ability to conduct or impede the flow of electrons. They range from extremely good conductors such as metals to very good insulators such as plastics and ceramics. Materials between these two extremes are referred to as semiconductors, but this does not mean that they have properties suitable for semiconductor devices. Only a few select inorganic materials such as doped silicon and gallium arsenide are useful in fabricating semiconductor devices. Organic

semiconductors have, as yet, not been useful in fabricating such devices. It is difficult to characterize a material as completely insulating or completely conducting since all materials are conductive to some degree, but in general, materials may be classified according to their volume resistivities as follows in Table 1.13.

Table 1.13. Classification of Materials by Volume Resistivities

Materials	Resistivities
Good conductors	10^{-6} to 10^0 ohm-cm
Semiconductors	10^0 to 10^8 ohm-cm
Good insulators	10^8 to $>10^{12}$ ohm-cm

Organic coatings are generally good electrical insulators and widely used in electronic equipment. Although their resistivities are high, even a small current flow can be critical in some electronic assemblies. Therefore, a knowledge of the electrical tolerances that a circuit or device must meet is important in selecting a coating. Volume resistivities of some familiar materials are compared in Fig. 1.5. Note the large difference (up to 24 orders of magnitude) between the most conductive materials such as copper and silver and the least conductive such as polytetrafluoroethylene and polystyrene.

Insulation resistance should not be considered the equivalent of dielectric breakdown voltage. Although clean dry coatings may have very high insulation resistances, they may have poor dielectric breakdown voltages because of voids, pinholes, or other coating imperfections.

Variables Affecting Resistivity. Resistivity is a constant, a characteristic of a material, provided the material does not change in composition and is maintained free of contaminants such as moisture and ions. Changes in formulation or chemical composition can produce significant resistivity changes. For example, blending a flexible resin such as polyamide with an epoxy resin degrades the initial excellent electrical properties of the epoxy when the amount of polyamide exceeds 30%, as shown in Fig. 1.6. It may be assumed that degradation of electrical properties occurs after the stoichiometric amount of polyamide is exceeded.

Resistivity also depends on the degree of cure or extent of polymerization. As the cure progresses, resistivity increases and stabilizes until the cure is complete. Resistivity can thus be used to establish optimum cure conditions (Fig. 1.7).

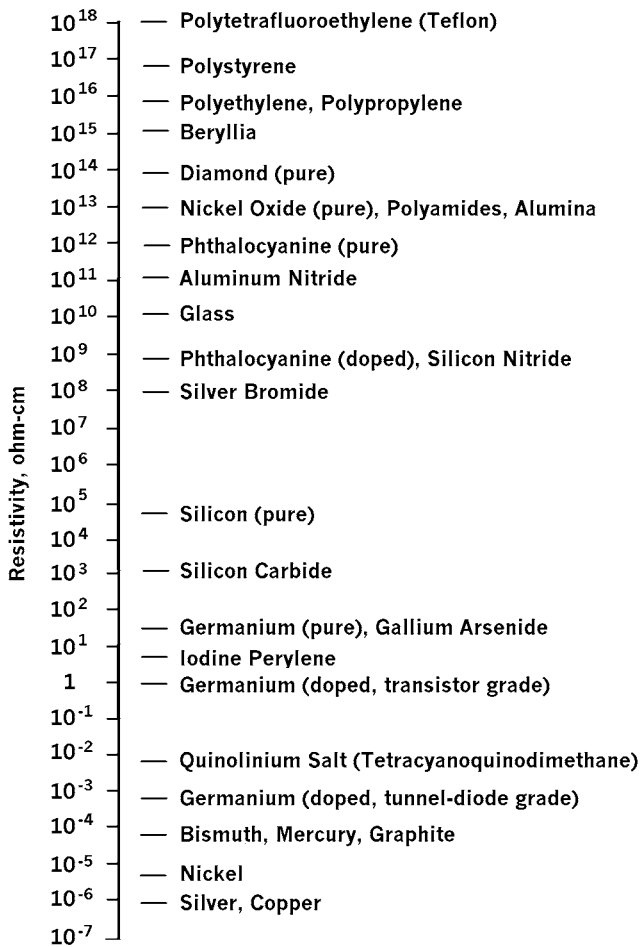


Figure 1.5. Comparative electrical resistivities of materials.

Besides the effects of gross changes in composition, minor amounts of impurities such as metal ions also affect resistivity values. Ionic impurities in low parts per million, especially when coupled with moisture, can lower resistivity values as much as 6 to 11 orders of magnitude.

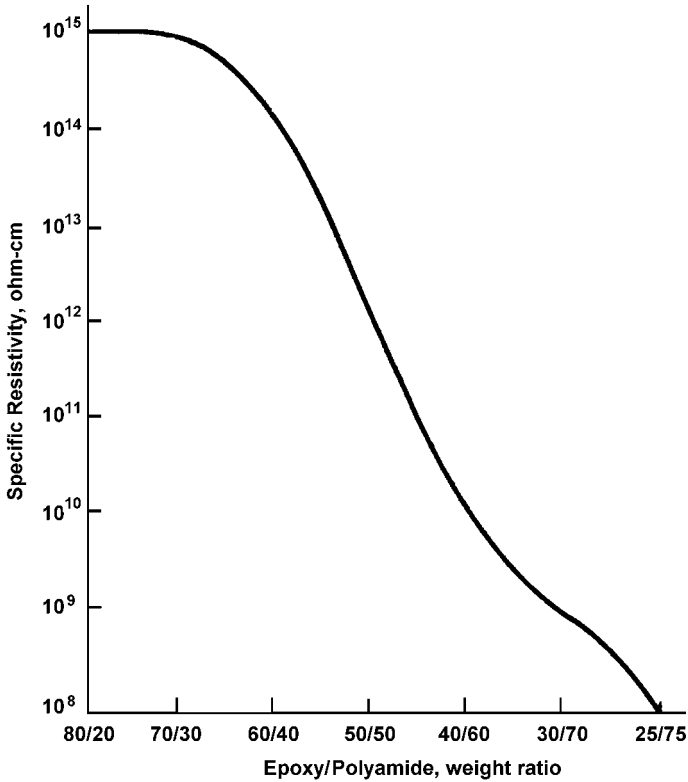


Figure 1.6. Variation of resistivity with change in epoxy-polyamide ratios.

Variation of resistivity with temperature is also important. Plastics, like inorganic semiconductors, but unlike metals, possess negative temperature coefficients of resistivity. Large decreases in values can occur at elevated temperatures. Hence, a coating that is an adequate insulator at room temperature may be completely unsatisfactory when the electronics are operating at higher temperatures. Examples of temperature-resistivity curves for some polymer coating types are given in Fig. 1.8. The temperature dependence of resistivity is given by the equation:

Eq. (1.3) $\rho = \rho_o e^{-E_a / KT}$

where ρ = resistivity at temperature T

ρ_o = a constant

K = Boltzmann's constant

E_a = activation energy

T = absolute temperature (Kelvin)

Finally, volume and surface resistivities are also dependent on frequency, voltage, pressure, light (photoconductivity of some organic crystals and polymers), and the conditioning of the sample.

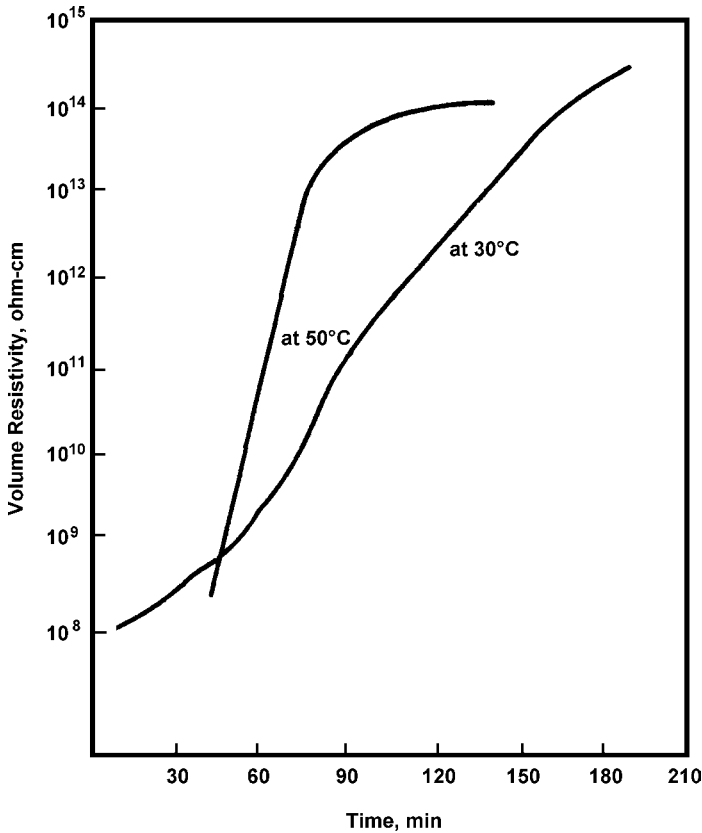


Figure 1.7. Isothermal polymerization of an amine-cured epoxy as a function of volume resistivity.^[41]

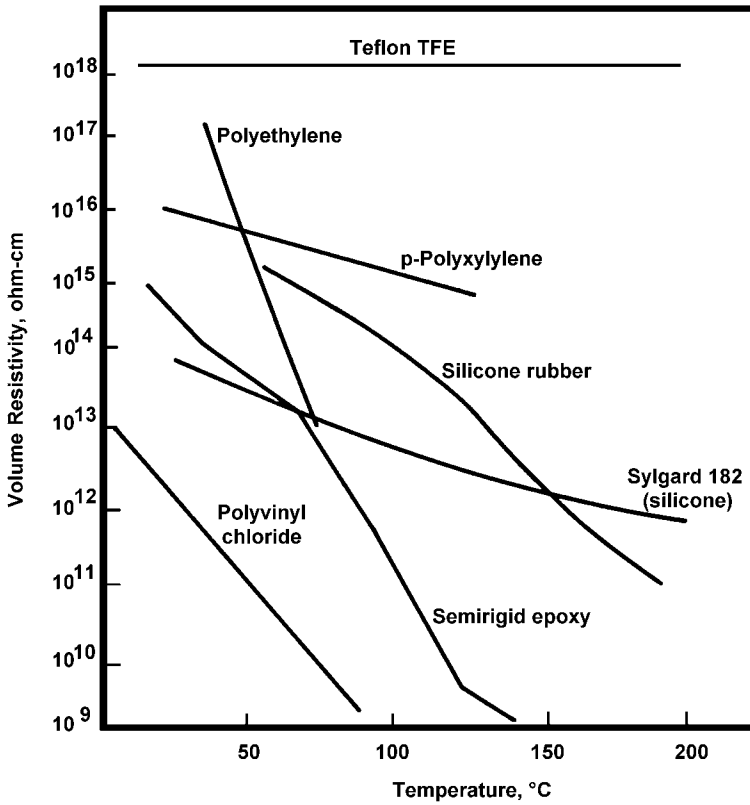


Figure 1.8. Electrical resistivity-temperature curves of polymer coating types.

Surface Resistivity. Moisture and contaminants have a more pronounced effect on surface resistivity than on volume resistivity. Whereas it may take several days or weeks for volume resistivity to change in humid or contaminating environments, surface effects are almost immediately discernible. Drastic reductions in surface resistivities occur through small amounts of ionic contaminants even for coatings that have high initial values.^[42] For example, reductions of 4 to 11 orders of magnitude in surface resistivities have been reported for polymers such as polymethylmethacrylate and polyethylene that had been contaminated with fingerprints and subsequently exposed to 96% relative humidity (Table 1.14).

Table 1.14. Effects of Contaminants on Surface Resistivity^[42]

Material	Surface Resistivity, ohms/square	
	At 50% Humidity	At 96% Humidity
Polyethylene		
As received	$>10^{18}$	2.4×10^9
Contaminated with fingerprints	...	4.6×10^7
Freshly shaved surface	...	2.2×10^{11}
Polystyrene		
As received	$\sim 10^{18}$	1.8×10^{11}
Contaminated with fingerprints	...	5.5×10^9
Polymethylmethacrylate		
As received	$\sim 10^{18}$	2.0×10^{14}
Contaminated with fingerprints	...	1.2×10^{12}
Silica glass, clean	10^{16}	5.0×10^8

Buchoff and Botjer^[43] studied the effects of humidity on the surface resistivity of epoxies cured with various hardeners. As shown in Fig. 1.9 surface resistivity as a function of relative humidity was highly dependent on the hardener used. Epoxies cured with aromatic amines were found to be stable at higher relative humidities than those cured with aliphatic amines or anhydrides. However, it should be noted that in the anhydride-cured sample resistivity leveled off to a value of 1×10^{12} ohms/square, a value still considered adequate for most electronic applications. Furthermore, unless there has been an irreversible hydrolytic degradation of the polymer, resistivities recover after removal from the humid environment. In that case as well, the aromatic amine-cured epoxies displayed the fastest rates of recovery. (Fig. 1.10)

1.4.2 Conductance and Conductivity

The reciprocal of resistance is conductance, expressed in units of ohm^{-1} or mhos, and the reciprocal of resistivity is the specific conductance or conductivity, expressed as $\text{ohm}^{-1}\text{-cm}^{-1}$ or mhos per centimeter. Electrically conductive and semiconductive coatings serve a number of functions in electronics such as screen-printed polymer thick-film (PTF) conductors

and resistors, organo-metallic compositions for thin-film conductors, coatings for radio frequency interference (RFI), and electrostatic dissipation coatings.

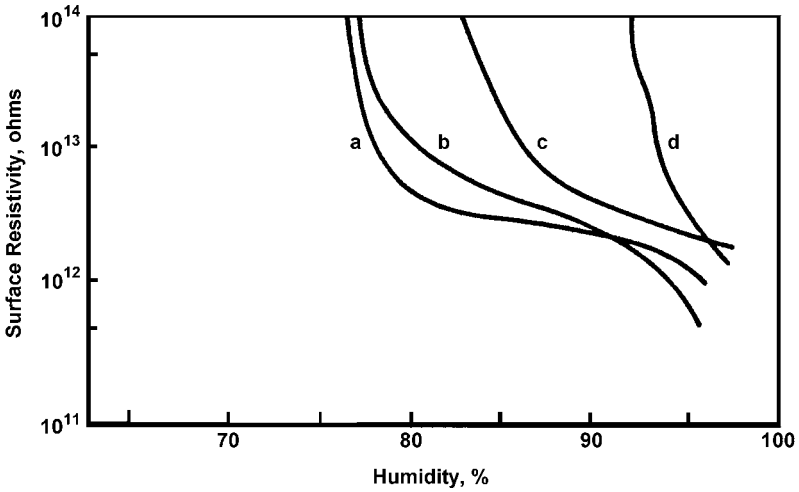


Figure 1.9. Effect of humidity on surface resistivity of epoxy resins cured with different hardeners at 35°C: (a) epoxy resin cured with methyl nadic anhydride, (b) epoxy resin cured with diethylenetriamine, (c) epoxy resin cured with aromatic amine, and (d) Novolac-epoxy resin cured with aromatic amine.^[43]

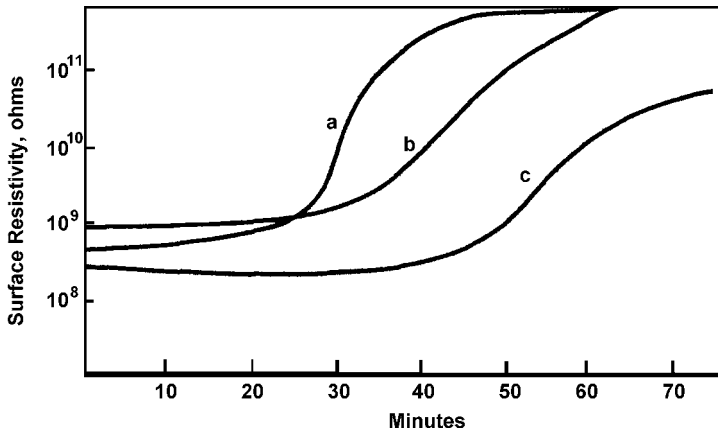


Figure 1.10. Recovery of surface resistivity for cured epoxy resins at 25°C after 80% humidity: (a) epoxy cured with aromatic amine, (b) epoxy cured with methyl nadic anhydride, and (c) epoxy cured with diethylenetriamine.^[43]

Table 1.15. Comparison of Conductive Fillers

Filler	Advantages	Limitations
Silver	Very high conductivity	High cost, silver migration can occur under certain conditions, tarnishes and corrodes if not protected
Gold	Very high conductivity, inert and stable	Higher cost than silver
Copper	High conductivity, low cost	Require extra steps for cleaning to remove oxides, conductivity decreases with age
Aluminum	High conductivity, low cost, good EMI shielding	Can oxidize, shielding decreases at higher frequencies
Steel	Low cost, good EMI shielding at low volume percent	Low conductivity
Graphite or Carbon Black	Low cost, good EMI and ESD shielding	Low conductivity, shielding decreases with rising frequencies

Metal-filled Polymers. The most practical method for rendering polymer materials conductive is to fill them with metal particles. Silver, gold, aluminum, copper, nickel, and carbon/graphite fillers are the most widely used fillers. Epoxies, silicones, acrylics, and polyurethanes are typical resin binders. A list of conductive fillers and their attributes is given in Table 1.15. Compositions are commercially available or may be formulated in a range of viscosities from thick pastes to sprayable liquids.

Conductivity values vary widely depending on the conductivity of the filler chosen, the technique used for cleaning and processing the filler particles, the percentage (loading) of the filler, and the degree of cure. Except for the noble metals (gold, platinum), meticulous cleaning of the metal particles is necessary to remove high-resistance surface oxide layers. Even after cleaning, metal oxides may slowly form again, and over long periods or under accelerated conditions, the conductivity will decrease.

The electrical conductivity of metal-filled plastics is a function of the extent to which the metal particles contact each other; the higher the filler content the greater the probability for metal-to-metal contact and the higher the conductivity. There is a limit, however, on the amount of filler that can be blended into a resin without affecting its flow properties and its ability to be dispensed. Filler concentrations greater than 80% by weight generally render the material impractical for use.

Finally, the degree of cure of the resin binder also affects conductivity. In general, higher values are obtained with the heat curing formulations than with room-temperature or low temperature curing types (Table 1.16). For high conductivity, silver or gold-filled resins are used; and, with an optimum formulation and cure schedule, conductivity values of the order of 10^{-4} to 10^{-5} ohm-cm are achieved.

Table 1.16. Conductivity Variations of Metal-filled Epoxies

Composition	Conductivity (mhos/cm)			
	Cure Conditions	Initial Value	After 40 days Humidity Cycling	After 50 hr 20% Salt Spray
Silver-filled epoxy	6 hr at 180°C	3,000	1,250	1,400
Silver-filled epoxy	36 hr at room temperature	100	700	--
Gold-filled epoxy	6 hr at 50°C	200-700	--	--

Inherently Conductive Polymers.In general, polymeric materials are good insulators. However, some have been synthesized and others formulated that inherently have semiconductive and even conductive properties. The main attractions of conductive polymers over conventional metals are their ease of processing, low cost, light weight, and robustness. Although the potential for inherently conductive polymers and coatings is quite large, actual introductions to commercial practice have been minimal. Applications that have been studied or envisioned include antistatic coatings, flexible flat-panel displays for TV and computers, semiconductor devices, capacitors, biosensors and chemical sensors, batteries, and antiradiation coatings.^[44]

Inherently conductive polymers have been synthesized by doping, with either an electron donor or an electron acceptor available, linear conjugated polymers that have electrons in easily excited valence bands. Although considerable research has been conducted, the conduction mechanism in organic materials is still not clear or well defined. Many electrically semiconductive or conductive polymers lack the thermal or mechanical stabilities to render them useful in electronic applications. Some polymers that have been extensively studied are: polyacetylene, polypyrrole,

polyphenylene sulfide, polyparaphenylene, polythiophene, and polyaniline.^{[45]–[47]}

1.4.3 Capacitance

The capacitance of a coating and its contribution to the total capacitance of a circuit is critical for high-frequency, high-speed digital circuits. High capacitance results in delays in switching times and changes in component values. Present computer operations are limited by the coupling capacitance between circuit paths and integrated circuits on multilayer boards. The computing speed between integrated circuits is reduced by high capacitance and the power required to operate them is increased.

For high-speed, high-frequency circuits, it is critical to select materials that contribute little capacitance. Reductions in parasitic capacitances may be achieved in several ways through both the selection of materials and design of the circuit geometries. Capacitance (C) is directly proportional to the dielectric constant (ϵ) of the insulator separating the conductors, directly proportional to the area (A) between the conductors, and inversely proportional to the distance between the conductors (d). Thus:

$$\text{Eq. (1.4)} \quad C = \epsilon A / d$$

Hence, capacitance can be minimized by using an insulator having a low dielectric constant and designing the circuit so that the conductor area is small and the insulator is thick.

1.4.4 Dielectric Constant

If the space between the plates of a parallel-plate capacitor is filled with a dielectric material, the capacitance will be increased by a factor that is a constant for that material. This constant ϵ is referred to as the dielectric constant or permittivity and is represented by the equation:

$$\text{Eq. (1.5)} \quad C_m = \epsilon C_v \text{ or } \epsilon = C_m / C_v$$

where C_m is the capacitance of the dielectric material and C_v is the capacitance of a vacuum. The *dielectric constant* of a material may, therefore, be defined as: the ratio of the parallel electrical capacitance with

the material between the plates to the capacitance when a vacuum separates the plates. Because dielectric material affects the force with which two oppositely charged plates attract each other, the dielectric constant may also be defined as the relative effect of the medium on this force of attraction, according to Coulomb's equation:

$$\text{Eq. (1.6)} \quad F = QQ'/\epsilon d^2$$

where F = force of attraction between the two plates

Q = charge on one plate

Q' = charge on the second plate

ϵ = dielectric constant

d = distance between plates

Thus, the higher the dielectric constant of the material between the plates, the more attenuated will be the force of attraction between the plates. The dielectric constant of vacuum is 1. Of air, it is slightly above 1, which for all practical purposes is also taken as 1. This simplifies the measurement somewhat. Details of sample preparation, test methods, and equipment for measuring dielectric constants are given in ASTM D150.

The dielectric constants of gases are only slightly greater than 1, but values up to 100 are common for many organic compounds, especially the highly polar types. Values of up to 1000 are known for some inorganic materials, such as barium titanate. The dielectric constants of materials arise from their electronic polarization abilities. Materials with polar groups are those having permanent dipole moments, such as the keto group (C=O) or carboxyl group (-O-C=O). They have large dielectric constants because of the orientation of the dipoles in an applied field.^{[48]–[49]} Polar polymers also tend to absorb moisture from the atmosphere, which further increases their dielectric constants and degrades their electrical insulation properties. It is for these reasons that non-polar polymers such as polyethylene, polystyrene, and fluorocarbons have better insulation properties than the highly polar polymers such as polyamides, alkyds, urea-formaldehydes, and some epoxies.

Dielectric constants for insulating or protective coatings range from 2 to 8. Preferred electrical insulating coatings have low dielectric constants and low dissipation factors, and retain these low values over wide temperature, humidity, and frequency ranges. Those combining high dielectric constants and low dissipation factors are useful as capacitors. Dielectric

constants of 4.5 maximum at 1000 Hz and 25°C are normally considered satisfactory as insulating materials for electronic assemblies. These are the minimum requirements specified in MIL-I-16923. However, as mentioned earlier, for microelectronic circuitry operating at high frequencies and speed, capacitance effects must be minimized. Materials having low dielectric constants, preferably below 2.0, are desirable. Unfortunately, there are few known materials with dielectric constants below 2. Experimental work is in progress to synthesize dielectrics with controlled, built-in, air-filled pores (*nanoporous dielectrics*) to reduce the already low dielectric constants of materials such as silicon dioxide, silicones, and fluorocarbons.^[50]

The dielectric constant of a polymer coating may increase or decrease depending on variations in its composition. For example, the addition of ceramic fillers that have fairly high dielectric constants will increase ϵ values. The blending of resins having high ϵ with those having low ϵ will increase the ϵ of the lower ϵ resin in proportion to the amount and type of resin added. A typical curve for blending of the high- ϵ polysulfide with a low- ϵ epoxy is given in Fig. 1.11.^[51]

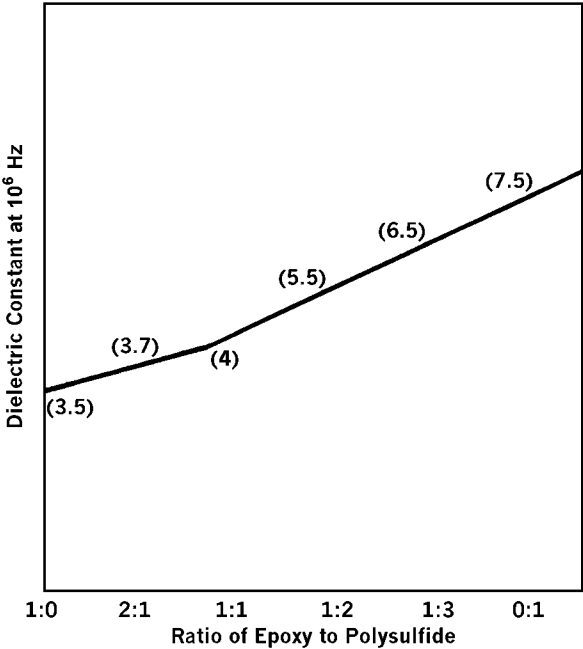


Figure 1.11. Variation of dielectric constant of epoxy-polysulfide blends.^[51]

If experimental data are not available, a rough approximation of the dielectric constant of a composite may be calculated by the following equation.^[52]

$$\text{Eq. (1.7)} \quad \log \varepsilon_x = v_1 \log \varepsilon_1 + v_2 \log \varepsilon_2$$

where ε_x = dielectric constant of the composite

v_1 = volume fraction of the first component

ε_1 = dielectric constant of the first component

v_2 = volume fraction of the second component

ε_2 = dielectric constant of the second component

1.4.5 Dissipation Factor and Power Factor

The *dissipation factor* (D) is the ratio of the resistive (loss) component of current I_r to the capacitive component of current I_c and equals the tangent of the dielectric loss angle δ as follows:

$$\text{Eq. (1.8)} \quad D = I_r / I_c = \tan \delta$$

The *power factor* (PF) is a ratio of power dissipated to the current (volts times amperes) and is a measure of the dielectric loss in the insulation acting as a capacitor. It is related to dissipation factor by the equation:

$$\text{Eq. (1.9)} \quad D = \frac{PF}{\sqrt{1 - (PF)^2}}$$

Because values for dielectric materials are low, dissipation factors are essentially equal to power factors and these terms are often used interchangeably. Military specifications such as MIL-I-16923 call for dissipation factors not to exceed 0.020 at 1 kHz and 25°C.

The loss factor is the product of the power factor and dielectric constant and is a measure of signal absorption according to the equation:

$$\text{Eq. (1.10)} \quad \text{Loss Factor} \approx \text{Watts loss} \approx \varepsilon \tan \delta \approx \varepsilon D$$

Low values are desirable for all these parameters, especially for high-speed, high-frequency circuits operating in the gigahertz range. A low value indicates low conversion of electrical energy to heat energy and reduced power loss for the network. The dissipation factor, as well as other electrical parameters, depends on frequency, temperature, humidity, and purity of the sample.

1.4.6 Variation of Dielectric Constant and Dissipation Factor with Temperature

In general, at constant frequency, both the dielectric constant and the dissipation factor of an insulating coating will increase with increasing temperature. Because coating formulations are not homogeneous, and because they contain constituents that become volatile or change on heating, electrical values may be quite erratic. No simple linear relationship with temperature exists. Figures 1.12 and 1.13 show the variations of dielectric constant and dissipation factor with temperature for an epoxy coating cured with an anhydride-castor oil adduct. The temperature was allowed to stabilize for about 25 minutes prior to taking the measurements. Therefore, part of the change attributed to temperature may have been due to further curing of the polymer at each temperature step.

1.4.7 Variation of Dielectric Constant and Dissipation Factor with Degree of Cure

The rate of change of dielectric constant and dissipation factor with increasing temperature can be used as an indication of the degree of cure of a polymer. The electrical properties of a polymer change very little with increasing temperature after the polymer is fully cured. This is in contrast to the rapid changes that occur in a partially cured polymer. As illustrated in Figs. 1.12 and 1.13, an additional 8 hours of cure at 75°C resulted in a lower rate of change of both the dielectric constant and dissipation factor. At room temperature, the electrical properties of the two samples were almost identical. Thus, at this temperature one cannot differentiate between the two cure conditions. Further data on the change in dielectric constant and dissipation factor with degree of cure are given in Table 1.17. In these studies, the temperature was held constant at 23°C. At all frequencies, dielectric constants and dissipation factors decreased progressively as the cure schedule was increased. The coating tested was Epon® 828 cured with an anhydride-castor oil adduct.

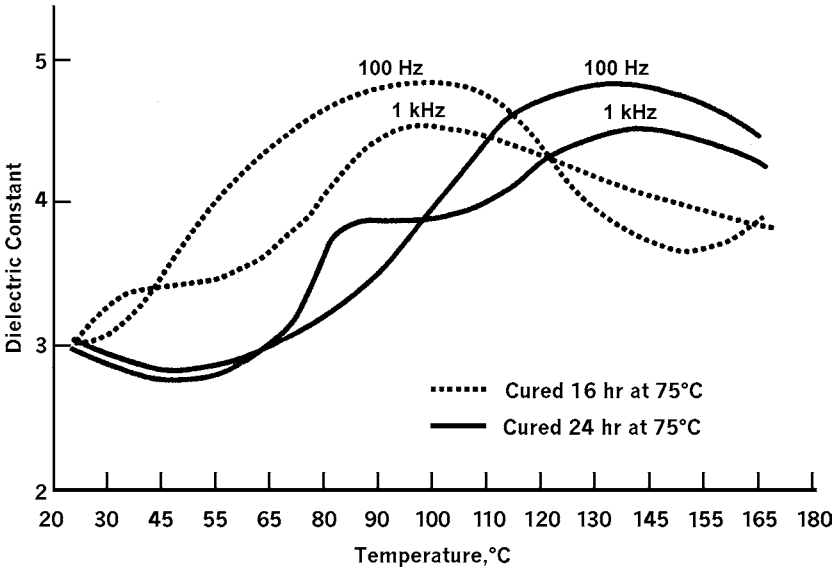


Figure 1.12. Variation of dielectric constant with temperature, degree of cure, and frequency for an epoxy coating cured with anhydride-castor oil adduct.

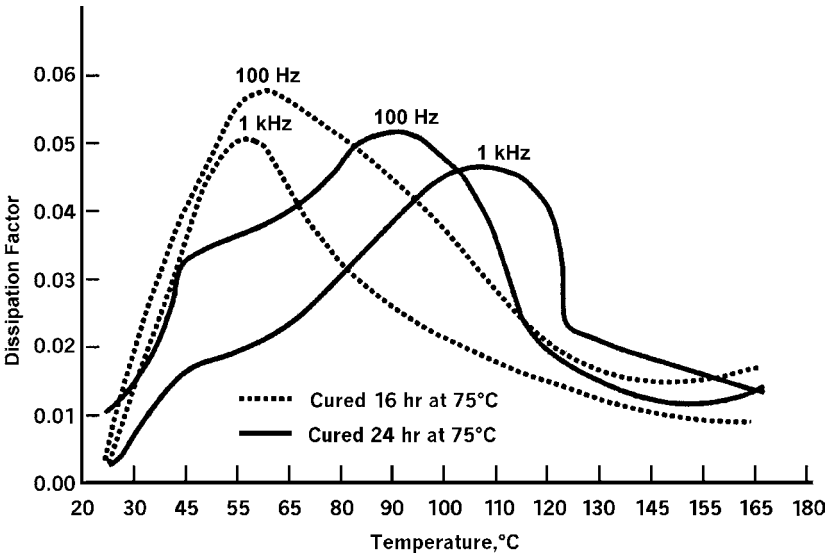


Figure 1.13. Variation of dissipation factor with temperature, degree of cure, and frequency for an epoxy coating cured with anhydride-castor oil adduct.

Table 1.17. Effect* of Cure on Electrical Properties of Epoxy Cured with Anhydride-Castor Oil Adduct

Sample	After Cure of 16 hr at 74°±2°C	After Postcure of 5 hr at 74°±2°C	After Additional Postcure of 16 hr at 120°±2°C
Dielectric Constant			
At 100 Hz			
1	4.31	3.77	3.08
2	4.30	3.73	3.04
3	4.32	—	3.07
At 1 kHz			
1	3.91	3.52	3.07
2	3.87	3.49	3.02
3	3.93	—	3.07
At 10 kHz			
1	3.63	3.39	3.05
2	3.57	3.35	3.00
3	3.65	—	3.04
At 100 kHz			
1	3.45	3.28	3.03
2	3.40	3.24	2.96
3	3.49	—	3.01
Dissipation Factor			
At 100 Hz			
1	0.0844	0.0664	0.0039
2	0.0912	0.0690	0.0040
3	0.0841	—	0.0036
At 1 kHz			
1	0.0626	0.0385	0.0037
2	0.0668	0.0396	0.0038
3	0.0586	—	0.0035
At 10 kHz			
1	0.0433	0.0257	0.0051
2	0.0452	0.0266	0.0053
3	0.0398	—	0.0048
At 100 kHz			
1	0.0371	0.0254	0.0091
2	0.0380	0.0259	0.0094
3	0.0343	—	0.0083
* Measured at 23°C.			

The optimum curing time and temperature obtained from a plot of the dielectric constant or dissipation factor versus time at constant temperature are even more apparent for the epoxy system shown in Figs. 1.14 and 1.15. Initial values, after mixing a two-part coating or upon activating a one-part coating, are high, but decrease as polymerization and hardening progress. Ultimately, at some optimum time, these values level off and stabilize. It can be seen that the cure for this epoxy resin is essentially complete in 3.5 hours at 120°C, but requires 12 hours at 66°C to achieve the same degree of cure.^[53]

Other investigators have shown that the degree of cure or cross-linking of an epoxy system may be followed by dielectric measurements over a frequency range from 30 Hz to 10¹⁰ Hz.^[54] A correlation of mechanical properties with electrical properties may also be made, and once the correlation has been established and standard curves prepared, they may be used for rapid quality control testing.

1.4.8 Dielectric Strength and Breakdown Voltage

Yet another important electrical property is the dielectric strength, that is, the ability of a coating to withstand an applied voltage without breakdown. *Dielectric strength* is defined as the maximum voltage (usually reported in volts per mil thickness) at or below which no breakdown occurs. Some prefer to speak about *dielectric breakdown voltage*, the voltage threshold at or above which actual failure occurs. This is also reported in volts per mil thickness and the two terms are often used interchangeably. The physical breakdown of coatings at a critical voltage is believed to be due to a large increase in electrons (electron “avalanche” effect) within the insulating coating.^[55] Even the best insulation materials contain a small number of ions and free electrons owing to thermal agitation or molecular imperfections. In such cases, very high voltages will be required to initiate breakdown. Other, less perfect insulators, that contain impurities, voids, and moisture will have lower breakdown voltages.^[56]

Accurate dielectric strength data are important in designing reliable high-density electronic circuits intended to operate at high voltages. For both low- and high-voltage operation, organic coatings are widely used because of their high dielectric strengths. In general, dielectric strengths of organic coatings are much higher than those of inorganic or ceramic coatings.

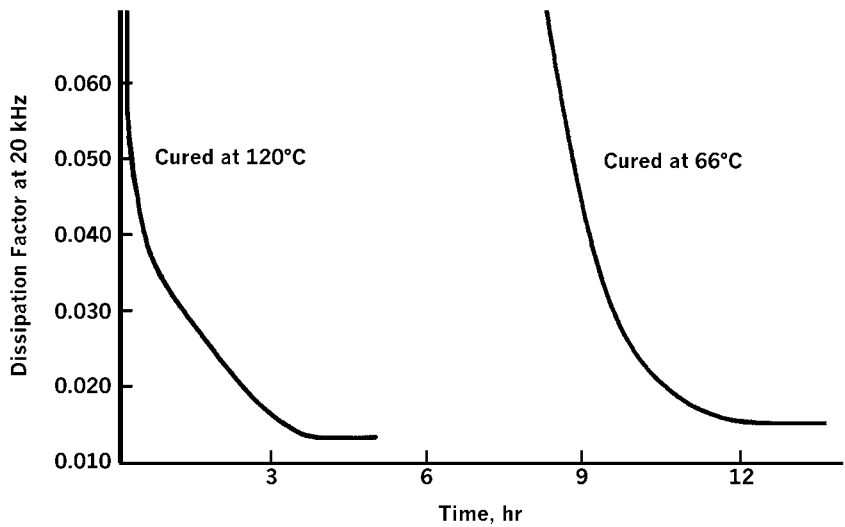


Figure 1.14. Establishment of epoxy cure schedule from dissipation factor data.^[53]

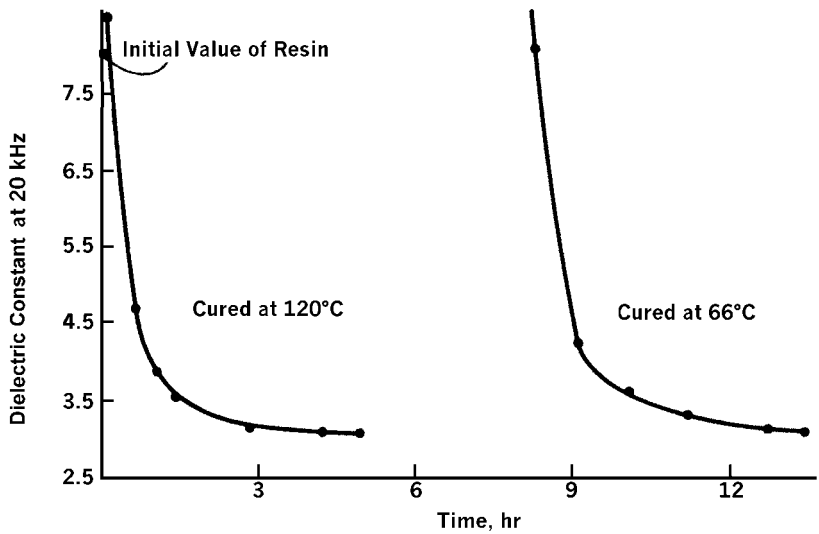


Figure 1.15. Establishment of epoxy cure schedule from dielectric constant data.^[53]

Dielectric strengths should be measured carefully under specified conditions in order to obtain reproducible results and an accurate comparison among various coating materials and their cure conditions. Numerous test conditions are known to affect dielectric strength values. For example, it is important to standardize the electrode configuration and the thickness of the sample. All values are ultimately reduced to volts per mil of thickness. The thickness of the sample has a marked effect on the values obtained (Fig. 1.16). Generally, thin specimens result in higher values than thick specimens. In most cases, the 17-mil thickness specified in the ASTM D149 method is too thick to easily prepare samples of coatings. The same test procedure, however, may be followed using 2 to 5 mil thick samples. Other variables affecting the readings include the manner in which the voltage is applied (continuously or stepwise), the rate of voltage increase, the frequency of the applied power, the integrity of the coating (lack of pinholes and air voids), and the purity of the sample. In general, the dielectric strength of a polymer coating decreases with an increase in imperfections or impurities in the coating.



Figure 1.16. Effect of coating thickness on dielectric strength for Teflon TFE.

Ambient conditions, such as temperature and humidity, under which the test is performed also affect the dielectric strength values. A plot of dielectric strength versus temperature shows the same general curve for all polymers. There is less change at low temperatures, but a rapid decline above a critical temperature is characteristic of the coating being tested (Fig. 1.17).^[57]

Although elevated temperatures and exposure to moisture cause pronounced reductions in dielectric strength, in some cases, final dielectric strength values may still be sufficiently high to be of little concern. As an

example, the dielectric breakdown voltage of an 8-mil-thick silicone coating (Dow Corning DC-630) having an initial value of 1000 volts/mil dropped to 400 volts/mil after a 24 hour immersion in distilled water and to 500 volts/mil after a 24 hour exposure at 260°C. Yet, these values are still sufficiently high for most applications.^[58]

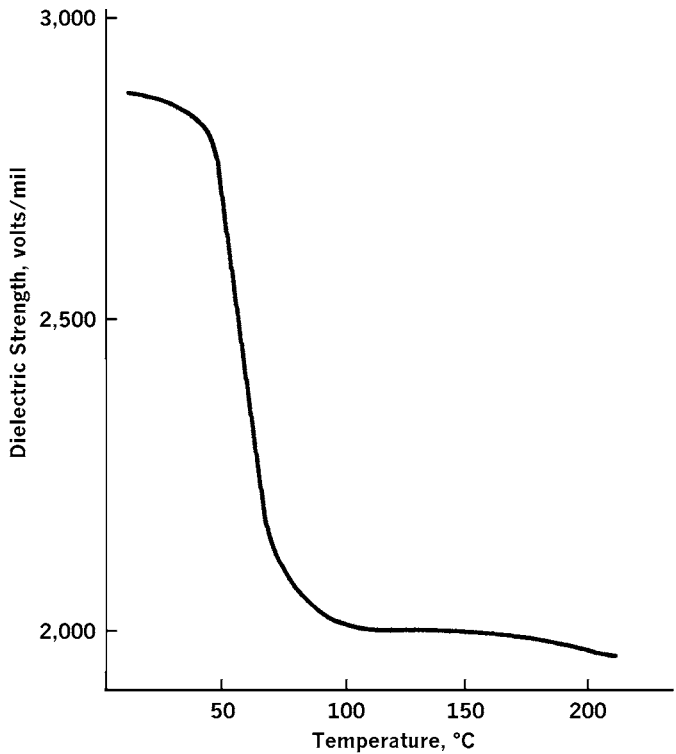


Figure 1.17. Temperature dependence of the dielectric strength of polytetrafluoroethylene (5-mil-thick film, 1/4 in electrode).^[57]

Measuring the dielectric strength under ambient conditions may result in readings that are difficult to interpret, because of electrical discharges and surface arcing around the sample. In such cases, the samples may be tested while immersed in a highly stable fluid having a minimum breakdown voltage of 26,000 volts with 0.1 inch separation between the electrodes.^[59] Examples of such high dielectric-strength fluids include some silicones and various hydrocarbon and transformer oils. There are several standard methods for measuring dielectric strength, such as ASTM D149 and IPC-TM-650, Method 2.5.7.

1.4.9 Arc Resistance

Arc resistance, also known as tracking resistance, is the time in seconds that an arc may exist on the surface of a material before electrical breakdown of the surface occurs. A high-voltage, low-current arc is used to simulate service conditions such as those existing in ac circuits operating at high voltages and currents limited to the low milliamperage region. A commonly used test method for arc resistance is described in ASTM D495. Several arc testers that comply with this test method are commercially available. According to ASTM D495, the specimens are placed between the electrodes and an arc is generated at scheduled intervals and at specified current densities.

There are three modes by which failures due to arcing can occur:

- By tracking; that is, by the formation of thin wire-like lines between the electrodes.
- By carbonization of the surface due to heating. A conductive path is formed because of carbonaceous decomposition products that have lower resistance to the flow of current than the original surface.
- By self-ignition of the coating without the formation of any visible conducting path.

Arc resistances of coatings vary widely, depending on their molecular structures, formulation ingredients such as fillers and curing agents, and the physical and chemical condition of the surface. In the case of epoxies, aromatic amine and anhydride curing agents result in higher values than aliphatic amines. Fillers also have a pronounced effect, generally improving the arc resistance of a coating. Studies of the effects of fillers such as mica, alumina, silica, and gypsum on the arc resistance of an epoxy resin were made by Delmonte^[60] and by others.^[61] In general, it was found that the addition of fillers could easily double or even triple the arc resistance of an unfilled epoxy resin system.

Not all coatings may be defined in terms of precise arc-resistance values. Some melt, gum up, or crack during the course of testing. When precise reproducible values are obtained, they are the result of the inherent stability of the material, its purity, and its surface cleanliness. Arc resistance can be improved by keeping the surface dry and free of contaminants. Even touching the surface will reduce arc resistance due to moisture, salts, and oils transferred from the fingers. The arc resistance of polymer resins may be increased two- to threefold by formulating them with glass or mineral fillers.

In addition to its usefulness as a design criterion, arc-resistance testing may be used as a quality control method and as a means of determining changes that a surface undergoes on aging, irradiation, and exposure to temperature or humidity.

1.4.10 Corona

Corona, also known as *partial discharge*, occurs when a sufficiently high voltage causes a breakdown of the surrounding medium, usually air or oil, resulting in a conductive path. This creates discharges to the polymer surface and degradation. The discharges produce humming or sizzling sounds that are most pronounced at locations having high moisture adsorption or absorption. The *corona inception voltage* is a measure of the onset of discharge. Polymers that oxidize readily such as polyolefins are especially prone to corona discharge while others such as silicones and polyimides are very resistant.

1.5 THERMAL FUNCTIONS

Organic coatings are seldom used for the primary purpose of conducting heat. Unfilled polymers and polymer coatings have low thermal conductivities. As such, they are good thermal barriers and thermal insulators. Furthermore, there is little difference in the thermal conductivities of the major polymer types; values generally lie between 3 and 8×10^{-4} cal/(sec)(cm)(°C) or 0.125 to 0.335 in W/mK (Table 1.18). These values are hundreds to thousands of times lower than those for metals or ceramics. As with electrical conductivity, the thermal conductivities of coatings can be increased somewhat by formulating them with metal or inorganic fillers. However, compositions containing metal fillers also become electrically conductive and as such are not suitable for electronic applications that require electrical isolation. Among the best non-metallic, high-thermally-conductive fillers are beryllia, aluminum nitride, boron nitride, and diamond. Each of these fillers has some limitation, such as the toxicity of beryllia powder and the high cost of diamond powder. Other more practical fillers, although not as effective, include aluminum oxide (alumina), silicon oxide (silica), and carbon. As can be seen from Table 1.19, the amount of filler and its physical nature affect the thermal conductivity.^{[62]–[63]} A need still exists

for very high thermally conductive polymers that are also electrically insulative, especially for high-density microelectronics where heat dissipation is critical to the reliability of the modules. No polymer material yet exists that combines the high thermal conductivity and electrical high insulation resistance of beryllia, aluminum nitride, or diamond.

If some degree of thermal conductance in organic coatings is required, either or both of the following approaches may be used:

- Employ a coating that is filled as much as possible with a thermally conductive filler.
- Employ as thin a coating as possible, since thermal conduction is inversely proportional to thickness.

In practice, it is found that any gain in thermal conductivity resulting from the use of a filler is often offset by the coating becoming thixotropic, thicker, and difficult to apply.

The use of fillers generally increases the thermal conductivity of unfilled polymers. For example, the thermal conductivity of an Epon 828/diethylenetriamine (DETA) epoxy formulation was improved three- to fourfold by adding silica, aluminum, or beryllia fillers, but these values are still far lower than the thermal conductivities of the fillers alone. The incorporation of conductive particle fillers in a resin can increase the thermal conductivity tenfold over the unfilled resin, but also decreases the electrical insulation resistance sometimes from 1×10^{15} ohm-cm to 10 ohm-cm. Carbon-filled polymers such as epoxies have been used for many years as low-cost screen-printable resistors known in the trade as Polymer Thick Films (PTF). Different sheet resistances are produced depending on the amount and nature of the carbon filler. Carbon-filled coatings are also used for EMI/RFI shielding and as antistatic coatings. Some investigators have attempted to increase the inherent thermal conductivity of epoxies by further cross-linking the molecules by postcuring or by exposure to gamma radiation, but were able to achieve, at most, only a 5% improvement.^{[64]–[65]} The addition of selected fillers still remains the most effective method of increasing the thermal conductance of plastics and polymer coatings.

Other more detailed discussions of thermal conductance may be found in the literature^{[66]–[69]} and in various test methods (see Ch. 7).

Table 1.18. Thermal Conductivities of Various Materials*

Unfilled Polymers	Thermal Conductivity, W/m.K
Acrylic	0.167–0.21
Alkyd	0.33
Depolymerized rubber	0.134
Epoxies Cured with diethylenetriamine Electrostatic spray coating (Hysol DK-4) Epon 828 (71.4%), DEA (10.7%)	0.125–0.25 0.2 0.276 0.22
Fluorocarbons Teflon FEP Teflon TFE	 0.24 0.29
Phenolics	0.125–0.25
Polyamide Nylon 6,6 Nylon 6,10	 0.24 0.22
Polyester	0.08–0.2
Polyethylene	0.33–0.46
Polyimide, Pyre ML Enamel Pyre ML Varnish	 0.15 0.3
Polypropylene	0.12
Polystyrene	0.13
Polyurethane	0.1
Polyvinyl chloride formal	 0.08 0.15
Polyvinylidene chloride fluoride	 0.083 0.15
Polyxylylene, Parylene N	0.125
Silicones Flexible casting resin Gel coating RTV type Sylgard varnishes and coatings	 0.29 0.155–0.29 0.21–0.31 0.15–0.31

(cont'd.)

Table 1.18. (cont'd.)

Metals, Alloys, and Ceramics	Thermal conductivity, W/m.K
Aluminum	247
Aluminum nitride	140–200
Aluminum oxide 99+ % alumina 96% alumina	36–40 17–20
Beryllium oxide, Beryllia 99.9%	276
Boron nitride	60–80
Chromium	66
Copper	398
Copper-molybdenum	155
Copper, 20% tungsten	248
Diamond single crystal CVD	2300 800–1300
Gallium arsenide	43–50
Glass	1.57
Gold	315
Gold-Platinum	130
Gold-Silicon Eutectic	294
Gold-Tin (20%)	57
Indium	78
Indium arsenide	7
Indium phosphide	68
Invar	11
Kovar	16.7
Lanxide (Al-SiC)	200
Lead	35
Low Temperature Cofired Ceramic (LTCC)	3–5
Molybdenum	130
Nickel	92
Palladium	70
Platinum	71

(cont'd.)

Table 1.18. (cont'd.)

Metals, Alloys, and Ceramics	Thermal conductivity, W/m.K
Quartz (X'line SiO ₂)	1.4
Sapphire (X'line Al ₂ O ₃)	33.5
Silicon	114-125
Silicon carbide	270
Silicon-germanium	114
Silver	427
Silver-palladium	150
Solder (Sn 60, Pb 40)	53
(Sn 40, Pb 60)	42
Stainless Steel	15
Tin	64
Titanium	20
Tungsten	178
*Values for other materials may be found in the Merck Index or the Handbook of Chemistry and Physics, CRC Press. Values were generally taken at 25°C. Values are for comparative purposes only since values for specific compositions, processing conditions, and temperatures will vary.	

Table 1.19. Effect of Fillers on Thermal Conductivities of Epoxies

Polymer	W/m.K
Epon 828/DETA (A)	0.17
A + 50% aluminum	0.46
A + 50% beryllia	0.52
A + 50% silica	0.42
A + 70% aluminum	0.54
A + 70% beryllia	0.745
A + 70% silica	0.50
Epoxy, flexibilized (B)	0.226
B + 64% by vol tabular alumina	2.09
B + 66% by wt tabular alumina	0.75
Epoxy, diamond filled	11
Epoxy, silver filled	1.56–1.87
Epoxy, silica filled	0.83

1.5.1 Ablative and Intumescent Coatings

Some coatings have been specifically engineered and formulated to remove large amounts of heat when subjected to high temperatures for short periods of time. Among these are the thermally *ablative coatings* that have been used to protect components during missile and rocket liftoffs. The coatings, when applied to heat sensitive parts such as electronic enclosures or nozzle control units, protect the inside surfaces from temperatures as high as 3000°F generated from the rocket engines during blast-off. At the temperature of ablation, the exterior layers of the coatings decompose and char. Thus, the coating absorbs considerable heat (heat of ablation) while the inside surfaces remain sufficiently cool. The coating must be applied at a sufficient thickness and must ablate at a controlled rate, so that sufficient coating remains at the end of the thermal exposure. Ablative coatings consisting of filled epoxies and silicones were used to protect the nozzle control unit of the Minuteman missile during take-off. A similar coating was used on the Apollo capsule to protect the astronauts from the intense heat of reentry into the Earth's atmosphere.

Intumescent coatings are used to protect electronic boxes and structures from fire. They contain fillers or have molecular structures that decompose and evolve into flame-retardant gases such as carbon dioxide.

REFERENCES

1. Licari, J. J., and Browning, G. V., *Plastics for Packaging: Handle With Care*, *Electronics* (Apr. 1967)
2. Ritchie, B., *Conformal Coating over Solder Mask, No-clean Soldering and Alternate Cleaning Technologies*, *NEPCON West* (1994)
3. *Commercialization of Military and Space Electronics Conference*, Los Angeles (Feb. 12–15, 2001)
4. Baer, E. (ed.), *Engineering Design for Plastics*, Reinhold, NY (1964)
5. *Permeability and Other Film Properties of Plastics and Elastomers*, *Plastics Design Library Handbook Series*, Wm. Andrew Publ. (1995)
6. Lee, H., and Neville, K., *Handbook of Epoxy Resins*, McGraw-Hill (1967)
7. ASTM D570-98, *Standard Test Method for Water Absorption of Plastics*, Am. Soc. for Testing and Mater., West Conshohoken, PA
8. ASTM E96-00, *Standard Test Methods for Water Vapor Transmission of Materials*, Am. Soc. for Testing and Mater., West Conshohoken, PA

9. ASTM D1653-93, *Standard Test Methods for Water Vapor Transmission of Organic Coatings*, Am. Soc. for Testing and Mater., West Conshohoken, PA
10. Baer, E., (ed.), *Engineering Design for Plastics*, Reinhold, NY (1964)
11. Kohman, G. T., Hermance, H. W., and Downes, G. H., Silver Migration in Electrical Insulation, *Bell Systems Tech. J.*, 34:6 (Nov. 1955)
12. Short, O. A., Silver Migration in Electrical Circuits, *Tele-Tech and Electronic Ind.*, Vol. 15 (Feb. 1956)
13. Riemer, D. E., Material Selection and Design Guidelines for Migration-Resistant Thick-film Circuits with Silver-bearing Conductors, *Proc. 31st Electronic Components Conf.* (1981)
14. Williams, J. C., and Herrmann, D. B., *Surface Resistivity of Non-porous Ceramic and Organic Insulating Materials at High Humidity with Observations of Associated Silver Migration*, I.R.E. Trans. on Reliability and Quality Control, PGROC-6 (Feb. 1956)
15. Chaikin, S. W., *Study of Effects and Control of Surface Contaminants on Dielectric Materials*, Final Report, U. S. Army Signal Engineering Labs., DA-36-039SC-64454, Stanford Research Inst. (Jan. 1958)
16. *Corrosion Control and Treatment Manual*, TM-584C, Revision C, Kennedy Space Flight Center (Nov. 1994)
17. MIL-STD-889, *Military Standard Dissimilar Metals*
18. ASTM D1434, *Standard Test Method For Determining Gas Permeability Characteristics of Plastic Film and Sheeting*, Am. Soc. for Testing and Mater., West Conshohoken, PA
19. Smits, P., *Metal Progress*, 80(3):75 (1961)
20. Ritchie, P. D., (ed.), *Physics of Plastics*, Van Nostrand (1965)
21. Linde, D. R. (ed.), *CRC Handbook of Chemistry and Physics*, 73rd Ed., The Chemical Rubber Co., Boca Raton, FL (1992-93)
22. Moore, D. T., Precision of the Sward Hardness Rocker, *Paint, Oil, Chem. Rev.*, 113(21):41 (1950)
23. Tech. Bull., TS-6083, Spencer Kellogg, Div. Textron
24. Koleske, J. V., (ed.), *Paint and Coating Testing Manual*, ASTM Manual 17 (1995)
25. King, J., Qualification of Dow Corning Q3-6527 as a Particle Getter, Singer Internal Report YS57A834 (1985)
26. King, J., Use of Silicone Gel Particle Getters For Microcircuits Packaging, *Proc. ISHM* (1985)
27. Madigan, M. T., Martinko, J. M., and Parker, J., *Brock Biology of Microorganisms*, 8th Ed., Prentice Hall, NJ (1997)

28. Swatch, F. E., Fungus Testing, *Environmental Quarterly*, 1(1) (Jan. 1961)
29. Landfield, H., and Taylor, W. S., Protecting Vinyl Compounds from Microorganisms, *Plastics Technol.*, 8(8) (Aug. 1962)
30. Trautman, N., and Olynciw, E., Compost Microorganisms, Cornell Composting, *Science and Engin.*, Cornell U., Ithaca, NY
31. Zedler, R. J., *Metal Finishing*, 60(12):57 (1962)
32. Baseman, A. L., Antimicrobial Agents for Plastics, *Plastics Technol.* (Sep. 1966)
33. Metal Finishing Guidebook and Directory Issue, *Metals and Plastics Publ.*, Hackensack, NJ (1982)
34. Magnesium Finishing, Dow Chemical Co., Midland, MI (1963)
35. Stevens, J. A., Designing For Long Service, A Primer of Magnesium Finishing, *Magnesium Topics* (Oct.–Dec. 1958)
36. Warwick, M., Solder Trends in Microelectronics, *Chip Scale Review* (Oct. 2001)
37. Whiting, L. R., and Wangner, P. F., *Coating Compositions for Metals*, U. S. Patent 2525107 (Oct. 10, 1950)
38. Hayward, J. A., Vinyl Coatings: Latest Aspects in Anti-corrosion, *Corrosion Technol.* (Sep. 1965)
39. Tech. Bull. 7030A, Hughson Chemical Co., Div. of Lord Corp.
40. Von Hippel, A., (ed.), *Dielectric Materials and Applications*, M.I.T. Press (1961)
41. Warfield, R. W., Studying Electrical Properties of Casting Resins, *SPE J.*, 14(11) (Nov. 1958)
42. Mathes, K. N., Electrical Properties of Insulating Materials, *Proc. 7th Elec. Insulation Conf., Chicago* (Oct. 15–19, 1967)
43. Buchoff and Botjer, Effect of Humidity on Surface Resistance of Filled Epoxy Resins, *Proc. Ann. Tech. Conf. SPE, Chicago* (Jan. 1960)
44. Ashley, S., Electric Plastics, *Mech. Engin. Magazine* (Apr. 1998)
45. Skotheim, T., Elsenbaumer, R., and Reynolds, J. R., (eds.), *Handbook of Conducting Polymers*, 2nd Ed., Marcel Dekker (1998)
46. Chandrasekhar, P., (ed.), *Conducting Polymers, Fundamentals and Applications*, Kluwer Acad. Publ. (1999)
47. Cotts, D. B., and Reyes, Z., *Electrically Conductive Organic Polymers for Advanced Applications*, Noyes Publications, Park Ridge, NJ (1987)
48. LeFevre, R. J. W., *Dipole Moments*, Methuen, London (1953)
49. Nave, C. R., *HyperPhysics*, Georgia State U. (2000)

50. Low Dielectric Constant Materials for Advanced Microelectronics, IBM, <http://www.almaden.ibm.com>
51. Volk, M. C., Lefforge, J. W., and Stetson, R., *Electrical Encapsulation*, Reinhold, NY (1962)
52. Lechterecher, K., and Rather, K., *Phil. Z.*, 32:255 (1931)
53. Knudsen, J. J., Dielectric Measurements for Process and Product Evaluation, *13th Ann. Exhibit Conf. Soc. of Plastics Ind., Reinforced Plastics Div.*, Chicago (1958)
54. Kobale, M., and Lobl, H., *Z. Elektrochem*, 65:662–669 (1961)
55. O'Dwyer, J. J., An Examination of Avalanche Theories of Dielectric Breakdown in Solids, *Electrical Insulation Conf.*, Natl. Acad. Sci./Natl. Res. Council Publ. 1356 (1966)
56. Philofsky, H. M., and Fort, E. M., Degree of Correlation of $\tan \delta$ and Electric Strength of Insulation, *Proc. 7th Elect. Insulation Conf.*, Chicago (Oct. 15–19, 1967)
57. Oakes, W. J., *Proc. IEEE*, 96(1):37 (1949)
58. Dow Corning Bulletin 07-062 (May 1963)
59. O'Dwyer, J. J., *The Theory of Dielectric Breakdown of Solids*, Oxford, NY (1964)
60. Delmonte, J., Arc Resistance of Epoxies, *Plastics Technol.* (Mar. 1958)
61. Comparative Properties of Filled Epoxy Electrical Potting Compounds, Union Carbide Report (1959)
62. Wolf, D. C., *Proc. Natl. Electronic Packaging Symp.*, New York (Jun. 1964)
63. Gershman, A. J., and Andreotti, J. R., *Insulation* (Sep. 1967)
64. Janssen, J. E., and Torborg, R. H., *ASME Thermodynamics and Transport Properties of Gases, Liquids, and Solids*, McGraw-Hill, New York (1959)
65. Evans, A. G., and Palanys, M., *Nature*, pp. 152, 738 (1943)
66. Sherman, L. M., Plastics that Conduct Heat, *Plastics Technol.* (2001)
67. Rabilloud, G., *High-Performance Polymers, Conductive Adhesives Chemistry and Applications*, Institut Francais du Petrole Publications, Paris (1997)
68. Wunderlich, B., *Thermal Analysis*, Academic Press, New York (1990)
69. Altoz, F., Thermal Management, *Electronic Packaging and Interconnection Handbook*, Ch. 2, (C. Harper, ed.), McGraw-Hill (1991)

Chemistry and Properties of Polymer Coatings

Almost any polymer type can and has been formulated as a coating, but the types most widely used as coatings for microelectronic applications are the acrylics, epoxies, polyurethanes, silicones, polyimides, fluorocarbons, and, more recently, benzocyclobutenes (BCB) and p-polyxylylenes (parylenes). A discussion of other polymer types used largely in commercial and consumer items is included for comparison. Among these are the polyesters, polyvinyls, phenolics, and polyamides.

In this chapter, the chemistry and properties of polymer coatings are treated together because of the interrelationship and dependence of properties with chemical structures. For example, both the dielectric properties and moisture affinities of polymers are related to their polarities and molecular structures. Whether the polymers are linear or cross linked and the degree of cross-linking also affect properties such as thermal expansion, shrinkage, softening temperature, resistance to solvents, and thermal stability. Formulations with fillers and additives further enhance certain properties such as thermal conductivity, electrical conductivity, and flame retardancy. Thus, in the discussion of each of the major polymer types, both the chemistry and the generic properties associated with that type will be given.

2.1.2 Properties

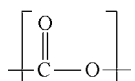
Acrylics are thermoplastic polymers noted for their excellent optical characteristics and resistance to outdoor environments. Acrylic coatings are used in many optical applications where their high light transmittance of 92% and refractive index of 1.48 are well suited. Besides their use as molded plastics for commercial uses such as lenses, light fixtures, and decorative household items, acrylics have a long history of use as conformal coatings for the protection of high reliability, printed wiring boards, and are one of the five coating types specified in MIL-I-46058. Acrylic coatings are characterized by long-term resistance to weather deterioration, good scratch and abrasion resistance, continuous service in temperatures from -65° to 125°C, and excellent electrical properties. An important benefit of acrylics as a coating for high-end expensive printed wiring assemblies is reparability. Acrylics can be easily removed by dissolving in organic solvents such as xylene or Freon. They may also be soldered through making repair and rework easy.

The physical properties of some acrylic resins prior to curing are given in Table 2.1 while the physical and electrical properties of the cured coatings are given in Table 2.2.

Among limitations are that some formulations discolor and degrade on prolonged humidity/temperature exposure. Acrylics are susceptible to attack by organic solvents such as ketones, esters, chlorinated and fluorinated solvents, and aromatic hydrocarbons. This poor solvent resistance, as already mentioned, becomes a benefit for rework and repair since the coatings can be selectively or completely dissolved and removed.

2.2 POLYESTERS

The term *polyester* is a very broad one encompassing any polycondensation product of a dicarboxylic acid with a dihydroxy alcohol. Polyesters are characterized by the ester group,



a repeating unit along the polymer chain. More specifically, polyesters may be divided into two types: unsaturated polyesters and alkyd polyesters.

Table 2.1. Properties of Liquid Acrylic Coating Resins

HumiSeal Type	1B12	1B31	1B31LSE*	1B73	1B73LSE
Specific wt., lbs/gal.	7.3	7.6	7.7	7.7	8.0
% Solids, by wt.	20	35	33	30	29
Viscosity, Centipoise	40	220	420	270	400
Flash Point, °F	30	30	62	30	62
VOC, g/liter	701	592	184	647	240
Dry Time, min.	10	10	20	30	20
Cure Schedule	24 hr/RT or 30 min/77°C	24 hr/RT or 30 min/77°C	24 hr/RT or 30 min/77°C	24 hr/RT or 2 hr/77°C	24 hr/RT or 1hr/77°C
Time for Optimum Properties, days	7	7	7	7	7
Shelf Life at RT, months	12	12	12	12	12
*Legal Solvent Emission. (Courtesy HumiSeal, Div. of Chase Corp.)					

Table 2.2. Physical and Electrical Properties of Cured Acrylic Coatings

HumiSeal Type	1B12	1B31	1B31LSE*	1B73	1B73LSE
Continuous Use Temp. Range, °C	-65 to 125	-65 to 125	-65 to 125	-65 to 125	-65 to 125
Thermal Shock	Passes	Passes	Passes	Passes	Passes
Flammability (self-extinguishing)	Yes	Yes	Yes	Yes	Yes
CTE, ppm/°C	56	55	55	55	55
Young's modulus, psi	9782	7154	7154	1606	1606
T_g , °C	32	15	15	43	43
Dielectric Constant, 1 MHz @ 25°C	2.8	2.5	2.5	2.6	2.6
Dissipation Factor, 1 MHz @ 25°C	0.01	0.01	0.01	0.01	0.01
Dielectric Withstanding Voltage	>1500	>1500	>1500	>1500	>1500
Insulation Resistance, ohms $\times 10^{12}$	250	800	800	550	550
Insulation Resistance after Moisture** ohms $\times 10^9$	30	60	60	72	72
Resistance to Solvents	Poor	Poor	Poor	Poor	Poor
*Legal Solvent Emission **Per MIL-I-46058, 3.13 (Courtesy HumiSeal, Div. of Chase Corp.)					

Free radicals may be initiated by thermal energy, ultraviolet light, or chemicals—notably the organic peroxides.

The use of unsaturated polyesters as coatings or encapsulants for electronic hardware may present several problems:

- Hydrolytic instability of the ester groups, resulting in deterioration and “whitening” of the coating.
- High shrinkage during cure, often as high as 10%, creating high stresses and separation from glass or metal substrates.
- With peroxide cures, the possibility of corrosion of copper owing to the interaction of peroxide catalysts with copper.

2.2.2 Chemistry of Alkyd Polyesters

Alkyd resins are polyesters produced by the condensation of saturated dicarboxylic acids with polyhydric alcohols as depicted in Fig. 2.3.

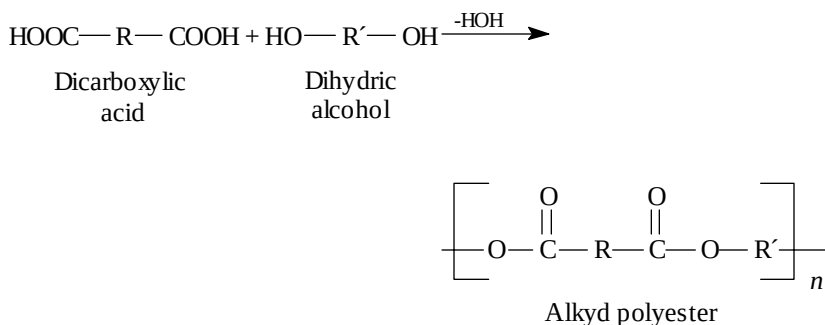


Figure 2.3. Alkyd polyester synthesis.*

*In these structures and throughout this book, the symbol R represents an organic group, either aromatic (ring structure) or aliphatic (straight or branched chain). This is a general method of indicating that a series of compounds is possible in which the R group varies in structure.

Among the most commonly used alkyd polyesters are those produced from phthalic anhydride (source of phthalic acid) and glycerol. These resins are also referred to as glyptals. They are seldom used as such, but are modified with unsaturated oils or fatty acids, such as oleic or linoleic acids, in order to achieve rapid air-drying properties. The first step in their preparation is the partial esterification of glycerol with the fatty acid. In the second step, phthalic anhydride reacts with one or more of the remaining hydroxyl groups of the partially esterified glycerol resulting in the alkyd polymer (Fig. 2.4).

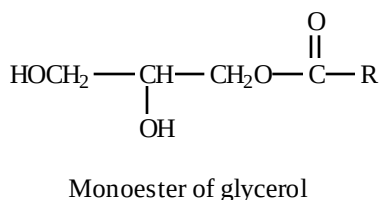
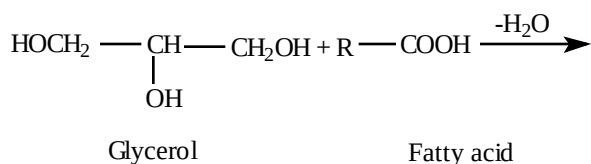
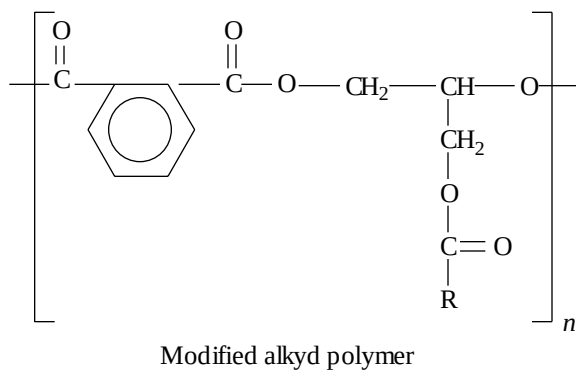
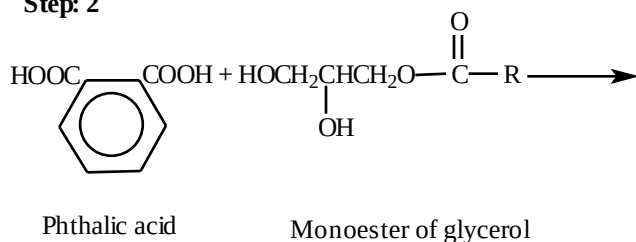
Although glycerol and phthalic acid are the most commonly used starting materials, other polyols and dibasic acids can be used. Other polyols include pentaerythritol, polyglycerol, and the mono- and diglycerides of fatty acids of linseed oil. Other dibasic acids include isophthalic, terephthalic, hexahydrophthalic, maleic, tetrachlorophthalic, and adipic acids.

Alkyds can be further modified with rosin, styrene, phenolic resins, or silicones, depending on the characteristics desired. More detailed discussions of the chemistry and formulation of alkyd polyesters appear in the literature.^{[1]–[3]}

2.2.3 Properties of Alkyd Coatings

The alkyds and modified glyptals have been used for many years as coatings, paints, and varnishes.^[4] They are used primarily as protective and decorative coatings for consumer products. For electronics, they are of interest more as finishing systems for metal enclosures, housing for electronic assemblies, and computer chassis than as primary insulation coatings. As corrosion-protective coatings for metals, many proven and well-defined alkyds are available and covered by federal specifications such as TT-E-508 and TT-E-489.

Alkyd coatings may be either air-drying or baking types. The air-drying types, as mentioned previously, have been modified chemically by incorporating unsaturated fatty-acid groups into the polymer structure. Experimental studies have shown that the greater the percentage of these fatty acids in the formulation, the shorter will be the drying time. Drying times may also be reduced by adding metal oxides such as those of lead, cobalt, or calcium, by using branched polyhydric alcohols such as pentaerythritol, or by substituting isophthalic acid for phthalic acid. The baking-type alkyds are modified with hardeners such as melamine or urea resins.

Step: 1**Step: 2****Figure 2.4.** Steps in the formation of a modified alkyd polymer.

2.3 POLYVINYL S

Polyvinyls are among the oldest types of polymers and consist of many structural variations. However, lacking either thermal stability or stable electrical properties under severe stresses, they are seldom used as protective or dielectric coatings, especially for the more advanced electronics. Among the most widely used polyvinyls are the polyvinyl chlorides and polyvinyl formal (Formvar) used as wire insulation.

2.3.1 Chemistry

Vinyl polymers are prepared by the free-radical addition polymerization of monomers containing one or more double bonds. The monomers join head-to-tail to form long-chain linear polymers of high molecular weight without releasing any by-products. Ultraviolet light, heat, or catalysts are used to initiate the free-radical reaction. The best accelerators are peroxide catalysts such as benzoyl peroxide or dicumyl hydroperoxide. For example, the polymerization mechanism for styrene (a vinyl benzene) using a catalyst is shown in Fig. 2.5.

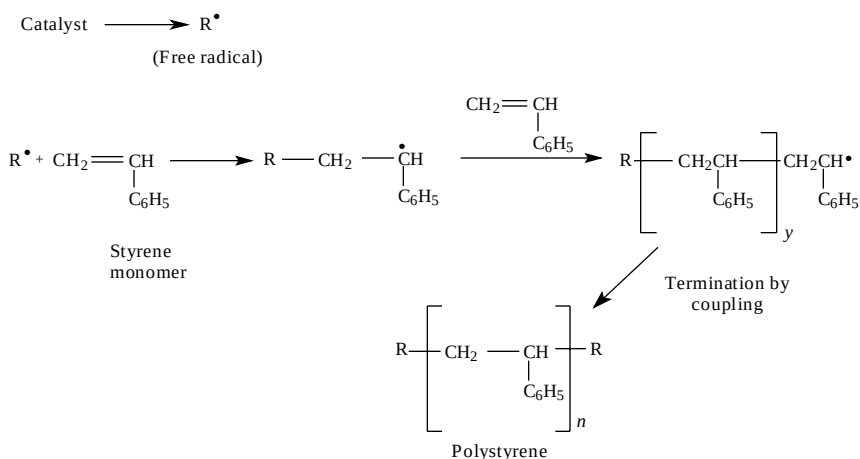


Figure 2.5. Free-radical polymerization mechanism for styrene.

Included in the vinyl classifications are many well-known monomers and their associated polymers as listed in Table 2.3. Most of these

polymers are formed directly from the polymerization of the vinyl monomer without further alteration and are referred to as *primary vinyls*. Others, formed by subsequently reacting the primary vinyls with reagents that alter the groups along the polymer chain, are called *secondary vinyl resins*. For example, some of the acetate groups of polyvinyl acetate may be hydrolyzed, and the resulting hydroxy groups then co-reacted with aldehydes to yield acetal derivatives. There are three such derivatives of importance to the electronics industry: polyvinyl formal (Formvar), polyvinyl acetal, and polyvinyl butyral. Polyvinyl formal and polyvinyl acetal are widely employed as tough, temperature-resistant wire insulation while polyvinyl butyral is useful as a surface coating and as a resin system in many wash primers (see Ch.1).

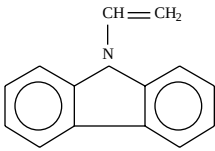
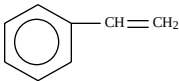
Acrylics, polyethylenes, polypropylenes, and other polyolefins may also be classified as vinyl types, but are often treated separately because of their great commercial importance. The polymers listed in Table 2.3 represent a small fraction of the numerous vinyl modifications that are possible. Additionally, many copolymers can be prepared by reacting two or more of the monomers. Such resins will be more soluble and possess properties half-way between those of the respective homopolymers. An example of a vinyl copolymer is given in Fig. 2.6.

2.3.2 Properties

Of the many vinyl types discussed, those most widely used as protective and electrically insulative coatings are the polyvinyl chlorides, polyvinyl fluorides, polyvinylidene chlorides and fluorides, polyvinylaldehydes, and polymethylmethacrylates. These polyvinyl coatings are used as moisture barriers, primary wire insulation, corrosion-protective coatings, dielectric impregnants, baking enamels, and as capacitor dielectrics. Some of the best electrical-grade and moisture-barrier coatings are formulated from vinyl monomers.

Polyvinyl Formals. The electrical properties of polyvinyl formals are extremely good, rendering them especially useful as wire enamel coatings. Their dielectric strengths range from 860 to 1000 volts/mil and dielectric constants typically are 3.3 to 3.6. Coatings are applied to wire from a solution containing small amounts of phenolic resin, which functions as a cross-linking agent. Polyvinyl formals are generally insoluble in alcohols and hydrocarbons, but soluble in acetic acid, dioxane, nitrobenzene, and tetrachloroethane.

Table 2.3. Vinyl Monomers and Polymers

Monomer	Monomer Structure	Polymer	Polymer Structure
Primary Types			
Vinyl Chloride	$\text{CH}_2=\text{CH}-\text{Cl}$	Polyvinyl Chloride	$\left[\begin{array}{c} \text{CH}_2-\text{CH} \\ \\ \text{Cl} \end{array} \right]_n$
Vinyl Fluoride	$\text{CH}_2=\text{CH}-\text{F}$	Polyvinyl Fluoride	$\left[\begin{array}{c} \text{CH}_2-\text{CH} \\ \\ \text{F} \end{array} \right]_n$
Vinyl Acetate	$\text{CH}_2=\text{CH}-\overset{\text{O}}{\underset{\text{ }}{\text{C}}}-\text{CH}_3$	Polyvinyl Acetate	$\left[\begin{array}{c} \text{CH}_2-\text{CH} \\ \\ \text{O} \\ \\ \text{C}=\text{O} \\ \\ \text{CH}_3 \end{array} \right]_n$
Vinylidene Chloride	$\text{CH}_2=\underset{\text{Cl}}{\underset{ }{\text{C}}}-\text{Cl}$	Poly-vinylidene Chloride	$\left[\begin{array}{c} \text{CH}_2-\text{C} \\ \quad \\ \text{Cl} \quad \text{Cl} \end{array} \right]_n$
Vinylidene Fluoride	$\text{CH}_2=\underset{\text{F}}{\underset{ }{\text{C}}}-\text{F}$	Poly-vinylidene Fluoride	$\left[\begin{array}{c} \text{CH}_2-\text{C} \\ \quad \\ \text{F} \quad \text{F} \end{array} \right]_n$
Vinyl Carbazole		Polyvinyl Carbazole	$\left[\begin{array}{c} \text{CH}-\text{CH}_2 \\ \\ \text{N} \\ \\ \text{Carbazole Ring} \end{array} \right]_n$
Ethylene	$\text{CH}_2=\text{CH}_2$	Polyethylene	$\left(\text{CH}_2-\text{CH}_2 \right)_n$
Propylene	$\text{CH}_2=\text{CH}-\text{CH}_3$	Poly-propylene	$\left[\begin{array}{c} \text{CH}_2-\text{CH} \\ \\ \text{CH}_3 \end{array} \right]_n$
Styrene		Polystyrene	$\left[\begin{array}{c} \text{CH}_2-\text{CH} \\ \\ \text{Benzene Ring} \end{array} \right]_n$

(cont'd.)

Table 2.3. (cont'd.)

Monomer	Monomer Structure	Polymer	Polymer Structure
Primary Types			
Methyl-methacrylate	$\text{CH}_2=\text{C}(\text{CH}_3)\text{COOCH}_3$	Polymethyl-methacrylate	$\left[\text{CH}_2-\text{C}(\text{CH}_3)(\text{COOCH}_3) \right]_n$

Secondary Polymer Types	
Polymer	Polymer Structure
Hydrolyzed Polyvinyl Acetate	$\left[\text{CH}_2-\underset{\begin{array}{c} \\ \text{O} \\ \\ \text{C}=\text{O} \\ \\ \text{CH}_3 \end{array}}{\text{CH}}-\text{CH}_2-\underset{\begin{array}{c} \\ \text{OH} \end{array}}{\text{CH}} \right]_n$
Polyvinyl Formal	$\left[\text{CH}_2-\underset{\begin{array}{c} \\ \text{O} \\ \\ \text{C}=\text{O} \\ \\ \text{CH}_3 \end{array}}{\text{CH}}-\text{CH}_2-\underset{\begin{array}{c} \\ \text{O} \\ \\ \text{CH}_2\text{OH} \end{array}}{\text{CH}} \right]_n$
Polyvinyl Butyral	$\left[\text{CH}_2-\underset{\begin{array}{c} \\ \text{O} \\ \\ \text{C}=\text{O} \\ \\ \text{CH}_3 \end{array}}{\text{CH}}-\text{CH}_2-\underset{\begin{array}{c} \\ \text{O} \\ \\ \text{HCOH} \\ \\ \text{C}_3\text{H}_7 \end{array}}{\text{CH}} \right]_n$

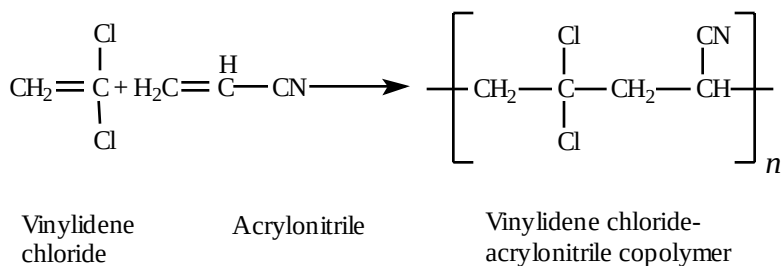


Figure 2.6. Vinyl-copolymer reaction.

Polyvinyl Alcohols and Acetates. Polyvinyl alcohols (PVA) and polyvinyl acetates are seldom used in electrical applications because of their high dielectric constants and dissipation factors, low thermal stabilities, and the rapid and extensive degradation of their electrical properties when exposed to humid conditions.^[5] In fact, under normal ambient conditions, sufficient water is absorbed to render electrical measurements useless.^[6] Polyvinyl alcohols coatings also suffer from poor thermal stability at temperatures as low as 95°C in air. They are sometimes used as temporary coatings such as maskants that are easily dissolved in warm or hot water. On the whole, polyvinyl alcohol and acetate resins find greater use in non-electrical applications such as paper coatings, packaging films, and house paints.

Polyvinyl Chlorides. Polyvinyl chloride (PVC) is widely used as wire and cable insulation because of its good electrical insulating properties, resistance to moisture and chemicals, inherent flame resistance, and relatively low cost. For these applications, the material is extruded from a dry blend or from hot fluxing.

The molecular weights of commercially available polyvinyl chloride resins range from 50,000 to 150,000. As with other polymers, toughness, viscosity, and chemical and solvent resistance increase with an increase in chain length and molecular weight. The average molecular weight of the resin largely determines its application. High molecular weight resins are used for wire insulation and extruded flexible tubing, whereas the intermediate and lower molecular weight resins are used in the production of films.

Polyvinyl chloride is seldom used in its pure form. It is usually formulated with plasticizers for flexibility, with stabilizers to prevent thermal degradation, and with lubricants and other additives to facilitate processing and increase its impact strength (Table 2.4).^[7] However, compounding with large amounts of plasticizers or other additives will degrade electrical properties, increase moisture absorption, or render the coating fungus nutrient. There are hundreds of plasticizers on the market, and judicious use must be made to minimize these effects. Fillers such as clay or calcium carbonate are added at about 15% loading to reduce the price of the plastic and improve its electrical resistivity. Amounts greater than 15%, however, degrade mechanical properties such as abrasion resistance, tensile strength, elongation, and flexibility.

Stabilizers are added because of the tendency of polyvinyl chlorides to decompose during high-temperature processing, cure, or operational use. Decomposition results in the release of hydrogen chloride which, in the

presence of small amounts of moisture, quickly forms hydrochloric acid and chloride ions. Hydrochloric acid and chloride ions are the main culprits in causing corrosion of metal and degradation of other plastics. They also act as catalysts, further attacking the polyvinyl chloride and releasing even more hydrochlorides. This catalytic process is accelerated at elevated temperatures, under high humidity, on being irradiated, or in the presence of certain metals such as iron or zinc. Stabilizers consist of compounds that react with and remove trace amounts of hydrogen chloride as soon as it is formed, thus preventing catalytic “unzipping” of the polymer chain. Examples of stabilizers include lead, epoxy compounds, and plasticized urea-formaldehyde resins. Because of the risk of degradation and the evolution of hydrogen chloride, polyvinyl chloride is classified as a reliability-suspect material in space applications and in many military applications according to MIL-HDBK-1547.

Table 2.4. Vinyl Wire-coating Formulation^[7]

Ingredient	Proportion, pbw
Polyvinyl Chloride Homopolymer (medium mol. wt.)	100
Primary Plasticizer	30
Secondary Plasticizer	15
Pigment 33 (clay filler)	10
Calcium Carbonate Filler	8
Mark OHM Stabilizer	2
Total	165

2.4 POLYSTYRENES

Except where high temperatures are involved, polystyrenes may be used for some electronic applications. They have very low dielectric constants and power factors (Table 2.5), placing them in a class with polyethylenes, fluorocarbons, and silicones. Polystyrenes also have high dielectric strength values (comparable to mica) and volume resistivities that do not vary much at high frequencies or in the presence of moisture. Because of these properties, polystyrenes are especially suited as capacitor

dielectrics, especially in commercial markets where moderate temperatures are encountered. Another outstanding property is their transparency. Unmodified polystyrene coatings are clear, colorless, and capable of transmitting 88 to 92% of light. Their refractive index is 1.59 to 1.60. They are, therefore, used in coating lenses and other optical equipment. Polystyrenes also have very good tinting and coloring properties, giving them a wide range of transparent, translucent, and opaque colors for decorative uses.

Table 2.5. Electrical Properties of Polystyrenes

Property, Tested by ASTM Methods	Value
Dielectric Strength, volts/mil	500–700
Dielectric Constant, 60 Hz	2.45 to 2.65
Power Factor, 60 Hz	1×10^{-5} to 3×10^{-4}
Volume Resistivity, ohm-cm	1×10^{16}
Arc Resistance, sec	60–80

Among the more serious limitations of polystyrenes are their inherent flammability and their upper temperature limit of 85°C, which is much too low for most military electronic applications.

2.5 DIALLYLPHTHALATE AND OTHER ALLYLIC POLYMERS

Polymers based on diallylphthalate or those derived from monomers containing the functional allylic group $\text{—CH}_2\text{—CH=CH}_2$ are referred to as *allylic polymers*. They may also be regarded as a specific class of polyesters or as a class of vinyls. Diallylphthalate, the simplest and most commonly used monomer, is an ester of orthophthalic acid and allyl alcohol. In its synthesis (Fig. 2.7), the orthophthalic anhydride may be employed instead of the acid. Other commonly used ester monomers include diallyl-isophthalate, triallylcyanurate, diallylmaleate, and diallylchloredate.

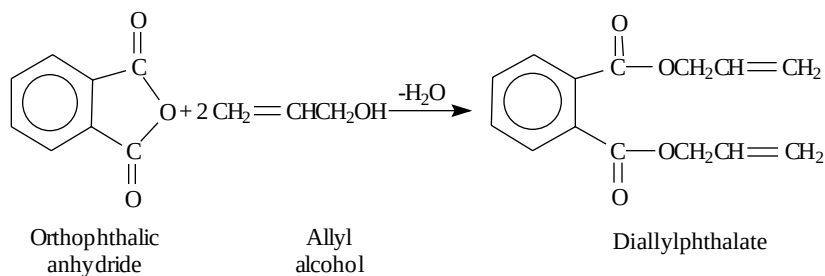


Figure 2.7. Synthesis of diallylphthalate monomer.

All allylic polymers are formed by a free-radical addition-type polymerization that occurs through the vinyl groups in a manner similar to the polymerization of styrene or other vinyl monomers. As such, no by-products are released during polymerization. A large variety of polymers and copolymers is possible, depending on the monomers used. However, the diallylphthalates and diallylisophthalates are the ones most used as coatings, varnishes, and impregnants. Diallylphthalates possess excellent electrical properties, chemical resistance, and thermal stability. The triallylcyanurate polymer is reported to be stable up to 300°C .^[8] Among limitations are the high shrinkages that occur during polymerization; up to 12% has been reported.

2.6 EPOXIES

Epoxy resins form the basis for a wide variety of polymer materials used in electronics ranging from conformal coatings to adhesives, encapsulants, and printed wiring board laminates. The extensive use of epoxies is due to their combination of low cost, ease of processing, and excellent thermal, electrical, mechanical, and moisture barrier properties. However, because of the numerous formulations possible and available from different vendors, there can be wide variations in their properties. Epoxies were initially developed in the early 1930s, but production for commercial applications did not begin until the 1950s. Initially, epoxy resins were developed and promoted by Ciba and the Shell Chemical Company. Today there are numerous manufacturers and formulators. Since 1960, epoxies have been formulated and applied to the rapidly growing field of electronics. They are widely used as die-attach adhesives, laminates for

printed wiring boards, conformal coatings, encapsulants, underfill adhesives for flip-chip and ball-grid-array modules, glob-top encapsulants, and transfer molding compounds for PEMs (plastic encapsulated microcircuits).

2.6.1 Chemistry

Epoxyes are based on the high reactivity of the strained three-member epoxy ring, also referred to as the *oxirane ring*. When mixed with acidic or alkaline compounds or with compounds that contain labile hydrogen atoms, the epoxy rings open up and a polymerization reaction occurs, resulting in useful epoxy coatings, adhesives encapsulants, and laminates (Fig. 2.8). Besides the epoxy group, the pendant hydroxyl groups of an epoxy resin are also reactive. Further cross-linking or lengthening of the polymer chain occurs through these groups.

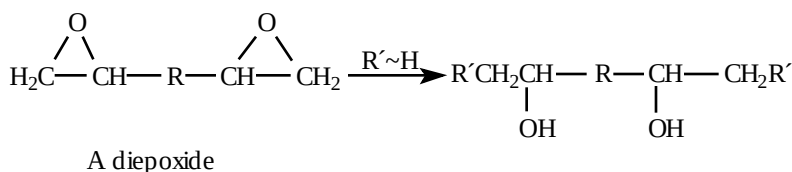


Figure 2.8. Epoxy chemistry.

Bisphenol A Epoxy Resins. The synthesis of di- and polyfunctional epoxy resins has been well described in the literature and will not be treated in any detail here.^{[9][10]} The most commonly used resins are based on Bisphenol A. When Bisphenol A reacts with epichlorohydrin, the simplest epoxy resin called the diglycidyl ether of Bisphenol A (DGEBA) is formed (Fig. 2.9). A series of epoxy resins based on Bisphenol A can be prepared and are commercially available. The generalized formula for this series is given in Fig. 2.10. In this structure, n , the number of repeating units, may range from 0 to 24. The resins will be liquids at low n values (1 or less) and solids of increasing molecular weights and melting points as the value of n increases. These resins, therefore, differ in their degree of polymerization, molecular weight, and viscosity. They also differ in their *epoxy equivalents*,

defined as the weight of resin that contains one gram-equivalent of epoxy, important in calculating how much hardener to add in order to get a stoichiometric ratio. There are many manufacturers of Bisphenol A-type epoxy resins, each using a different designation for essentially the same resin.

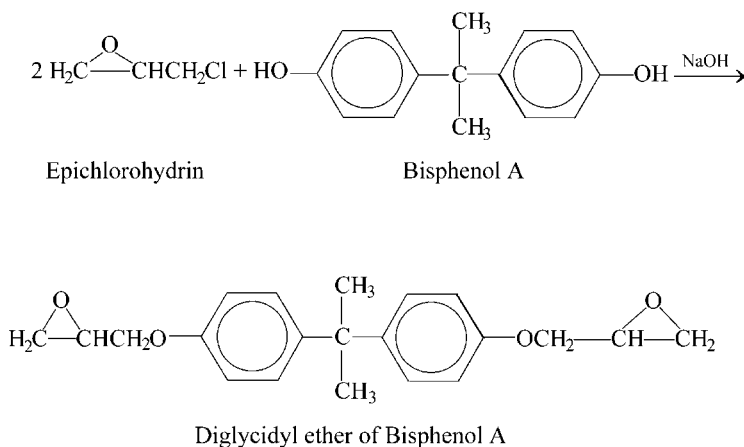


Figure 2.9. Preparation of diglycidyl ether of Bisphenol A epoxy resin.

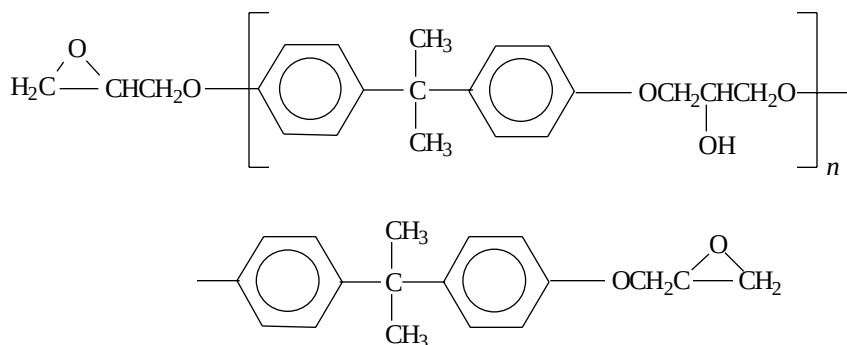


Figure 2.10. Generalized structure for Bisphenol A epoxy resins.

Numerous Bisphenol A analogs have been synthesized and evaluated; the synthesis of 84 bisphenol compounds and their corresponding epoxy resins have been reported.^[11] Of these, only a few, such as the halogenated Bisphenol A epoxy resins, are of any commercial consequence. Halogenated epoxy resins are useful because of their inherent flame-retardant properties. Examples include the chlorinated and brominated derivatives (Fig. 2.11).

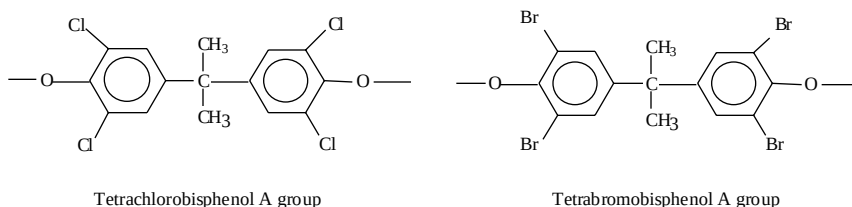


Figure 2.11. Examples of halogenated bisphenol groups used for flame-retardant epoxy resins.

Novolac Resins. Besides Bisphenol A, other phenolic and polyhydroxy aromatic compounds react with epichlorohydrin to yield epoxy resins having a variety of properties. Some widely used resins are derived from novolac, a phenol formaldehyde resin. Reaction of the hydroxyl groups of this resin with epichlorohydrin yields an epoxy-novolac resin (Fig. 2.12). Novolac resins are characterized by their high epoxy functionality, resulting in coatings with a high cross-linking density and high temperature stability.

Other Epoxy Types. Epoxy resins may also be prepared by reacting unsaturated compounds (compounds containing double bonds) with oxidizing agents such as peroxides or peracids. Epoxies from both linear and cyclic unsaturated compounds may be prepared in this manner (Fig. 2.13). The peracetic acid method is being used commercially; epoxy resins, so prepared, are known as *peracetic acid epoxies*.^[12]

Epoxidized polyolefin resins possess a molecular structure quite different from that of the Bisphenol A series. The one thing they have in common is the epoxy ring, but, even so, there is a difference in the position of the epoxy rings. In the epoxidized polyolefins, the epoxy rings are present along the chain as well as at the end of the chain, whereas in the bisphenol series, the epoxy rings are always at the end of the chain. Epoxy polyolefin resins may be cured with any number of hardeners or catalysts commonly

used to cure the bisphenol epoxies, but also with free-radical initiators because of the many double bonds along the chain that were not epoxidized (Fig. 2.14). Hence, dicumyl peroxide and other peroxide catalysts may be used.

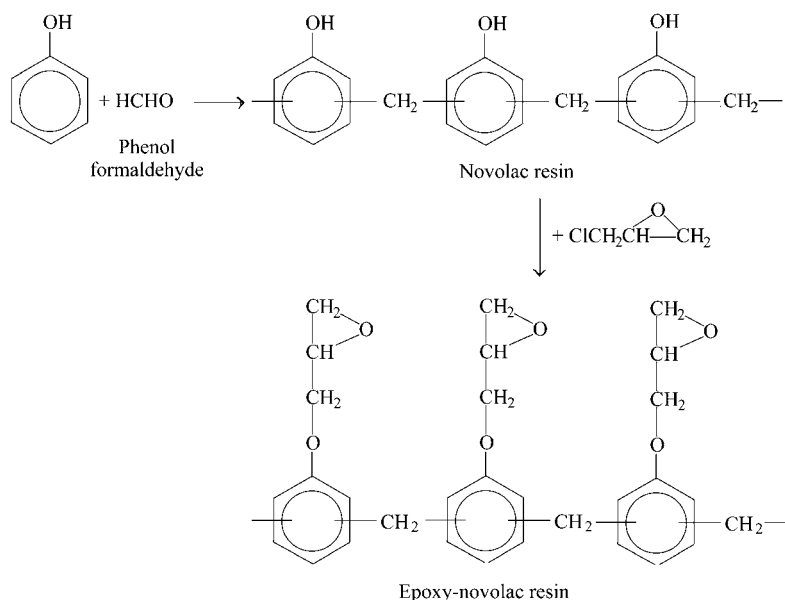


Figure 2.12. Formation of novolac and epoxy-novolac resins.

The peracetic acid resins have an advantage over bisphenol epoxy resins in possessing lower densities. The uncured resins are approximately 20% lighter in weight, a property that is desirable for some airborne electronics.

2.6.2 Curing

By adding suitable curing agents, epoxy resins polymerize to highly cross-linked, three-dimensional solids either by an addition mechanism or a catalytic mechanism. According to the addition mechanism, the curing agent, also known as a hardener, combines chemically with the epoxy resin and serves as a bridge to cross link a number of resin molecules into a macromolecular structure. This type of polymerization is referred to as

heteropolymerization. In the catalytic mechanism, a catalyst promotes the self-polymerization of the epoxy resin. The catalyst is regenerated and does not become part of the final structure. This type of polymerization is known as *homopolymerization*. A large number and variety of catalysts and hardeners are commercially available, and, as in the case of the resins, an almost infinite number are synthetically possible. The hardener or catalyst selected governs the rate of polymerization and dictates the resulting properties of the cured coating. The hardener also determines the curing schedule (time and temperature) necessary to achieve optimum properties.

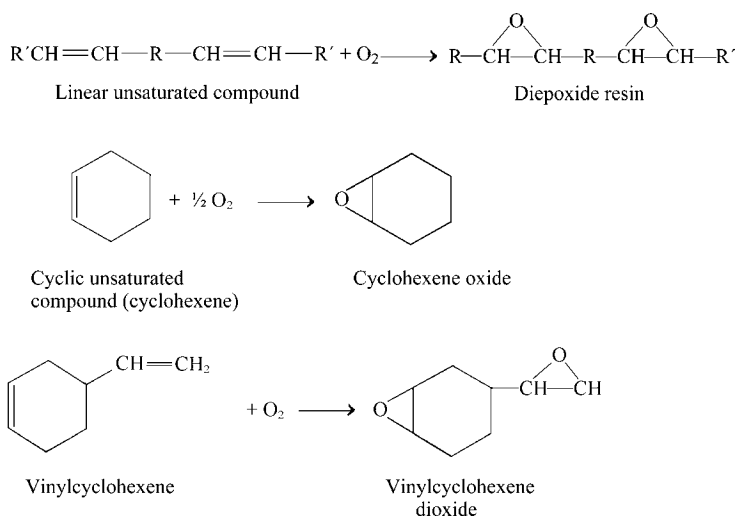


Figure 2.13. Epoxy resins formed by epoxidation of unsaturated compounds.

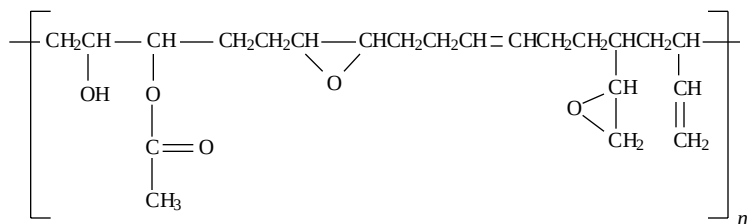


Figure 2.14. Typical structure for an epoxidized polyolefin.

The choice of a hardener or catalyst for a specific application becomes a critical factor in determining the performance and reliability of the coating. The advantages and limitations of various epoxy curing agents are summarized in Table 2.6. It should be noted that, with proper precautions and suitable equipment, many of the limitations listed can be avoided.

Table 2.6. Epoxy Curing Agents: General Comparison

General Type	Advantages	Limitations
Polyamines (primary, secondary, and tertiary amines)	• Rapid cures • Cure at room temperature • Excellent wettability and adhesion	• Short pot life (20–30 min) • Require careful and accurate weighing and mixing • High exotherms may be difficult to control • May result in slightly colored films • May have noxious odor or be irritating to the skin
Polyamides	• Result in flexible coatings with high vibration, impact, and shock resistance • Are nonirritating • Coatings have high degree of adhesion; surface preparation and cleanliness are not as critical to adhesion as with other curing agents • Pot lives are longer than for amine-cured epoxies • Peak exotherm temperatures are lower than for amine-cured epoxies	• Electrical properties not as good as with other curing agents • Moisture absorption and permeability are higher than for polyamines
Anhydrides	• Long pot life at room temperature • Good thermal resistance (to 260°C) • High heat-distortion temperatures • Low peak exotherm temperature • Coatings do not discolor on aging	• Require tertiary amine or other catalyst to accelerate cure • Require higher temperatures (80°–260°C) and longer time (up to 24 hr) to affect cure
Boron Trifluoride Complexes	• Very rapid cures	• High exotherm • Some have short pot lives • Some are hygroscopic

Catalytic Curing. Both Lewis bases and Lewis acids initiate polymerization of epoxy resins producing high molecular weight polyethers. Lewis acids are compounds, such as boron trichloride, boron trifluoride, or aluminum chloride, that easily accept an electron pair from another compound to form a complex. Conversely, Lewis bases, such as the tertiary amines, easily donate a pair of electrons.

Most tertiary amines require slightly elevated temperatures when used to cure the low molecular weight liquid glycidyl ether resins. However, room-temperature cures are possible with the high molecular weight epoxies because of the larger number of hydroxyl groups that they contain. Tertiary amine catalysts are used in quantities of 5 to 15 phr (parts per hundred resin), whereas Lewis base amine complexes are used in amounts of 2 to 4 phr.

Both Lewis acids and bases in the free state must be handled with care. Most are highly corrosive or irritating gases or liquids that cause skin irritation. Those having a high vapor pressure are also noxious or toxic. They are also highly reactive exhibiting extremely short pot lives after mixing. For example, boron trifluoride is one of the most reactive catalysts known for curing epoxies. Its extreme reactivity makes it almost impossible to handle in a practical situation. To obviate this problem, these highly reactive catalysts are sold and used as latent complexes, modified so that their vapor pressures and toxicities are reduced and their pot lives extended. Hence, boron trifluoride is employed as an amine complex such as aniline boron trifluoride or triethylamine boron trifluoride. These complexes dissociate gradually at room temperature, but more rapidly on heating, liberating the active catalysts.

The mechanism for curing epoxies with tertiary amines is depicted in Fig. 2.15. The tertiary amine first opens up an epoxy ring, forming a quaternary base and leaving an oxygen atom with a pair of unsatisfied electrons. This negatively charged oxygen atom then proceeds to open up more epoxy rings, and so on. In this manner, long-chain polyethers are formed.

Curing with Amines. Amine compounds are widely used as curing agents for epoxy coatings, providing rapid cures at room temperature in 1 to 2 hours, or sooner at higher temperatures. Polyamines are used in concentrations of 4 to 20 phr. The resultant coatings have excellent chemical and solvent resistance, electrical properties, and thermal and vacuum stability. These properties are enhanced when the coatings are postcured or cured at elevated temperatures. Amine compounds that may be used to cure epoxies fall into 12 generic types (Table 2.7).

As with tertiary amines, the primary and secondary amines may also cause skin irritation, possess a noxious odor, or emit corrosive fumes. They are, therefore, sold as modified variations under many proprietary names. They may be used as eutectic mixtures, adducts with low molecular weight epoxies, or as complexes with boron trifluoride. In all cases, their vapor pressures are reduced and the possibility of skin irritation is also reduced. The use of modified amines is also beneficial in controlling and extending the pot life of the mixed formulation.

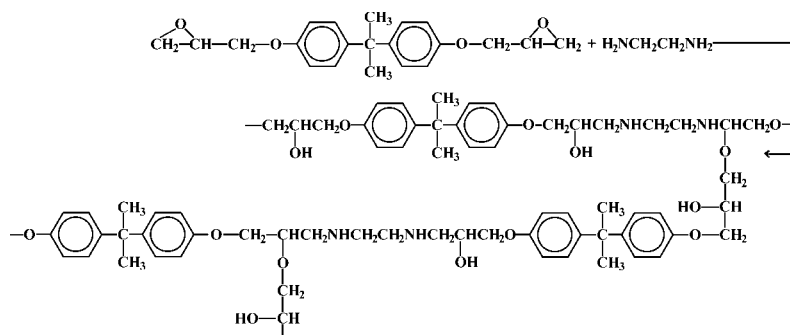


Figure 2.16. Mechanism of epoxy cured with ethylenediamine.

Primary and secondary amines of both the aliphatic (straight chain) and aromatic (benzenoid ring) types react readily with epoxy resins in concentrations of 10 to 12 phr. An example of an epoxy cure using ethylenediamine is shown in Fig. 2.16. Other amines react similarly to give high molecular weight thermosetting epoxies.

Curing with Acids and Acid-Anhydrides. Organic dicarboxylic acids and acid anhydrides derived from them are also widely used to cure epoxies. They will open up the epoxy rings and cross link the molecules by becoming incorporated into the structure as an ester (Fig. 2.17). Oxalic acid, (HOOC–COOH), the simplest dicarboxylic acid, is used in some coating formulations. These formulations have a pot life of several days and may be cured at 125° to 175°C for 1 hour or longer. Other dicarboxylic acids of the series HOOC–[CH₂]_n–COOH, where *n* is greater than 1, are generally not used due to their poor solubilities, difficulty in mixing with resins, and tendency to foam. Anhydrides derived from the dicarboxylic acids are much more commonly used. Compared with the amine-cured epoxies, the anhydride-cured systems are noted for their greater thermal resistance, higher

heat distortion temperatures, higher glass transition temperatures, and improved electrical properties. Low dielectric constants, for example, 2.8 to 3, have been achieved with some formulations. Anhydride-curing agents are used in concentrations of 30 to 140 phr, depending on the epoxy resin used and the stoichiometry desired. They usually require accelerators or catalysts, without which, they react sluggishly, especially with liquid epoxies. By adding small amounts of a tertiary amine catalyst (0.1 to 5 phr), epoxy compositions can be formulated that are stable up to 12 hours, maintaining a low viscosity at room temperature, but curing rapidly at 120°C.^[13] If the epoxy resin contains more hydroxy groups than epoxy groups, as with solid Bisphenol A resins, the higher hydroxy functionality is effective in initiating the reaction without the need for a tertiary amine catalyst. Some commonly used anhydrides are: dodecenylsuccinic anhydride, phthalic anhydride, trimellitic anhydride, nadic methyl anhydride, hexahydrophthalic anhydride, and chlorendic anhydride.

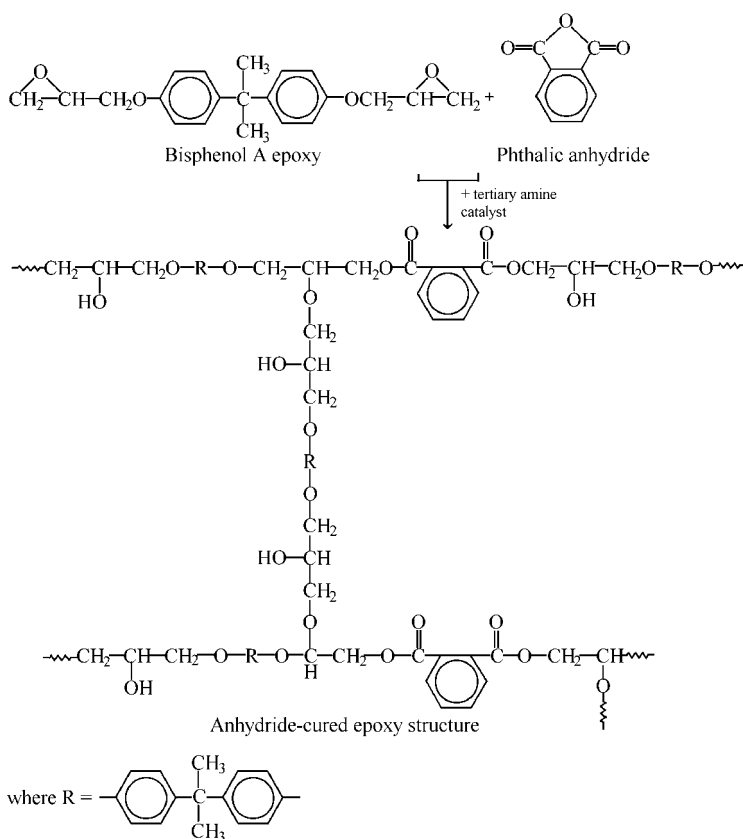


Figure 2.17. Mechanism of epoxy cured with anhydride.

Dicy is used extensively in solution coating formulations for impregnating glass fiber and fabricating epoxy prepreg used for printed wiring board laminates, for adhesive bonding of electrostatic shields or heat sinks to circuit boards, and for bonding layers of laminates together to form multilayer circuit boards. A typical solution coating consists of Epon* 1001F, dicy, and benzyldimethylamine. Tertiary amines such as benzyldimethylamine or quaternary ammonium salts such as benzyltrimethylammonium chloride accelerate the otherwise sluggish reaction.

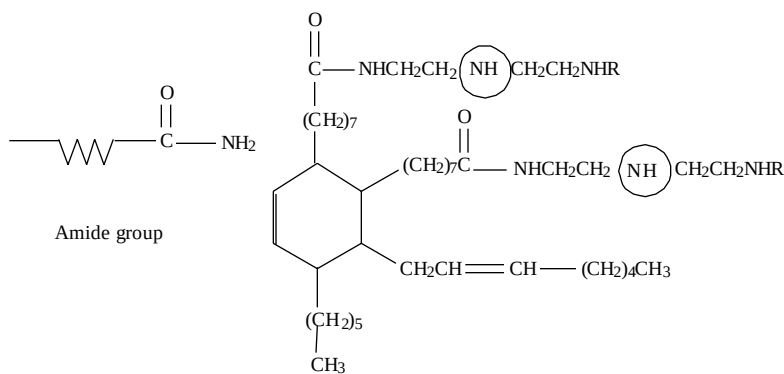


Figure 2.18. Linoleic acid-diethylenetriamine polyamide resin.

Ultraviolet (UV) Curing. Epoxy resins that can be cured on exposure to uv light are also available. The benefits of uv curing over heat curing include: short cure cycles, energy conservation, low VOC emissions, and selective curing by employing a photomask.

Ultraviolet curing involves a cationic mechanism; the epoxy ring opens up when exposed to uv light in the presence of a cationic photoinitiator. The epoxy rings open up, cross linking with themselves or with polyol compounds that have been added to the formulation. Cationic curing does not involve free radicals. In the first step, the photoinitiator, exposed to uv light, converts to an acid (a cation or proton donor) that acts as a catalyst. Commonly used photoinitiators are arylsulfonium hexafluoroantimonate ($\text{Ar}_3\text{S}^+\text{SbF}_6^-$) and arylsulfonium hexafluorophosphate salts ($\text{Ar}_3\text{S}^+\text{PF}_6^-$). In

*Epon is a tradename of Resolution Performance Products.

the second step, the acid donates its proton to the epoxy ring, activating the ring and allowing the hydroxyl-containing compound (a polyol) to open up the ring and add to it. Next the proton is recaptured by the anionic acid portion, thus regenerating the acid catalyst. Cross-linking then occurs among the generated hydroxyl compounds and the original epoxy resin (Fig. 2.19). Both cycloaliphatic epoxies and diglycidyl ether epoxies can be cured cationically, but faster cures have been achieved with the cycloaliphatic epoxies. A comprehensive review of the history and development of cationic photoinitiators has been authored by Crivello.^[16]

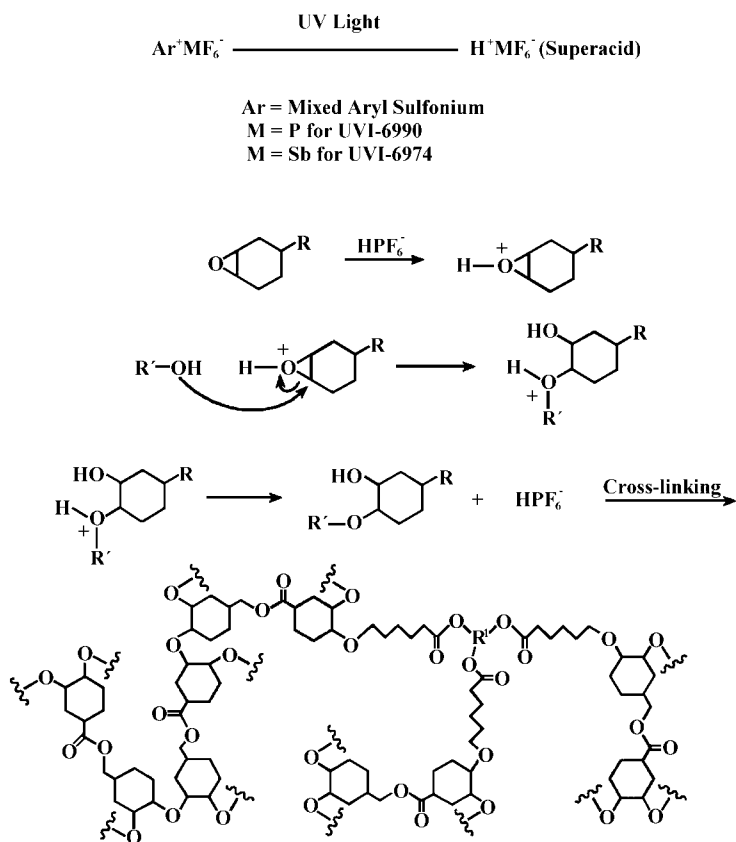


Figure 2.19. Cationic cure mechanism for cycloaliphatic epoxies.

Unlike the acrylates, uv-cured epoxies are not inhibited by atmospheric oxygen, but are inhibited by ammonia, amine-containing acrylates, other amines, and rhodamine pigments. High humidity conditions also suppress the rate of curing. When properly cured, coatings have excellent adhesion. The superior adhesion is attributed to the relatively low shrinkage, typically less than 5%, compared with uv-cured acrylics where shrinkages up to 25% are possible.

Epoxies are formulated to cure to a non-tacky, hard state during uv exposure, but properties of the exposed areas continue to improve even after the uv source has been removed. The acid catalyst generated from the photoinitiator continues to be active and reactants continue to cross link. Optimum properties may take up to 24 hours after uv exposure. A short heat cure following uv exposure is often recommended to speed up optimization of properties and to cure portions of the coating beneath components or coating that has become shadowed from the uv light by nearby components.

2.6.3 Classification of Epoxy Coatings

Epoxy coatings may be classified into three main categories: nonesterified solutions, esterified solutions, and 100% solids types.

Nonesterified Solution Coatings. These are two-part epoxy systems in which the curing agent may be an amine, polyamide, acid anhydride, or other compound containing an active hydrogen atom. Many solution coatings are prepared by dissolving high-molecular-weight epoxy resins such as Epon 1001F or Epon 1009F in suitable organic solvents. These solutions may be further modified with resins such as urea-formaldehyde, phenol-formaldehyde, or melamine-formaldehyde. Solution coatings may be cured at room temperature or at elevated temperatures, depending on the reactivity and amount of curing agent used. In heat-curing, care is necessary to allow evaporation of solvents through an initial room temperature or low-temperature exposure followed by step curing to the optimum temperature. The entrapment of solvents and volatiles can be a serious problem in using solution coatings. Incorporating pigments or fillers assists in releasing these solvents during the cure cycle.

Esterified Solution Coatings. Esterified solution coatings contain free hydroxyl groups along the polymer chain that have been pre-reacted with organic carboxylic acids. Thus, groups of unsaturated fatty-acid esters may be grafted onto the epoxy backbone structure according to several generalized equations (Fig. 2.20). One of the Epon 1000F series

epoxies is usually employed as the epoxy to be esterified with soybean oil, linseed oil, castor oil, or other unsaturated fatty acid. Driers such as metal naphthenates, conventionally used for alkyd coatings, are also used in the esterified formulations, hence, both air-drying and bake-type coatings can be formulated. Bake-type enamels cure in 20 to 60 minutes at temperatures of 60° to 180°C. The incorporation of unsaturated chains has the advantage of imparting to the resin the more classical air oxidation curing mechanism, lowering its cost, and achieving properties intermediate between those of nonesterified types and the alkyd esters. One of the early patents on esterified epoxies was granted to Greenlee in 1948.^[17]

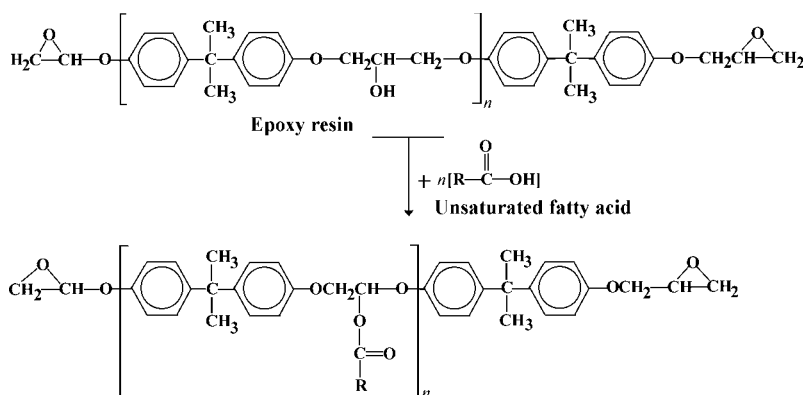


Figure 2.20. Preparation of esterified epoxy resins.

100% Solids Coatings. One hundred percent solids epoxy coatings are one-part or two-part systems that are formulated without solvents or other volatile ingredients. A resin of low enough viscosity is chosen so that it functions both as the reactive portion and as a vehicle. Non-solvent-containing (100% solids) coatings are gaining prominence because of OSHA and EPA restrictions on emissions of volatile organic compounds (VOC) into the atmosphere.

2.6.4 Properties

Epoxies, compared with other coatings and polymer types, are noted for their high resistance to chemicals, acids and alkalis, organic solvents,

moisture, and salt spray. They are also highly abrasion resistant and tough, finding numerous applications as protective coatings where harsh environments are encountered, especially in marine, automotive, and military hardware. Specially formulated, high-purity formulations also have excellent electrical properties and thermal resistance and are being used as interlayer dielectrics for multilayer interconnect substrates.

The three properties that single out epoxies from other coating types rendering them very useful for electronics are:

- Excellent adhesion to a wide variety of substrates without the use of primers and retention of adhesion under many harsh environmental conditions
- Excellent resistance to moisture, salt spray, organic solvents, and chemicals
- Good electrical characteristics and stability of these parameters under humidity and elevated temperature conditions

These desirable properties are primarily attributed to the thermosetting and highly cross-linked nature of the cured epoxy structure. However, this same structure renders epoxies less flexible than other coating types such as polyurethanes and silicones, resulting in higher shrinkage, embrittlement, and poor dissipation of stresses. Flexibility may be introduced by the use of flexible hardeners or plasticizers, but often at the expense of other critical properties such as electrical insulation and moisture resistance. Often, a compromise of properties must be accepted for lack of an ideal insulation coating.

Adhesion. Epoxies are noted for their excellent adhesion to a diversity of substrates and surface conditions. Adhesion is generally attributed to the highly polar, surface-active nature of the epoxy molecules that form both strong chemical bonds and mechanical interlocking with the substrate. The numerous ether linkages in an epoxy resin, with their available electron pairs (from oxygen atoms) provide sites for hydrogen bonding with the hydrogen atoms available from metal, ceramic, or plastic substrates. The aromatic ether from the bisphenol portion of the resin augments this ability to hydrogen bond because its oxygen is more electronegative owing to resonance effects of the phenyl ring.^[18] The hydroxyl groups present in an epoxy polymer also provide labile hydrogen atoms that take part in hydrogen bonding. Each hydrogen bond represents a van der Waals force of attraction of approximately 5 kcal/mole; thus, the very large number of such bonds account for the high total force of attraction of epoxies with the substrate.

Additionally, some epoxy rings can chemically interact with active hydrogen atoms from the substrate forming chemical bonds. For these reasons, epoxies are widely employed as adhesives, yielding lap-shear strengths of 1000 to 5000 psi on a variety of metal or plastic substrates.^[19] Many properties of epoxies that render them outstanding as coatings, such as resistance to abrasion, weathering, humidity, salt spray, and impact, are attributable to the adhesion characteristics just described. Epoxies adhere well to aluminum, magnesium, steel, titanium, beryllium, copper, most alloys, plastics, and ceramics. The sensitivity of adhesion to rough surfaces and contaminated or wet surfaces varies with the curing agent employed. Polyamide-cured epoxies are less sensitive to these situations than are epoxies cured with other agents. Polyamide-cured epoxy coatings have been applied in ambients of high relative humidity without subsequent loss of adhesion. One epoxy-polyamide ablative coating composition was even found to adhere well to aluminum surfaces containing oily residues,^[20] although thoroughly cleaned surfaces are always recommended.

Water and Salt-spray Resistance. Another outstanding property of epoxy coatings is their resistance to absorption and permeation of water and salt spray. Water absorption values generally reported are for 24-hour immersion in distilled water at room temperature. Under these conditions, epoxies cured with one of a large variety of anhydrides, aliphatic amines, aromatic amines, or boron trifluoride complexes were found to have water absorptions in a narrow range of 0.1 to 0.5%. Properly cured epoxies are stable even in boiling water and, compared with other polymer types, absorb only minimal amounts. Of 38 epoxy formulations in which both the resin and curing agent proportions were varied, the weight gain after 2-hours immersion in boiling water ranged from 0.13 to 2.3% with typical values of 0.5 to 1%.^[21] Water absorption values, however, may be higher than these values when non-stoichiometric quantities are used, that is, when a large excess of either the resin or the hardener is used such that they remain unreacted in the cured coating. High values will be obtained if the coating is undercured. There is a sparsity of data on long-term water absorption values and values at temperatures higher than room temperature. However, Lee and Neville^[9] show graphs for epoxies immersed in water for up to 5 years at temperatures up to 72°C. Major differences were reported among DGEBA epoxy resins cured with different curing agents; some polyamide-cured epoxies absorbed up to 7% after 300 days.

Besides moisture resistance, the salt-spray and salt-water resistance of epoxies is also superior to that of many other coating types. Epoxies

are used effectively to protect metal enclosures and equipment in marine environments. Equipment located outside the hull of underwater vehicles may be adequately protected with epoxy coatings. Laboratory tests, using aluminum and magnesium panels coated with both air-curing and baking-type epoxies showed no signs of corrosion or coating deterioration after being exposed for 800 hours in salt spray.

Electrical Properties. Epoxies are also noted for electrical insulating properties that render them suitable for many high-stress insulation applications. Properties such as insulation resistance, dielectric constant, and dissipation factor are fairly stable under a variety of environmental conditions such as temperatures up to 150°C and relative humidities to 100%.

Insulation resistance. The volume resistivities of epoxies, although quite high in the dry state (10^{12} to 10^{15} ohm-cm, or greater for some formulations), can drop to 10^6 ohm-cm or less when exposed to temperature/humidity cycling. This deterioration in electrical properties has been attributed to ionic impurities notably chloride, sodium, and ammonium ions, remaining in the epoxy from its manufacture or from additives and fillers. These ions become mobile in the presence of moisture and/or elevated temperatures, thus increasing the conductivity of the plastic. Purifying the epoxies or using alternate syntheses have improved their electrical properties. Other coatings that are inherently purer than epoxies such as the silicones and fluorocarbons remained stable over the same humidity and temperature conditions (Fig. 2.21). The reduction in volume resistivity of this epoxy, however, should not be considered typical of other epoxy formulations.

Changes in volume resistivity with temperature for a Bisphenol A epoxy formulation cured with diethanolamine are given in Table 2.8. Volume resistivity also degrades with the amount of water absorbed. The electrical properties of epoxies, however, are much more stable than those of polyesters or alkyds under the same conditions as was demonstrated by Graves and Pizzino.^[23] Flat specimens $2 \times 2 \times 0.125$ inch of the cast and cured materials were suspended over water at 70°C in a sealed container for various periods of time, removed, and tested electrically. Initial values for some epoxies were greater than 3.2×10^{12} ohms and dropped to 2.5×10^{12} ohms after 7 days, then to 3.5×10^{11} ohms after 14 days, and to 8×10^{10} ohms after 28 days. Other unfilled epoxies remained stable at values greater than 10^{12} ohms after 28 days of exposure. In contrast, both filled and unfilled polyesters showed poor performance, some even on only 4 days of exposure.

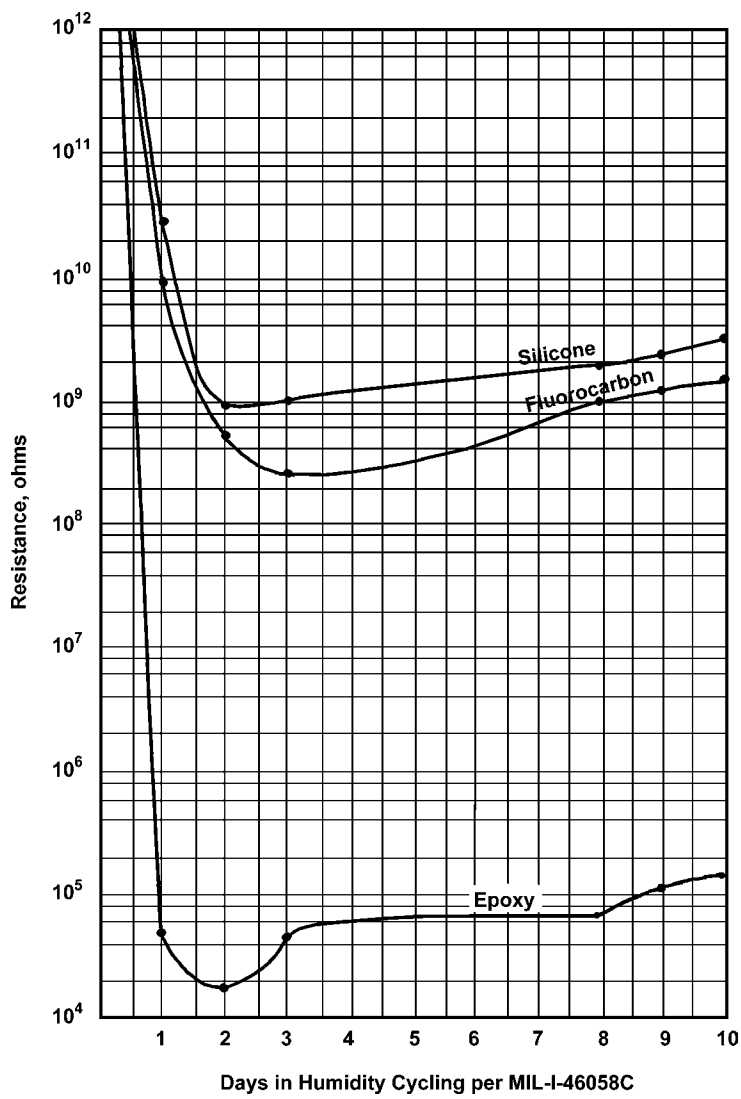


Figure 2.21. Effect of humidity on insulation resistance of polymer coatings.

Table 2.8. Variation of Volume Resistivity with Temperature for Epoxy-Amine Formulation^[22]

Temperature, °C	Volume Resistivity, ohm-cm
23	2.05×10^{14}
66	1.97×10^{13}
93	9.30×10^{10}
121	2.43×10^9
149	3.68×10^8

Dielectric constant and dissipation factor. Dielectric constants and dissipation factors for epoxies are low, ranging from approximately 3 to 6 and 0.003 to 0.03, respectively, at room temperature and at 60 to 1000 Hz. At higher frequencies, dielectric constants decrease slightly. The dielectric constants and dissipation factors for a novolac-epoxy formulation compared with a Bisphenol A formulation (Table 2.9) showed no significant differences when measured at room temperature.^[24]

Table 2.9. Electrical Values for Epoxy Formulations^[24]

Property	Novolac Epoxy*		Bisphenol A Epoxy**	
	Initial Value	Value after 24 hr in Water	Initial Value	Value after 24 hr in Water
Dielectric Constant				
60 Hz	3.78	3.82	4.12	4.19
10^3 Hz	3.74	3.8	4.07	4.15
10^6 Hz	3.39	3.44	3.55	3.61
Dissipation Factor				
60 Hz	0.0027	0.0021	0.0035	0.0043
10^3 Hz	0.012	0.012	0.015	0.016
10^6 Hz	0.024	0.025	0.032	0.032
Volume Resistivity, ohm-cm	3.8×10^{15}	1.83×10^{14}	1.81×10^{15}	2.31×10^{14}
*Cured for 1 hr at 95°C plus 16 hr at 180°C.				
**Cured with MNA for 16 hr at room temperature plus 4.5 hr at 150°C.				

Dielectric strength. The dielectric strengths of epoxies, as with many other polymer coating types, are high. Typical values range from 300 to 500 volts/mil for 0.125-inch-thick samples and may increase to 2000 volts/mil for 1-mil-thick samples. Dielectric strengths are only slightly affected by fillers, regardless of the types or amounts used.^[25]

Arc resistance. The arc resistance of unfilled epoxies may vary from 80 to 100 seconds. Fillers have a beneficial effect, increasing the arc-resistance values up to 125–225 seconds, depending on the type of filler and hardener used.^[25] The fillers studied included silica, mica, zirconium silicate, and hydrated alumina. Other investigators have attained improved anti-tracking properties by incorporating 45–60% by weight of hydrous magnesium silicate powder.^[26] Still further improvement in arc resistance was achieved by roughening the surface or allowing filler particles to project partially from the surface.^[27]

Thermal properties. Epoxies are generally stable up to 150°C, but some anhydride- and aromatic amine-cured formulations are stable to 200°C. Above these temperatures, decomposition, outgassing, and changes in electrical and mechanical properties occur. The thermal stability of epoxies is higher than that of polyurethanes, acrylics, and polyesters, but lower than silicones, polyimides, and fluorocarbons. Epoxy-novolac resins are more thermally stable than epoxy-Bisphenol A types because the methylene linkage of the former is more stable than the isopropylidene linkage in the latter.

The percentage of outgassing products after aging at elevated temperatures is a good measure of thermal stability. As an example, Fig. 2.22 shows the superiority of an epoxy over an alkyd polyester when vacuum baked at 150°C. The amount of outgassing from the epoxy had stabilized within 4 to 5 hours, whereas volatiles continued to evolve from the alkyd coating even after 55 hours.^[28]

Figure 2.23 compares the outgassing at 150°C of an anhydride-cured epoxy with an amine-cured epoxy. The samples were preconditioned at 100°C in vacuum for 7 hours prior to aging at 150°C. In a 5-hour cycle, the amine-cured epoxy evolved less than 0.2 ml of gas while the anhydride-cured epoxy evolved slightly more than 1.5 ml. In other tests, polyesters evolved over 2.5 ml and phenolics and alkyds about 1.5 ml under essentially the same conditions.^[28]

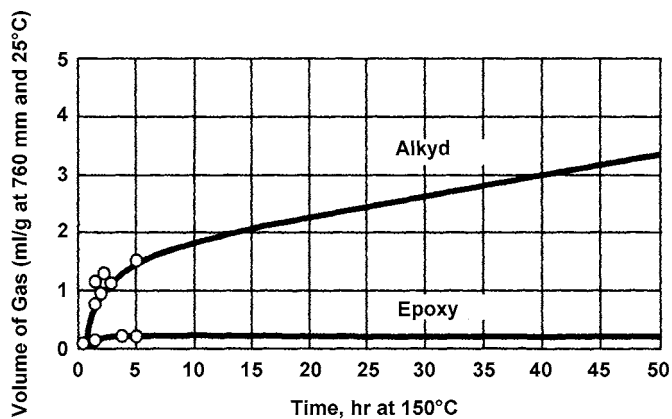


Figure 2.22. Gas evolution at extended thermal-vacuum exposure.^[28]

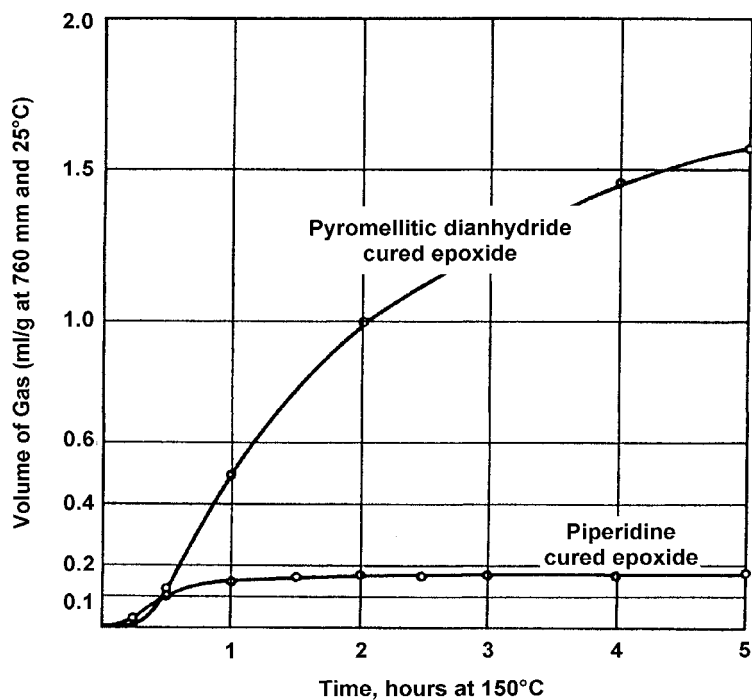


Figure 2.23. Gas evolution from anhydride-cured vs amine-cured epoxies.^[28]

Thermal gravimetric analysis (TGA) and differential thermal analysis (DTA) are excellent methods for determining the temperature at which a material starts to outgas. Initially small weight losses may be due to absorbed water, residual solvents, or low-molecular-weight species, but later, at higher temperatures, decomposition of the polymer and major outgassing occur. A TGA curve (pyrogram) for an anhydride-cured epoxy is shown in Fig. 2.24. Pyrograms for other epoxies have been reported by Ehlers.^[29] Thermal degradation of epoxies and other polymers has been treated by Conley.^[30]

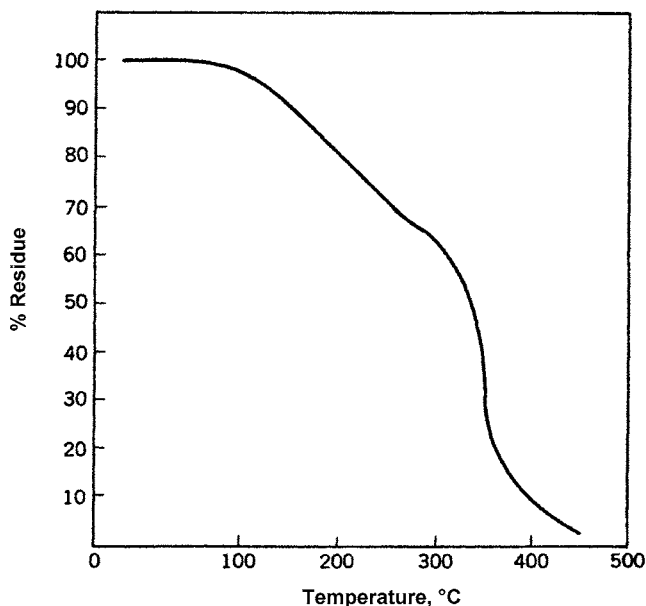


Figure 2.24. Pyrogram of Bisphenol A epoxy resin (100 pbw) cured with methyl nadic anhydride (80 pbw) and benzyldimethylamine (0.5 pbw).

2.7 POLYURETHANES

Polyurethanes were among the first coatings to be used for printed wiring board electrical insulation and protection from moisture, salt spray, and handling. Polyurethanes are also used as potting compounds for connectors and as vibration-damping fillets for large components. A key

attribute of most polyurethanes is the ability to rework defective components after a circuit assembly has been conformally coated. Polyurethanes can be softened and penetrated with a hot solder iron and residues may even act as a flux in resoldering a new component.

Almost all the early work and, in fact, most of the elucidation of the basic chemistry of the polyurethanes was performed by Bayer Corp. in Germany around 1937. Considerable work followed in the United States, primarily by DuPont, around 1940 resulting in a series of patents on the reaction products of polyisocyanates with various glycols, alkyd resins, polyamides, and polyesters. However, it was not until after World War II when much of the practical technology developed in Germany was transferred to the United States, that the commercialization and wide use of polyurethanes occurred.^[31]

2.7.1 Chemistry

The urethane technology developed in Germany was based on a series of addition polymers formed from polyisocyanates called *desmodurs* and polyesters called *desmophens*. These polymers soon became popular and widely used as coatings because of their flexibility, toughness, excellent electrical insulation properties, and excellent moisture, abrasion, chemical, and corrosion resistance.

The parent compounds for all polyurethane coatings are the di- or polyisocyanates of which the most widely used is tolylene diisocyanate (TDI). It consists of 2,4-tolylene diisocyanate or various mixtures of the 2,4- and 2,6- isomers (Fig. 2.25).

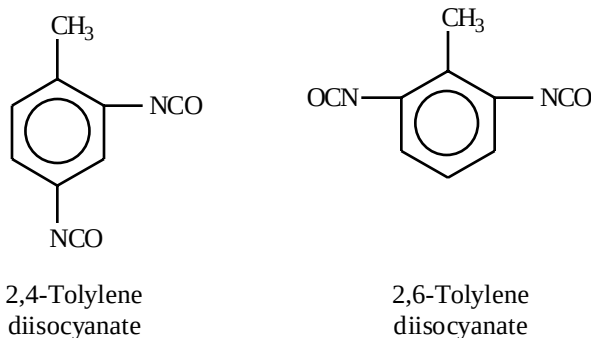
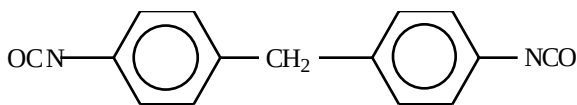


Figure 2.25. Structures for tolylene diisocyanates.

Methylene bis(4-phenylisocyanate), also referred to as p,p'-diphenylmethane diisocyanate (MDI) is another widely used diisocyanate.



These basic isocyanates, however, are not employed as such in commercial formulations because of their high vapor pressures and toxicities which are due to the free isocyanate (NCO) groups. To lower their vapor pressures and render them safe, they are modified by co-reacting some of the isocyanate groups with a polyol, for example, trimethylolpropane (Fig. 2.26). Trimethylolpropane combines with three of the six available isocyanate groups, producing an adduct that is safe to work with and that serves as one part of a two-part polyurethane system. In this structure, note that three isocyanate groups are still available for polymerization with other resins containing active hydroxyl groups.

In summary, the reaction common to all polyurethane chemistry is the addition of a hydroxyl group to an isocyanate group resulting in a urethane linkage as in Fig. 2.27 and polyurethanes as in Fig. 2.28.

2.7.2 Classifications

Polyurethanes have been classified and defined according to six types by the American Society for Testing and Materials (ASTM D-16). Four of these types are one-part systems and two are two-part systems. These types are described as follows:

- Type I. One-part, pre-reacted. These are urethane-oil or uralkyd types in which polyisocyanates have been reacted with a polyhydric alcohol ester of a vegetable fatty acid. They cure by oxidation at ambient or slightly elevated temperature in 5 minutes to 1 hour.
- Type II. One-part, moisture cured. These are resins that have free reactive isocyanate groups that can cross link and harden with ambient moisture. They are slower curing than Type I, requiring up to 24 hours at room temperature at a relative humidity of over 30%.

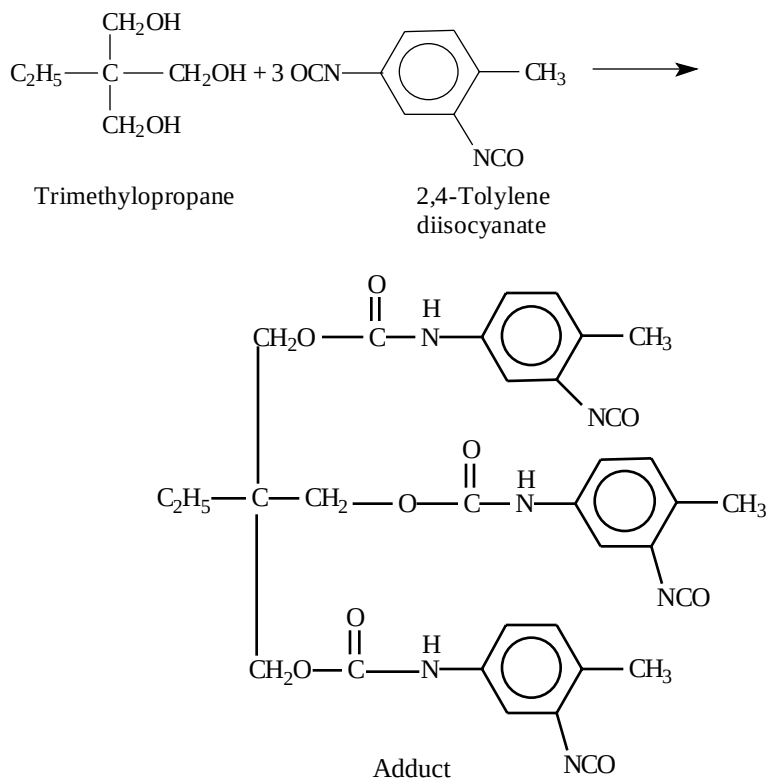


Figure 2.26. Preparation of low-vapor-pressure urethane prepolymers.

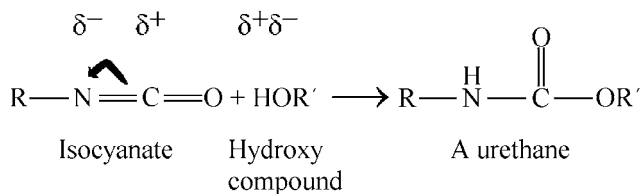


Figure 2.27. The basic urethane reaction.

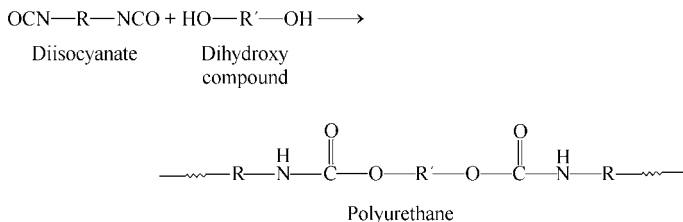
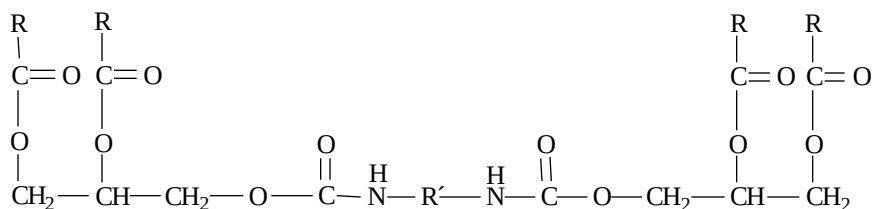


Figure 2.28. The basic polyurethane reaction.

- Type III. One-part, heat cured. These are phenol-blocked isocyanates that release the blocking agent and regenerate the reactive isocyanate on heating.
- Type IV. Two-part, catalyst cured. These systems consist of a pre-polymer or adduct having free isocyanate groups as one part and a catalyst as the second part. Small amounts of the catalyst will cross link the pre-polymer. Catalysts may consist of monomeric polyols or polyamines. The pot life after the two parts are mixed is generally short varying inversely with the amount of catalyst used.
- Type V. Two-part, polyol cured. In this type, the first part is a pre-polymer or adduct having free isocyanate groups while the second is a resin having reactive hydrogen atoms such as hydroxyl-terminated polyesters or polyols such as castor oil.
- Type VI. One-part, nonreactive lacquers. These are polymerized urethanes that are thinned with a solvent. The systems are characterized by the absence of any significant quantity of free isocyanates or other functional groups. These resins convert to solid films primarily by solvent evaporation.

One-part, Oil-modified Systems: Uralkyds (ASTM Type I).

One-part polyurethanes are based on urethanes containing as part of their structure modified drying oils such as linseed oil and are referred to as uralkyds, urethane oils, or oil-modified urethanes. In their manufacture, the oil is first partially de-esterified to give a mixed hydroxy ester. The free hydroxy group of this ester then reacts with a diisocyanate to give the pre-polymer resin.



where R represents a fatty acid portion containing double bonds, such as



This resin cannot polymerize further through free isocyanate groups since they have all been reacted, but it can continue to cross link and polymerize through the double bonds (ethylenic groups) available in the fatty acid R portion. Through air oxidation, free radicals are formed from the active methylene groups adjacent to the double bonds and several units may then combine to form high-molecular-weight polymers. The addition of a drying catalyst such as cobalt or manganese naphthenate accelerates the air curing so that tack-free times of 2 to 5 minutes are achieved. More specific information on the mechanism for this type of cure may be found in several references.^{[32][33]} The main feature of uralkyd resin coatings is their low cost compared with other polyurethane types. This is due to the low cost of the naturally occurring oils used in their synthesis. Like the alkyds, they exhibit very good moisture resistance, but are marginal in color and gloss retention. Uralkyds are not as extensively used in electrical applications as are the blocked polymers or the two-part systems (see below).

One-part, Moisture-cured Systems (ASTM Type II). Moisture-cured prepolymers are formed by reacting hydroxyl-containing compounds such as castor oil, hydroxyl-terminated polyester, or hydroxyl-terminated polyethers with an excess of tolylene diisocyanate. The prepolymer adducts so formed have some free isocyanate groups which can then react with moisture (Fig. 2.29). Thin films of these prepolymers cure on exposure to ambient moisture by a mechanism involving the cross-linking of molecules through the formation of urea linkages (Fig. 2.30). Moisture-cured polyurethanes are among the most durable and most abrasion-resistant coatings known (Tables 2.10 and 2.11). They are widely used as floor, wood, and appliance coatings. Their use in electronics, however, has been limited due to the unpredictable time required to achieve a complete cure which depends on the ambient humidity. Films, 1-to 2-mils thick, dry tack-free in 20–30

minutes, but require up to 24 hours at room temperature and a minimum of 30% relative humidity to harden to a full cure. Optimum physical and electrical properties require further air-moisture cure for an additional 5 to 7 days.

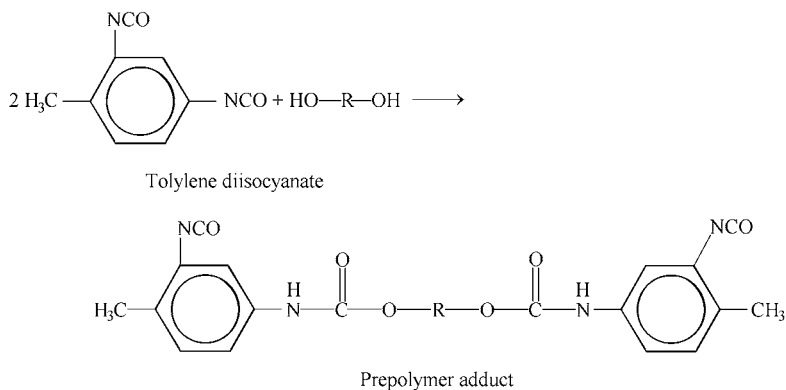


Figure 2.29. Prepolymer urethane-adduct formation.

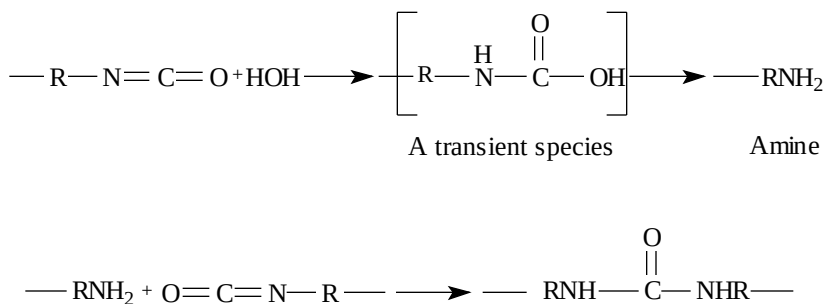


Figure 2.30. Moisture-cure mechanism for polyurethanes.

Table 2.10. Properties of a Typical Moisture-cured Polyurethane^[34]

Property	Rating
Nonvolatile Content, %	45
Solvent	Xylene
Viscosity (bubble)	A
NCO-OH Ratio	1.65
TDI, %	42.8
Sward Hardness Value	48
Impact	>160
Elongation, %	>14
Drying Time, hr	
Set to touch	0.4
Tack-free	6.0
Hard dried	6.0

Table 2.11. Abrasion Resistance of Polyurethane Coatings (mg/1000 cycles)^[35]

Isocyanate Curing Agent	Resin				
	Mondur TD-80	E-244	E-262	E-268	Mondur CB-60
Modified Alkyd (uralkyd)	72				
Polyether Prepolymer, moisture-cured	31	29	33		
Multron R-12				35	38

One-part, Blocked Polyurethanes (ASTM Type III). The one-part polyurethanes most widely used for electrical/electronic applications, especially for wire insulation, are those with blocked isocyanate groups. To provide the most desirable one-part system and to extend pot life, the active isocyanate groups are rendered latent by reacting them with other

organic compounds having active hydrogen atoms. In this condition, referred to as a *blocked isocyanate*, the prepolymer is non-reactive and has an indefinite shelf life. On heating, the blocking compound splits off, and the liberated isocyanate can then polymerize using a suitable hardener. Phenol is the most commonly used blocking agent, but other agents include cresol, methyl ethyl ketoxime, butanol, and caprolactam. The chemical mechanism for blocking and unblocking is given in Fig. 2.31. The temperature required to unblock the phenol adducts is about 160°C which limits their use for temperature-sensitive electronic components. However, they are ideal for wire and coil insulation and for coating other metal or ceramic parts. Other adducts having lower unblocking temperatures are available, for example, the malonic ester adduct that unblocks at 130°C.

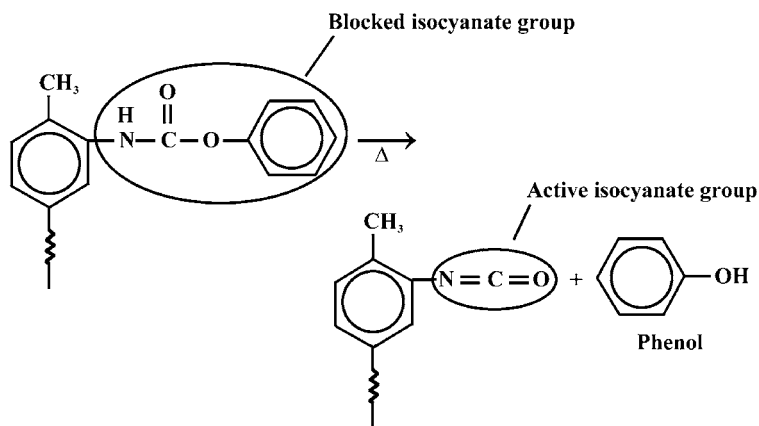


Figure 2.31. Mechanism for unblocking Type III polyurethane resins.

Two-part, Catalyst-cured Systems (ASTM Type IV). Type IV systems consist of a prepolymer or adduct having free isocyanate groups as one part of a two-part system and a catalyst, accelerator, or cross-linking agent, such as a monomeric polyol or polyamine, as the second part. The urethane reaction is base-catalyzed and small amounts (0.5 to 4%) of an alkaline compound may be used to initiate polymerization. Among the commonly used catalysts are the tertiary amines such as triethylamine, organo-tin and organo-cobalt compounds (Fig. 2.32). Some of these catalysts may also be used to accelerate the cure of other two-part polyurethane systems, for example, Type V. Although desirable from a manufacturing standpoint, precautions should be taken that the addition of such catalysts

does not alter critical engineering properties of the coating. Combinations of two different catalysts have been found to be more active than either one used alone. This synergistic enhancement achieved by combining two catalysts has been reported for organotin compounds and tertiary amines.^[36]

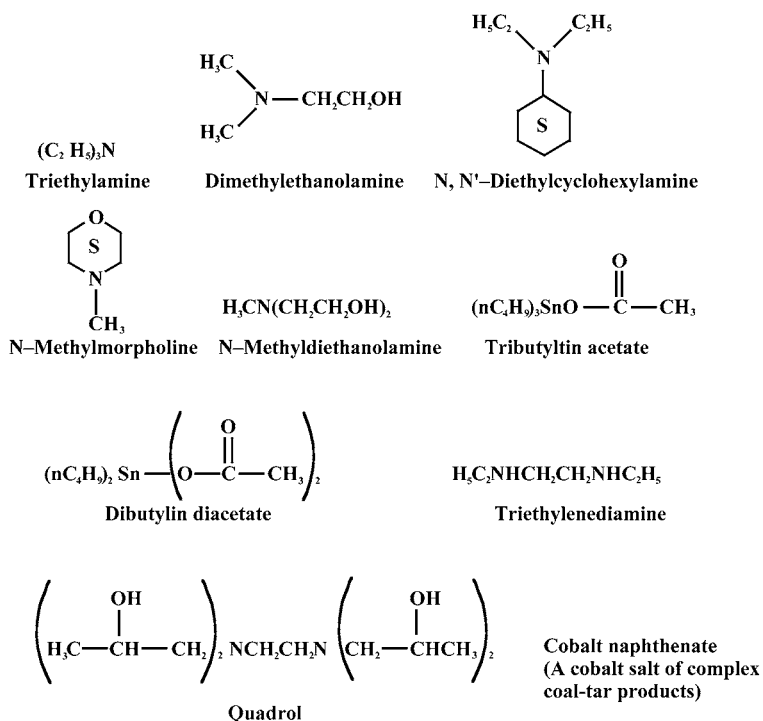
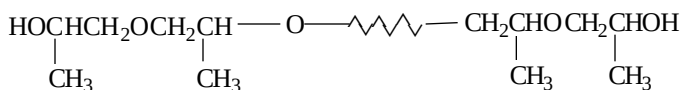


Figure 2.32. Typical catalysts for curing polyurethanes. (*Quadrol*[®] is a registered tradename of BASF Corp.)

Two-part Prepolymer: Polyol (ASTM Type V). Two-part Type V polyurethanes are widely used for high-reliability electrical insulating coatings and corrosion protective coatings. Part A is usually a tolylene diisocyanate or a polyisocyanate prepolymer, also known as an adduct. Part B is a hydroxyl-containing resin of which the most commonly used are hydroxyl-terminated polyesters, polyethers, polyols, castor oil, and some epoxy resins, the latter reacting through the free hydroxyl groups along the polymer chain. The polyethers are based on polypropylene oxide and are

termed polypropylene glycols. A large variety of these glycols, differing in molecular weight and viscosity, is commercially available.

Both polyethers and polyesters range from long-chain linear structures, as in the generalized formula for hydroxyl-terminated polyether to highly branched structures.



Through proper selection, the properties of the coating may be varied from highly flexible to very hard or brittle. As a rule, the more linear the structure, the more flexible the resulting film; the more branched, the harder and more chemically resistant the coatings will be. Almost all the polyethers and polyesters are hygroscopic and capable of absorbing as much as 2% by weight of water under high-humidity conditions. With proper containment and storage, moisture absorption can be kept to a minimum. The isocyanate part A is also sensitive to moisture. Water reacts with the free isocyanate groups releasing carbon dioxide and forming an amine compound which is also reactive combining readily with more free isocyanate to give substituted urea polymers. The released carbon dioxide can also cause bubbles to form in the coatings. In summary, moisture must be excluded because it competes with part B for the free isocyanate groups of part A.

Castor oil is a good choice for curing isocyanates resulting in excellent insulating and protective coating properties. However, oil-based coatings show strong yellowing and are, therefore, used primarily as primer coatings.

One-part, Non-reactive Systems (ASTM Type VI). These polymer solutions (lacquers) are pre-reacted and thinned with solvents such as alcohols, methyl ethyl ketone, toluene, or N-methyl-2-pyrrolidone. They may also be purchased as anionic colloidal urethane elastomeric dispersions in a water/solvent solution. These coatings are primarily used as impregnants for fabrics, leather, and paper and as primers and topcoats for other plastics. Type VI urethanes are not generally used for coating electronics.

2.7.3 Properties

Polyurethanes were among the first polymer coatings to be used as conformal coatings for the protection of printed circuit boards and continue

to be favored. They excel in abrasion resistance (Table 2.12), toughness (Table 2.13), humidity resistance, adhesion to a variety of surfaces, and retention of their excellent electrical insulation properties even after the 10-day humidity/temperature cycling test of MIL-I-46058. Typical electrical properties for some polyurethane coatings are given in Table 2.14. Polyurethanes may be cured at room temperature for extended periods of time or at moderately elevated temperatures for several hours.

Table 2.12. Abrasion Resistances of Polyurethanes Compared with Other Coatings^{[37]–[39]}

Coating Type	Taber Wear Index (mg/1,000 cycles)
Polyurethane, Type 1*	43–155
Polyurethane, Type 2	28–33
Polyurethane, Type 5	60
Alkyd	147
Vinyl	85–106
Amine-catalyzed Epoxy Varnish	38
Epoxy Polyamide	95
Phenolic Varnish	91–172
Epoxy Ester	116–121
Chlorinated Rubber	220
*Types defined under Classifications and Properties.	

Table 2.13. Toughness of Polyurethane and Alkyd Coatings^[37]

Coating Type	Energy of Rupture, in –lb/in ³
Polyurethane, two-part system	4,000–8,000
Polyurethane, one-part system	1,000–2,000
Alkyd	200–600

Table 2.14. Typical Electrical Properties of Polyurethane Coatings

Electrical Property	Conathane® CE-1155	Conathane® CC-1194
Insulation Resistance, ohms initial @ RT and 50% RH	$>2.5 \times 10^{13}$	2.5×10^{13}
Insulation Resistance, ohms after 10 days 65°C/95% RH	6.1×10^{10}	1.3×10^{10}
Volume Resistivity, ohm-cm @ 25°C	5.66×10^{14}	1.5×10^{15}
Dielectric Constant, 1 MHz	3.21	2.7
Dissipation Factor, 1 MHz	0.0162	0.020
Dielectric Withstanding Voltage, 1500 V ac	No flashover or breakdown	No flashover or breakdown
Dielectric Strength, V/mil	3000 (2-mil film)	3500 (1-mil film)
Values are typical and not intended for specification purposes. Conathane® is a registered tradename of Cytec Industries. (Courtesy Cytec Industries.)		

2.8 SILICONES

Silicones constitute a unique class of polymers due to their semi-organic structures. They are distinguished from other organic polymers in having a silicon-to-carbon backbone structure instead of the normal carbon-to-carbon structure. Because of this unique structure, silicones possess much higher thermal resistance than other polymers and, at the same time, possess and maintain excellent electrical properties at high temperatures and under humid conditions. A series of ultra-pure silicones were developed for the electronics industry in the early 1960s and today find extensive applications as circuit board conformal coatings, semiconductor junction coatings, encapsulants, and adhesives.

2.8.1 Chemistry

Unlike other polymers, silicones are not entirely organic. Chemically, silicones consist of alternate Si and O atoms linked to organic sidegroups such as aliphatic or aromatic hydrocarbons and, as such, are

more accurately classified as semi-organic. The --Si--O--Si--O-- backbone structure is referred to as siloxane. The general structure for a linear silicone polymer is represented in Fig. 2.33.

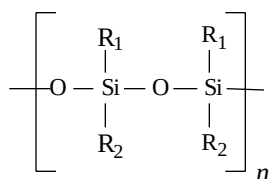


Figure 2.33. General structure for a linear silicone polymer.

In this structure, the group R_1 may be the same as or different from R_2 . These appendages may represent any one or combination of organic groups such as:

- methyl (CH_3)
- phenyl (C_6H_5)
- allyl ($\text{--CH}_2\text{CH=CH}_2$)
- vinyl (--CH=CH_2)
- trifluoropropyl ($\text{--CH}_2\text{--CH}_2\text{CF}_3$)

Silicone polymers are classified by the nature of these side groups according to ASTM D1418 (Standard Practice for Rubber and Rubber Lattices-Nomenclature) as follows:

Q	Siloxane
MQ	Dimethyl Siloxane
PMQ	Methyl Phenyl Siloxane
VMQ	Methyl Vinyl Siloxane
PVMQ	Methylphenylvinyl Siloxane
FVMQ	Fluoromethylvinyl Siloxane

Silicone chemistry was developed in the early 1940s at General Electric in Schenectady, NY, and at Corning in Corning, NY, and has been modified,

improved, and commercialized over the years by both General Electric and Dow Corning.

The basic silicone resins are prepared in several steps starting with the partial or complete hydrolysis of alkyl- or arylchlorosilanes by reaction with water. The starting materials, for example, may be mixtures of trimethylmonochlorosilane, dimethyldichlorosilane, and methyltrichlorosilane. In this mixture, the dimethyldichlorosilane dominates and is separated from the others by fractional distillation. Hydrolysis of the alkyl- or arylchlorosilanes results initially in silanols that readily condense in the presence of acid or base catalysts to give polysiloxane oligomers^{[40]–[42]} (Fig. 2.34). These resins are commercially available for further processing and application to electronics. The cross-linking of linear polymers, or the further cross-linking of partially cross-linked resins using heat, catalysts, or both, results in curing to produce elastomeric or rigid coatings, encapsulants, or adhesives.

There are essentially two cure mechanisms for silicone resins: condensation cure and addition cure.

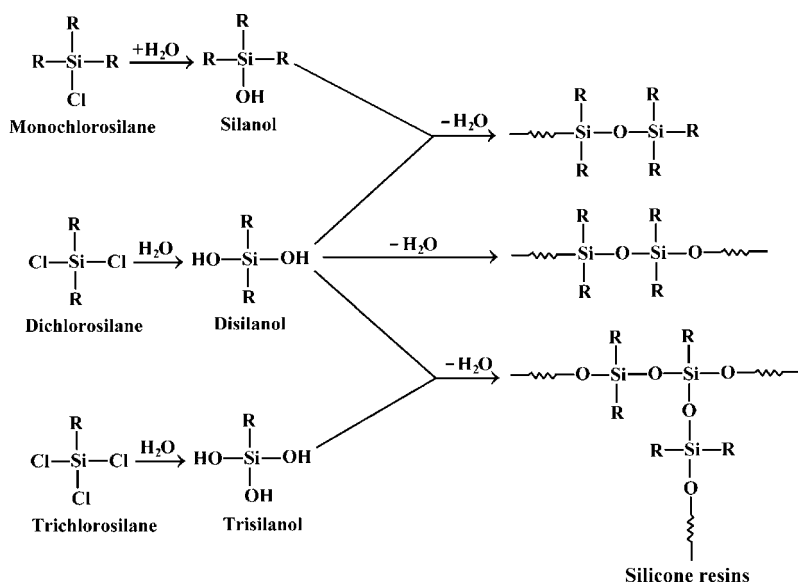


Figure 2.34. Synthesis reactions for silicone resins.

Condensation-cured Silicones. According to the condensation mechanism, hydroxyl-terminated silicones react with other hydroxyl-containing silicone species or with alkoxy silanes. In this process, either water or an alcohol is eliminated as a by-product. As an example, the mechanism for curing a hydroxyl-terminated silicone resin with propyl orthosilicate in the presence of a catalyst is shown in Fig. 2.35. Curing occurs at room temperature or at elevated temperatures in the presence of specific catalysts, such as dibutyltin dilaurate, zinc naphthenate, iron octoate, stannous octoate, or the metal salts of other organic acids. Amine catalysts, such as triethanolamine, may also be employed. Silicones prepared by this procedure are referred to as room-temperature vulcanizing (RTV) types. After mixing in the catalyst, they polymerize and cure at room temperature, generally in a 24-hour period for optimum properties, but their cures may be accelerated by elevating the temperature.

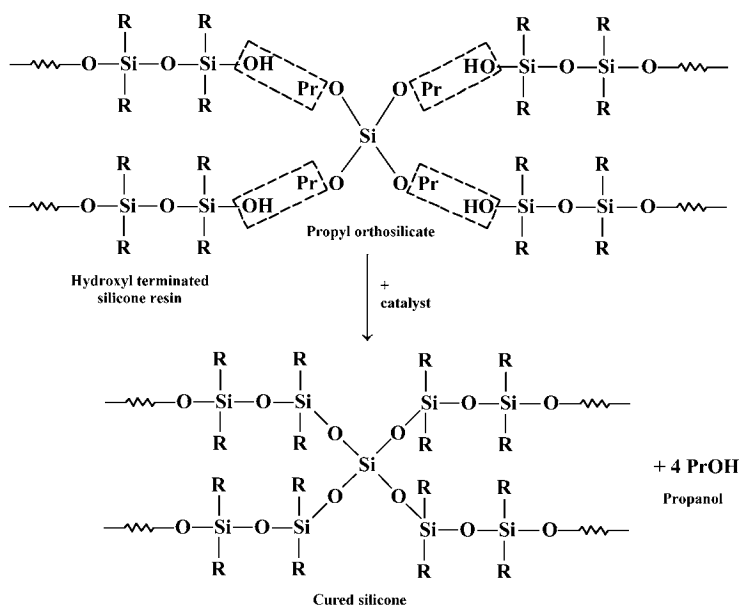


Figure 2.35. Condensation polymerization of silicones.

A simpler condensation cure mechanism, widely used today for conformal coating of microelectronics, starts with a silicone resin in which the hydroxyl groups have been converted to alkoxy groups, for example,

methoxy. These one-part systems polymerize by reacting with ambient moisture, releasing the alcohol, and linking the chains (Fig. 2.36). An originally introduced moisture-cured resin, in which the hydroxyl group was converted to acetoxy, is now seldom used for electronic applications because of the many failures caused by the release of corrosive acetic acid as the by-product. The released acetic acid corroded thin-film metallizations and chromium and cadmium plated parts, especially when confined in a sealed enclosure.

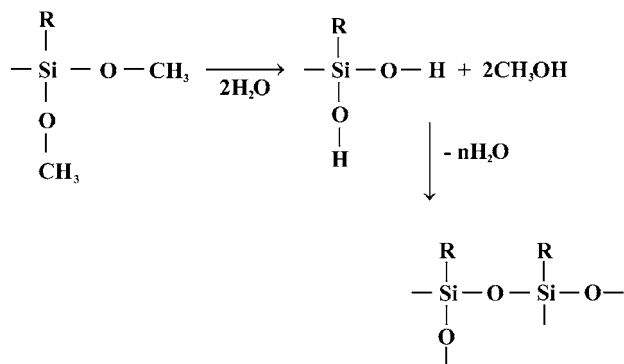


Figure 2.36. Condensation mechanism for moisture-cured silicones.

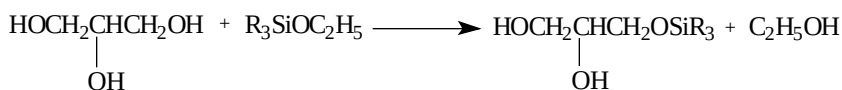
Addition-cured Silicones. Dimethyl siloxane polymers may also cure by a *free-radical mechanism* involving addition polymerization in which no by-products are eliminated. In such cases, the siloxane polymer must be terminated with an unsaturated group such as vinyl or allyl. Cross linking occurs through the formation of free radicals using a catalyst as a free-radical initiator. Two addition-cure mechanisms are reported. Both require a vinyl end-blocking group on one of the silicone constituents. The mechanism for curing a methyl vinyl siloxane using a peroxide catalyst is shown in Fig. 2.37. Dichlorobenzoyl peroxide, benzoyl peroxide, di-tertiarybutyl peroxide, and dicumyl peroxide may be used. On heating, each molecule of the peroxide catalyst, generically represented as R-O-O-R,

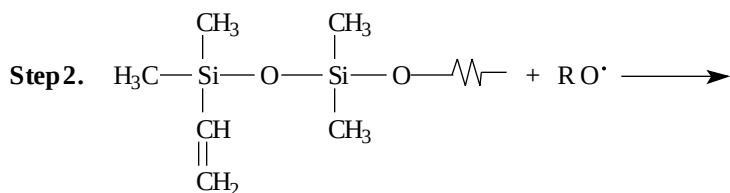
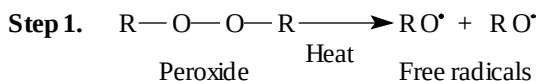
dissociates into two free-radicals (Step 1). One of these free radicals then adds to the vinyl group of the silicone resin (Step 2) creating a carbon free-radical. The latter, on contacting a methyl group from a neighboring polymer chain, abstracts a hydrogen atom and creates a methyl free radical. Simultaneously, the OR group is released as a free radical. There now remains an ethyl free-radical side group on one polymer chain and a methyl free-radical group on the other, that instantly couple to form a cross-link between the chains (Step 3). Note that the free radical from the peroxide has been regenerated and is, of course, available again to repeat the process. By a similar mechanism, dimethyl polysiloxane resins can be cross linked with a peroxide-initiated free-radical cure (Fig. 2.38).

A second addition cure mechanism also starts with a vinyl end-blocked siloxane prepolymer, but cross links with a methyl silane polymer in the presence of a organo-platinum or organo-rhodium complex catalyst and heat (Fig. 2.39). The platinum complex serves as a free-radical initiator opening up the vinyl group of the first silicone polymer and allowing it to add to the second.

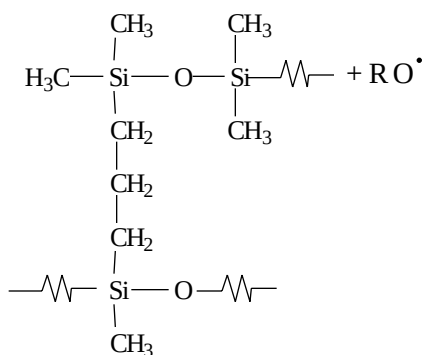
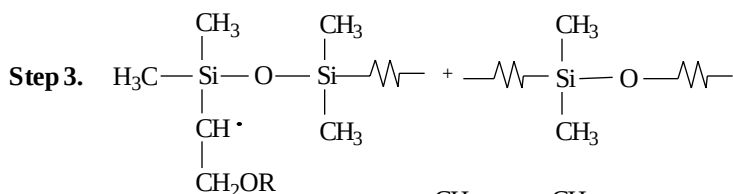
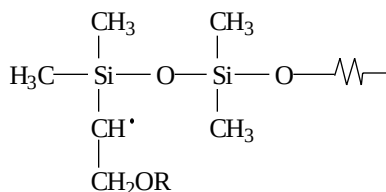
Silicones cured in this fashion are also referred to as *heat vulcanizing* types. They are of special interest for many electronic applications because no water, alcohol, or other by-products are released during their cure.^[43] Addition cure formulations require elevated temperatures to obtain full cure in a short and predictable time (cure schedules may range from a few hours at 100°C to 20 minutes at 150°C). Addition-cured silicones, however, are susceptible to the cure being inhibited by contaminants such as fluxes and solder residues. Amines and organosulfur compounds are also known to poison the platinum catalyst and inhibit the cure. Further details of the chemistry and cure mechanisms of these and other silicones are given in the literature.^{[44]–[46]}

Silicone Alkyds. Silicone alkyds are resins in which the silicone structure has been chemically combined with an alkyd polymer. They can be prepared by reacting glycerol with a silicone ester or with a silanol instead of with the fatty acids normally used in preparing alkyds.^[47]





Vinyl-terminated methylsiloxane



Cross-linked addition polymer

Figure 2.37. Free-radical addition mechanism. Polymerization of vinyl-terminated siloxane catalyzed by peroxide.

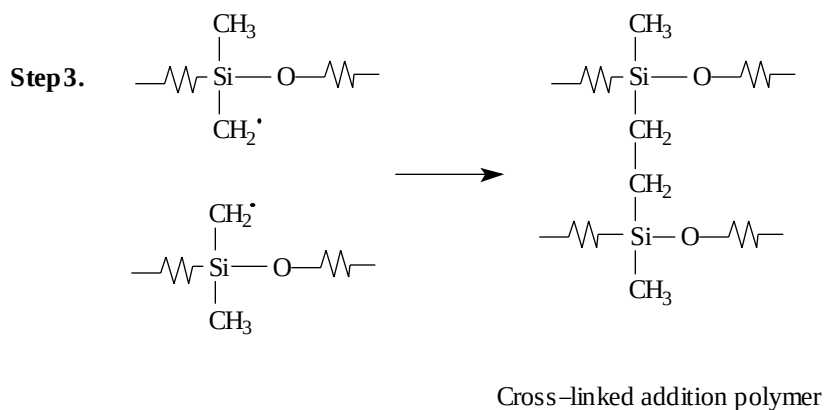
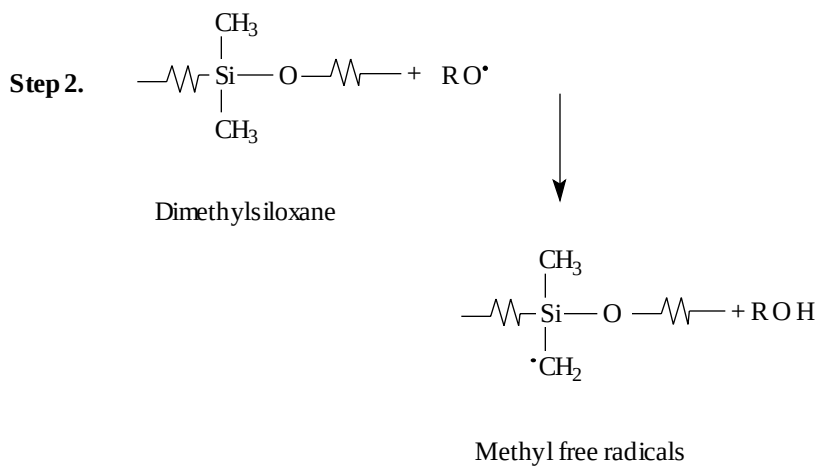
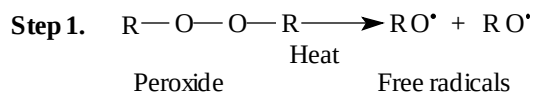
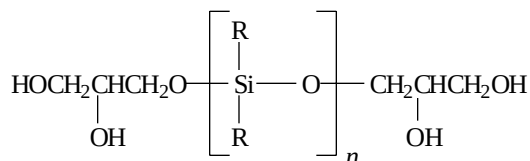


Figure 2.38. Free-radical addition mechanism. Polymerization of dimethyl polysiloxane catalyzed by peroxide.

Other silicone diesters and hydroxyl-terminated silicones may be used to give structures such as



Phthalic anhydride may then be condensed with these products to yield high molecular weight, highly cross-linked silicone alkyds of which a typical structure is given in Fig. 2.40.

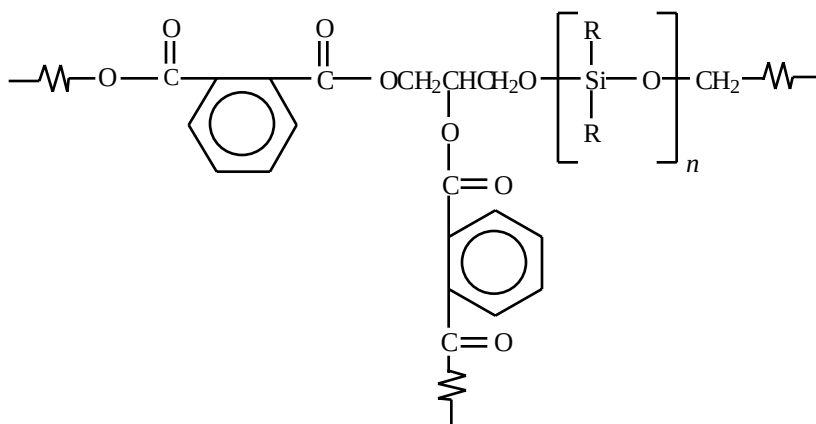


Figure 2.40. Typical structure of a silicone-alkyd polymer.

Numerous modifications of this basic chemistry are possible, giving rise to a multitude of proprietary silicone alkyd coatings. Silicone-alkyd coatings have greater flexibility, hardness, and thermal stability than alkyds, but lack the high thermal and oxidative resistance of the unmodified silicones and must, therefore, be considered intermediate in properties. Nevertheless, these intermediate properties are considered important in achieving a compromise between thermal stability and ease of handling for many applications. Silicone-alkyd coatings are widely employed as moisture-barrier and corrosion-protective coatings for electronic components such as resistors, transistors, and integrated circuits.

Halogenated Silicones. As with epoxies, silicones may be chlorinated or brominated to render them non-flammable or less flammable than their non-halogenated counterparts. Chlorinated diphenyl silicone and methyl chlorophenyl silicone are examples that have been synthesized and characterized.^[48]

2.8.2 Properties

Silicones range from soft (quasi-liquid) gels to hard coatings. For two-part systems, the hardness can be tailored by changing the ratios of the components. Silicones may be either solvent-based or solventless (100% solids) and either one-part or two-part systems. For electronic applications, the one-part, solventless (100% solids) formulations are preferred. One-part silicones generally cure by exposure to ambient moisture. A full cure may require from 24 to 72 hours, however, after an initial moisture cure, the cure may be accelerated by mild heating at 60–80°C and raising the humidity to 75%. Solvent-based silicones and heat-cured systems (10–15 minutes at 105–110°C) provide improved abrasion resistance. Solvent-based systems sometimes result in stresses and cracking or crazing of the coating and breakage of interconnect wires due to rapid solvent evaporation and shrinkage. Thus, the solventless formulations are preferred.

Thermal Properties. Because of their silicon-to-oxygen backbone structure ($-\text{Si}-\text{O}-\text{Si}-\text{O}-$), silicones enjoy both very low (-100°C) and very high temperature (300°C) stability and better thermal-oxidative stability than their totally hydrocarbon counterparts.^[49] For wire insulation, silicones have been classified as Class H insulation; that is, they may be used safely up to 180°C for long periods of time (5 to 10 years)^[50] (Fig. 2.41).

Before the introduction of silicones, electrical applications were limited to 130°C or less (Classes A and B). Sufficient data are now available to show that the life expectancy of equipment insulated with silicones may be increased a hundredfold over Class B-insulated equipment.

Electrical Properties. The electrical properties of silicones are superior to those of most polymer types, including many epoxies. For example, dielectric constants at room temperature and 100 Hz, for a large number of commercial silicone formulations, lie in a rather narrow range of 2.8 to 3.8. At higher frequencies, temperatures, and humidities, very little change occurs in either the dielectric constant or dissipation factor. In fact, unlike many plastics, values may even decrease with increasing tempera-

ture (Figs. 2.42 and 2.43). The dielectric constant, ϵ , for Dow Corning Sylgard[®] 183, for instance, drops from 3.3 at room temperature to 2.6 at 200°C.^[51] Silicones have been aged at 300°C for 1000 hours with little change in dielectric constant. Dielectric breakdown voltages for silicones are high, ranging from 500 to 2000 volts/mil, depending on the formulation and thickness of the film. Volume resistivities are all 10^{12} ohm-cm or higher.

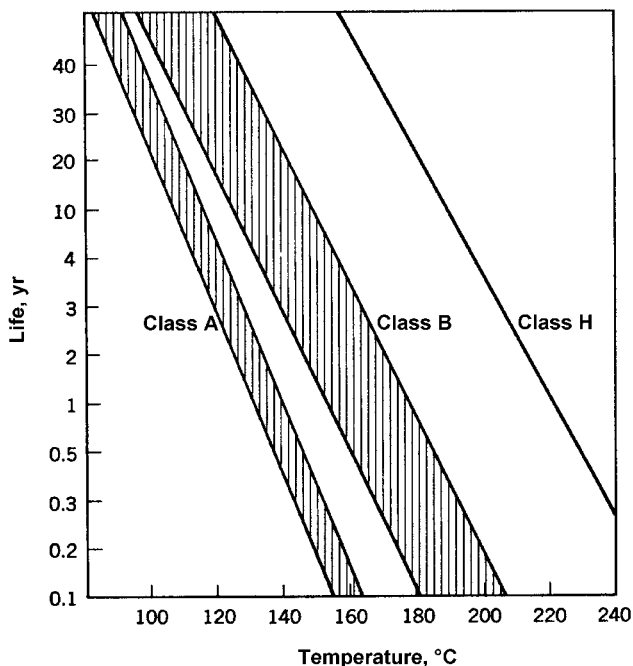


Figure 2.41. Insulation classes and their relationship to life expectancies.^[50]

Other Properties. Because of their low surface tension due to hydrocarbon groups appended to the silicon atoms, silicones have low water absorptions and repel water and, as such, are widely used as water repellents in many military and commercial applications. Paradoxically, in spite of their low water absorptions and water repellent properties, silicones have high moisture vapor transmission rates.

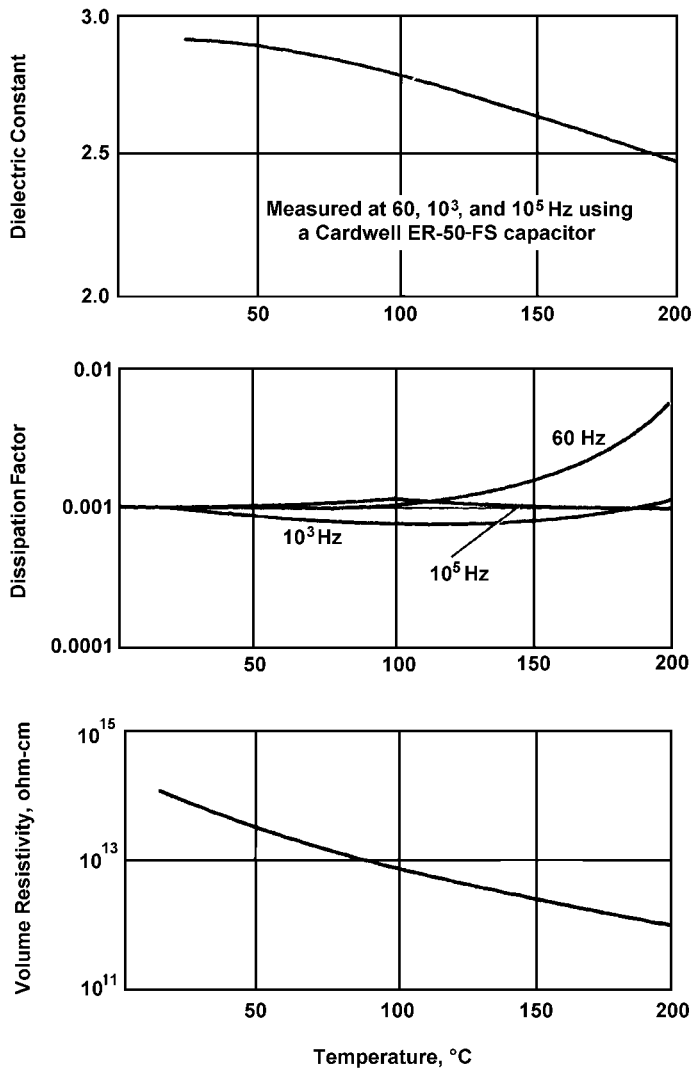


Figure 2.42. Electrical properties of cured Sylgard® 182 resin at elevated temperatures. (Courtesy Dow Corning Corp.)

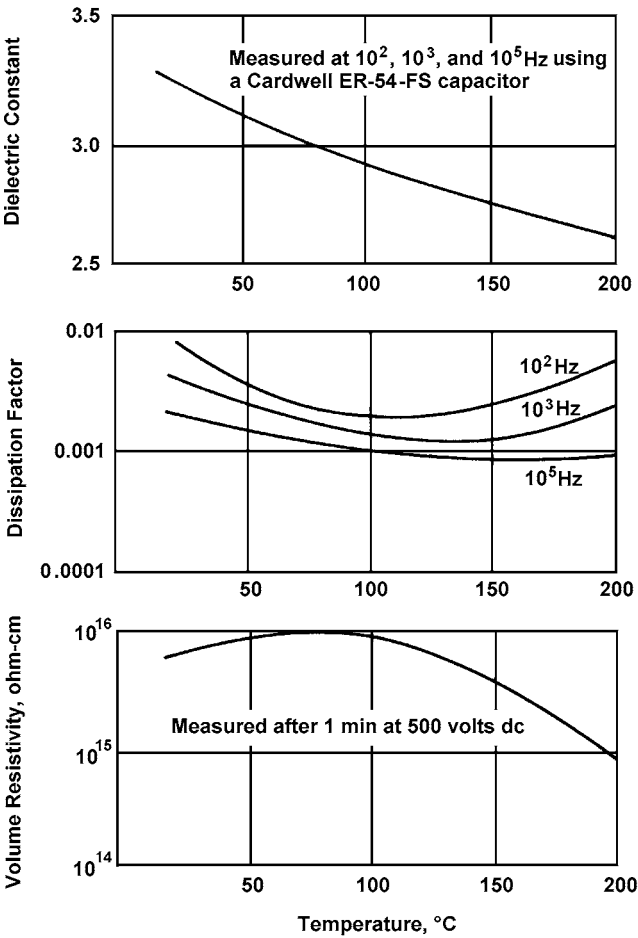


Figure 2.43. Electrical properties of cured Sylgard® 183* resin at elevated temperatures. (Courtesy Dow Corning Corp.)

*Discontinued.

Silicone coatings are transparent or translucent, but small amounts of ultraviolet indicator may be incorporated to facilitate inspection under a black lamp.

Silicones and parylenes are among the purest of known polymers. They contain little or no chloride, sodium, or potassium ions nor other deleterious ions or by-products. Both have a long history of use in high-reliability applications such as spacecraft, medical implants, automotive circuits, and military hardware. Silicones have been used for many years as moisture barrier conformal coatings for printed wiring assemblies and are one class of coatings specified in MIL-I-46058. They are also widely used in semiconductor applications as junction coatings to relieve and dissipate thermal mechanical stresses.

In summary, the key attributes of silicones are:

- Low and high temperature stability with a useful life range generally of -54° to 204°C . Some formulations are thermally stable even at 316°C for short periods. Others maintain their resiliency and other properties as low as -115°C .
- Low modulus of elasticity, thus affording thermal stress relief.
- Alpha particle protection.
- Excellent moisture resistance.
- Excellent electrical properties over a wide temperature and frequency range.
- High purity.
- Inherent non-flammability.
- Resistant to ozone and corona.
- Resistant to ultraviolet and other radiation.

The relatively high cost of silicones, compared with other polymer coatings, coupled with their low tensile and tear strengths have been drawbacks for some applications. Table 2.15 gives typical values for some Dow Corning silicones.

Some typical applications of silicone coatings for electronic hardware include:

- Circuit board conformal coatings.
- Semiconductor junction coatings.

- Wire and cable insulation.
- Electronic component protective coatings.
- Impregnating varnishes for coils (stator, rotor, generator, transformer).
- High-temperature stable, corrosion-protective paints.
- Ablative coatings.
- Insulating coatings for power supplies, connectors, relays, and magnetic amplifiers.
- Gel coatings for integrated circuits.
- Mold release agents.
- Water repellents.

Other non-coating applications include adhesives, lubricants, and potting compounds. Table 2.16 lists a number of commercially available silicones, their properties, and uses.

Silicone Gels. High-purity silicone gels were extensively studied as protective coatings and encapsulants for bare-chip devices and multichip modules and found to be essentially stress-free and compatible with the devices.^{[52]–[53]} However, because of their softness, silicone gels need to be contained. It was also reported that migration of low-molecular-weight species contained in the gel migrated to other parts of the module. These almost molecular layers can affect the adhesion of subsequent adhesive bonding operations and can contaminate optics and sensitive instruments.

Other soft silicones are used as stress relieving junction coatings for epoxy encapsulated, wire-bonded semiconductor devices. Junction coatings are soft, elastomeric materials designed to preserve the dielectric integrity of the semiconductor p-n junctions and wire-bond sites and relieve mechanical stresses that may be imposed by overmolding with epoxy encapsulants.

Block copolymers of siloxanes with α -methyl styrene are solvent-soluble coatings that have been used for particle immobilization in hermetically-sealed hybrid microcircuits and other sealed devices^[54] (See also Ch. 4 “Applications”). Silicone gels and other inherently tacky silicones have also been used as particle getters. They have been used to coat the inside of a lid prior to sealing a hybrid circuit or multichip module so that particles that may have been trapped or later generated within the hermetic enclosure may be gettered^[55] (see also Ch. 4).

Table 2.15. Selected Properties for Some Dow Corning Silicone Coatings

Designation	Type	Viscosity, Centipoise	Specific Gravity, g/cc	Tack-free Time @ RT minutes	Cure Time, hr	Dielectric Strength, V/mil	Dielectric Constant, • @ 100 kHz	Volume Resistivity, Ω -cm	Dissipation Factor @ 100 kHz
3-1753	1-part RTV solventless	385	0.99	8	24 @ 25°C	380	2.26	1×10^{15}	<0.001
3-1765	1-part RTV solventless	150	1.03	8	24 @ 25°C	-	2.25	2.1×10^{15}	<0.001
3-1744	1-part RTV solventless	60,000	1.04	15	24 @ 25°C	590	2.29	2.5×10^{15}	<0.001
3140	1-part RTV solventless	30,000	1.03	70	72 @ 25°C	445	2.52	2.1×10^{14}	<0.001
1-2577	1-part in solvent	725	1.04	20	72 @ 25°C or 10 @ RT + 10 @ 80°C	400	2.74	5×10^{13}	<0.001
1-2577 Low VOC	1-part in solvent	1250	0.88	20	72 @ 25°C	-	2.33	1.9×10^{14}	<0.001

(cont'd)

Table 2.15. (cont'd.)

Designation	Type	Viscosity, Centipoise	Specific Gravity, g/cc	Tack-free Time @ RT minutes	Cure Time, hr	Dielectric Strength, V/mil	Dielectric Constant, • @ 100 kHz	Volume Resistivity, Ω -cm	Dissipation Factor @ 100 kHz
1-2620	1-part RTV in solvent	135	1.00	20	72 @ 25°C	450	2.54	7.4×10^{13}	<0.001
1-2620 Low VOC	1-part RTV in solvent	250	0.88	20	72 @ 25°C	-	-	-	-
Q1-4010	1-part heat cure solventless	830	1.00	Not applicable	15 min @ 110°C	530	2.66	5.8×10^{14}	<0.001
1-4105	1-part heat cure solventless	470	0.97	Not applicable	10 min @ 105°C	500	2.63	2.7×10^{13}	<0.001
3-1944	1-part moisture cure solventless	60,000	1.03	13	10 min to 4 hrs @ RT	425	2.12	1.3×10^{15}	< 0.0002

Note: Values are typical and not intended for specification purposes. Contact Dow Corning for further information. (Courtesy Dow Corning Corp.)

Table 2.16. Typical Silicone Coatings: Properties and Uses

Coating	Properties and Uses
Dow Corning 1900 Series	100% solids, one-part conformal coatings, low VOC emissions, moisture/condensation cure at RT
Dow Corning Q3-6636 and Dow Corning Q3-6575	Dielectric gels to seal and protect microelectronic devices, temp. range from -80° to 200°C
Dow Corning 997	Coating and impregnating varnish for motors and transformers, reliable to 220°C
Dow Corning 1-2577	One-part, moisture-cure, conformal coating for rigid and flexible circuit boards, porous substrates and thick-film circuitry, resistant to uv, meets MIL-I-46058C
Dow Corning 94-003	A fluorosilicone dispersion coating to control corrosion
Dow Corning 96-082	Impregnant for high-voltage coils, transformers, and general purpose applications where long pot life is critical
Dow Corning HIPEC* 648	A 50% solids resin in xylene used in high temperature, high voltage applications, semiconductor passivation, and as an α particle barrier
Dow Corning HIPEC R-6101 and HIPEC R-6102	Solventless semiconductor junction coatings, protect IC and hybrid circuits, LED displays, and optoelectronics, α particle barrier
Dow Corning Sylgard* 170	Impregnant for high voltage transformers and coils, general purpose RTV encapsulant and potting compound for electronic and electrical circuits
Dow Corning Sylgard 184	Solventless resin with long pot life, general purpose RTV coating
Dow Corning Sylgard 527	Primerless gel to seal and protect delicate electronics and as a particle getter in hybrid microcircuits
Dow Corning Silastic* 734	A one-part, RT-curing, self-leveling coating for mechanical devices and electrical terminals
G.E. SR-17M	General purpose dipping and impregnating varnish used on transformers, coils, flexible tapes, and rotating equipment
*HIPEC, Sylgard, and Silastic are registered trademarks of Dow Corning.	

(cont'd.)

Table 2.16. (cont'd.)

Coating	Properties and Uses
G.E. SR-32	A 60% solids resin in toluene used in flexible electrical tapes and as an electrical insulating varnish. Thermally stable from -40° to 220°C with 5 to 10 minute surges up to 370°C
G.E. SR-80M	Air drying varnish used over 105° and 130°C insulation to protect from moisture, corrosive chemicals, and dust
G.E. SR-98	Varnish with good high temperature strength, hardness and abrasion resistance, used for bonding coils and insulating materials
G.E. SR-112	A 50% solids resin in xylene used for high heat and weather-resistant coatings and in formulations for resistor coatings
G.E. SR-125	A 50% solids resin in xylene used in resistor coatings and as a paint resin, has flexibility and excellent thermal shock resistance
G.E. ECC4865	A clear, one-part solventless, thermal curing PWB conformal coating, compatible with a broad range of clean fluxes and solder pastes
G.E. EJC301	Transparent, one-part, low viscosity silicone electronic junction coating
G.E. EJG3175	Black addition cure gel for electronic junction coating
G.E. RTV-11	A white two-part condensation cure elastomer for protecting switches, components, and coils from moisture, dust, and shock
Wacker SWS 960	A RTV dispersion coating, cures at RT without acidic by-products
Wacker RTV T-84	A one-part RTV, uv-fluorescent protective coating
Wacker T-12	A two-part coating, cures on exposure to air
Wacker T-162	A one-part water repellent coating
Wacker Semicosil Gel	Encapsulant and dip coating for semiconductor chips

(cont'd.)

Table 2.16. (cont'd.)

Coating	Properties and Uses
NuSil R-1400	One-part, Pt catalyzed vinyl methyl silicone for microchip coating and encapsulation
NuSil R-4701 and 4721	Polyvinylmethyl silicones, solventless, peroxide heat cured
NuSil R-1007	One-part, RT, moisture cure used as a thermal control coating
NuSil R-1010	One-part, high strength RTV dispersion coating, moisture cure, may be sprayed, dipped, or brushed
NuSil R-1075	One-part RTV dispersion in trichloroethane solvent, used as conformal coating for printed circuit boards
Loctite 5293	Ultraviolet cured conformal coating, no solvents, low VOC, used for automotive electronics, UL-746C approved
Loctite 5296	Heat-cured conformal coating for automotive electronics
Transene Silicoat*	One-part moisture-cure, clear conformal coating for PWBs, full cure 12 hrs @ RT, xylene thinner
Transene SSE*	Self-catalyzed semiconductor junction coating for ICs, diodes, transistors, and rectifiers, cure 4 hrs @ 200°C
Transene MBS*	One-part semiconductor junction coating, self-catalyzed, cure 15 min. @ 125°C plus 24 hr @ 150°C
Transene Translastic* S-2007	One-part semiconductor junction coating for rectifiers applied by transfer, dipping, or vacuum impregnation, cure 0.5 hr @ 90°C plus 4 hr @ 200°C
Transene Transplastic RTV 111	Two-part, catalyst cured, RT cure or elevated temp. to 200°C, coating of motor leads, cable junctions, modules, relays, power supplies, amplifiers, transformers, and connectors
*Transene Silicoat, SSE, MBS, and Translastic are registered tradenames of Transene Co., Inc. Note: These silicones represent only some of the formulations available from the suppliers.	

Room Temperature Vulcanizing (RTV) Silicones. Early silicone formulations required cures of over 24 hours at 120°C or higher. The introduction of the RTV silicones was a major step in reducing these extensive curing schedules and expanding the use of silicones in electronics. The RTV designation was first used by General Electric in reference to two-part silicones that, after mixing in a catalyst, could be cured at room temperature or at slightly elevated temperatures, obviating the need to expose sensitive electronic assemblies to high curing temperatures. The term RTV is now used more generically to encompass any silicone, either one- or two-part, that can be cured at room temperature. Hence, the moisture-cured, one-part silicones are also referred to as RTVs. Although the cure time is given as 24 hours at room temperature, a seven-day cure is recommended to achieve optimum properties. Cure time can be shortened by curing at temperatures up to 93°C.

Room temperature vulcanizing silicones are available in a wide range of viscosities and are generally 100%-solid types of various viscosities. They are most useful as potting compounds for connectors, transformers, and as thick coatings for electronic circuits. Some high-viscosity RTV silicones may, if thinned with compatible solvents, be used as coatings. In the two-part formulations, the curing agent (catalyst) is a metal salt of a long-chain fatty acid and is used in concentrations of 0.1 to 1% by weight. Higher catalyst concentrations provide faster cures, but also reduce the pot life of the mixture. Examples of commonly used catalysts include: dibutyltin dilaurate (DBT), lead 2-ethylhexoate, and stannous 2-ethylhexoate.

Besides their ease of application and curing, RTV silicones have an advantage over other polymers in their ease of removal for the rework and repair of faulty electronics. Since they are rubbery and soft, they may be cut away, softened with halogenated solvents and mechanically removed, or dissolved with some solvents.

As with other silicones, the electrical properties of RTV silicones are extremely good at room temperature and also at very low and very high temperatures. The effects of thousands of hours of aging at 200°C are shown in Fig. 2.44. The physical and electrical properties for RTV silicones from three manufacturers are given in Tables 2.17, 2.18, and 2.19.

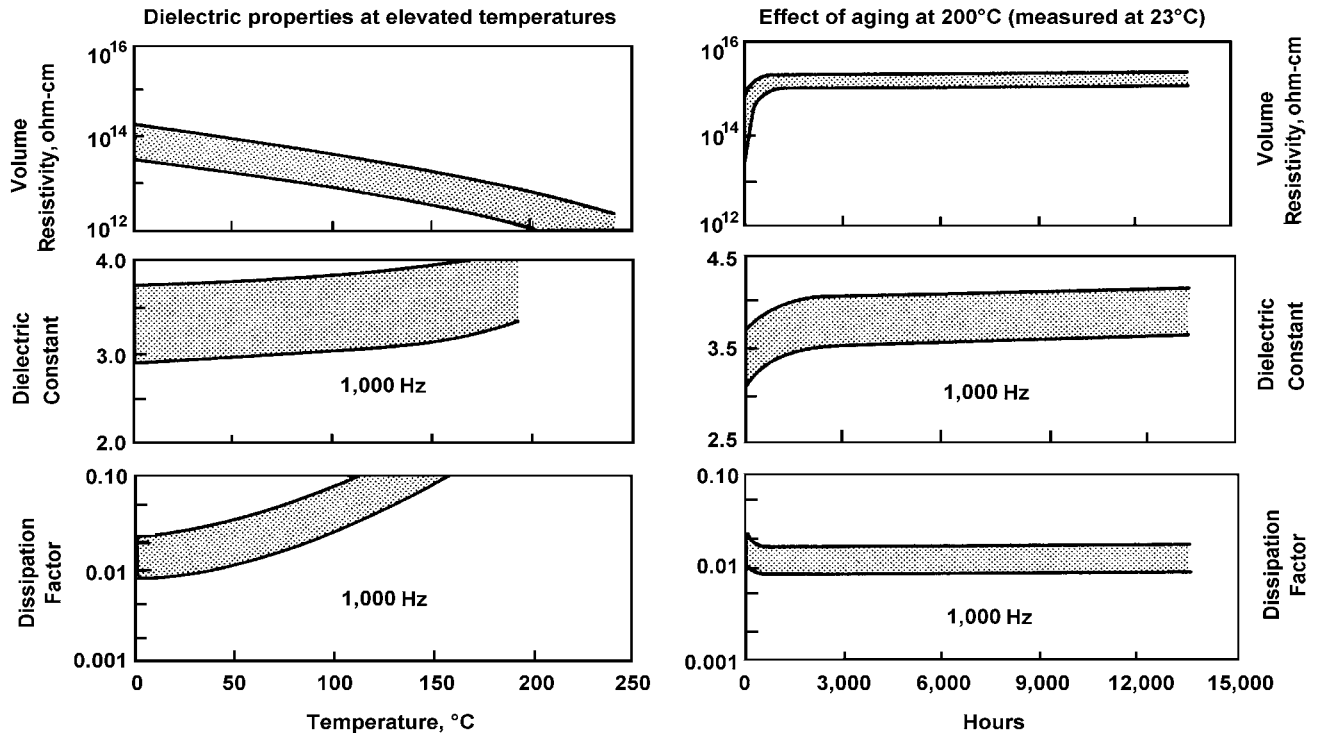


Figure 2.44. Effects of thermal aging on the electrical properties of RTV silicones. (Courtesy Dow Corning Corp.)

Table 2.17. Typical Properties of Some Dow Corning RTV Silicones

Property	Sylgard* 170	Sylgard 184	Sylgard 186	3110	3140
Viscosity at 25°C, cps	2,900	3,900	65,000	13,000	30,000
Specific Gravity at 25°C	1.37	1.03	1.12	1.14	1.03
Pot Life at 25°C, hr	15 min	>2	2	na	na
Cure Schedule, hr/°C	24 /25 20 min/70 15 min/85 10 min/100	48/25 45 min/100 20 min/125 10 min/150	48/25 30 min/100 15 min/150	room temp.	72/25
Useful Temperature Range, °C	-45 to 200	-45 to 200	-45 to 200	-55 to 200	-45 to 200
Hardness, Shore A Durometer	40	50	24	45	32
Thermal Conductivity (25° to 100°C), cal/cm · sec °C × 10 ⁻⁴	9.6	4.3	4.3	5.7	4.3
CTE, ppm/°C	270	310	330	na	315
Dielectric Constant at 100 Hz at 100 kHz	3.17 3.16	2.65 2.65	2.93 2.87	2.29 2.20	2.52 2.52
Dissipation Factor at 100 Hz at 100 kHz	0.003 <0.001	0.0005 <0.001	0.0012 <0.001	0.010 0.0010	0.004 0.001
Dielectric Strength, V/mil	480	540	450	434	445
Volume Resistivity, ohm-cm × 10 ¹⁴	0.31	1.2	1.1	0.73	2.1

* Sylgard is a registered tradename of Dow Corning Corp. Note: Values are typical and not intended for specification purposes. Contact Dow Corning for further information. (Courtesy Dow Corning Corp.)

Table 2.18. Typical Properties of Some General Electric RTV Silicones

Property	RTV 11 ^a	RTV 21 ^a	RTV 8111	RTV-31 ^a	RTV-615 ^b
Viscosity at 25°C, cps	11,000	26,000	9,900	25,000	4,300
Specific Gravity at 25°C	1.19	1.32	1.18	1.42	1.02
Work Time at 25°C, hr	1.5	1	0.5 to 0.75	2	4
Cure Schedule, hr/°C	24/25	24/25	24/25	24/25	24/25
Hardness, Shore A Durometer	41	45	40	54	44
Tensile Strength, psi	510	310	350	870	920
Elongation, %	190	210	160	170	120
Tear Strength, lb/in	20	40	24	29	-
Shrinkage, %	0.6	0.6	1.0	0.6	0.2
Dielectric Strength (1.9 mm thick), V/mil	515	420	500	430	500

(cont'd.)

Table 2.18. (cont'd.)

Property	RTV 11 ^a	RTV 21 ^a	RTV 8111	RTV-31 ^a	RTV-615 ^b
Dielectric Constant at 1 kHz	3.3	3.8	3.5 ^c	4.4	2.7
Dissipation Factor at 1 kHz	0.006	0.02	0.0055 ^c	0.03	0.0006
Volume Resistivity, ohm-cm	1.1×10^{15}	2.6×10^{14}	1×10^{15}	1.6×10^{14}	1.8×10^{15}
Useful Temp. Range, °C	-54 to 204	-54 to 204	-54 to 204	-54 to 260	-60 to 204
Thermal Conductivity (25 to 100°C), cal/sec · cm °C × 10 ⁻⁴	7	7.4	7.0	7.4	4.5
Coefficient of Thermal Expansion, ppm/°C	250	200	250	200	270
Specific Heat, cal/gm, °C	0.35	0.35	0.35	0.35	0.3
Note: Values are typical and not intended for specification purposes. Contact General Electric for further information. ^aProperties are for resins cured with 0.5 wt % Dibutyltin dilaurate (DBT) curing agent, cured 7 days at 25°C and 50% RH. ^bCured 1 hr at 100°C. ^cAt 103 Hz. (Courtesy General Electric Corp.)					

Table 2.19. Typical Properties of Some NuSil* RTV Silicones

Property	R-1009	R-1010	R-1075	R-2010	R-2550
Viscosity at 25°C, cps	6,500	6,500	7,500	40,000	9,000
Specific Gravity at 25°C	1.1	1.1	1.06	1.12	1.07
Work Time at 25°C, min	10	10	10	10	2 hr
Tack-free Time, hr	1	0.5	0.5	4	24
Cure Schedule, days/°C	7/25 ^a	7/25	7/25	7/25	7/25
Hardness, Shore A Durometer	40	40	40	45	35
Tensile Strength, psi	1100	800	450	400	400
Elongation, %	750	750	350	200	200
Tear Strength, lb/in	130	130	50	20	20
Shrinkage, %	-	-	-	-	0.5
Dielectric Strength, V/mil	500	500	-	500	500
Volume Resistivity, ohm-cm	1×10^{15}	1×10^{15}	-	1×10^{15}	1×10^{15}
Useful Temp. Range, °C	-65 to 240	-65 to 260	-	-65 to 240	-115 to 260
Coefficient of Thermal Expansion, ppm/°C	276	276	276	276	276
*NuSil is a registered tradename of NuSil Silicones. Note: Values are typical and not intended for specification purposes. Contact NuSil Silicones for further information. (<i>Courtesy NuSil Silicones.</i>) ^a Full cure					

2.9 POLYIMIDES

Polyimides, noted for their high thermal stabilities and chemical and radiation resistance, were first developed by DuPont and introduced on the market in 1961. Subsequently other manufacturers entered the market, notably Ciba Geigy and Hitachi. In 1997, Hitachi and DuPont created a joint venture called HD MicroSystems to produce polyimides for the microelectronics industry. Meanwhile, Ciba Geigy's polyimide technology, developed in the 1970s, was augmented in the 1980s by their licensing the photosensitive polyimide technology from Siemens. Then, in 1990, Ciba Geigy and Olin formed a joint venture which later transitioned to Olin Microelectronics and

has now passed on to Arch Chemicals who markets polyimide coatings under the Durimide tradename.

Besides the changes in the companies that developed them, the applications for polyimides have also undergone considerable changes. Whereas early applications were for varnishes, wire coatings, and impregnants for magnetic parts, now polyimide coatings are also used as stress buffers and passivation in the processing of ICs and as interlayer dielectrics to fabricate very high density multilayer substrates. In addition, polyimides are used in processes to redistribute bond pads on integrated circuit chips and wafers, rendering them amenable to flip-chip bonding. They are also used as plating resists in the fabrication of micromachined parts (See Ch. 4 on “Applications”).

Like other polymer classes, there are hundreds of polyimide formulations on the market, but only a few meet all the requirements for use on ICs and microelectronic assemblies. Of the many engineering properties desired of a dielectric, three are critical and should be measured for initial screening and selection. These are dielectric constant, moisture absorption, and coefficient of thermal expansion (CTE); all of which should be low. Of course, there are many other engineering properties and numerous manufacturing properties that must be considered to achieve high yields, low cost, and reliability.

2.9.1 Chemistry

Three basic types of polyimides, differing in their molecular structures, curing mechanisms, and properties, are commercially available. These are classified as:

- Condensation cured
- Addition cured
- Photocured

Condensation-cured Polyimides. Condensation-cured polyimides start as polyamic-acid or polyamic ester precursors dissolved in an organic solvent. Upon evaporating the solvent, generally N-methyl-2-pyrrolidone, and heating in steps up to 400°C, water or alcohol molecules are released from the vicinal amide-acid or amide ester groups, respectively, resulting in ring closures along the chain and formation of the thermally stable cyclic imide rings (Fig. 2.45). This process, referred to as *imidization*, results in the formation of heterocyclic rings that render the polymer

extremely temperature stable and resistant to solvents. The synthesis of the original polyamic-acid resin from pyromellitic dianhydride (PMDA) and oxydianiline (ODA) is also shown in this figure. Pyralin[®] PI-2611, a widely

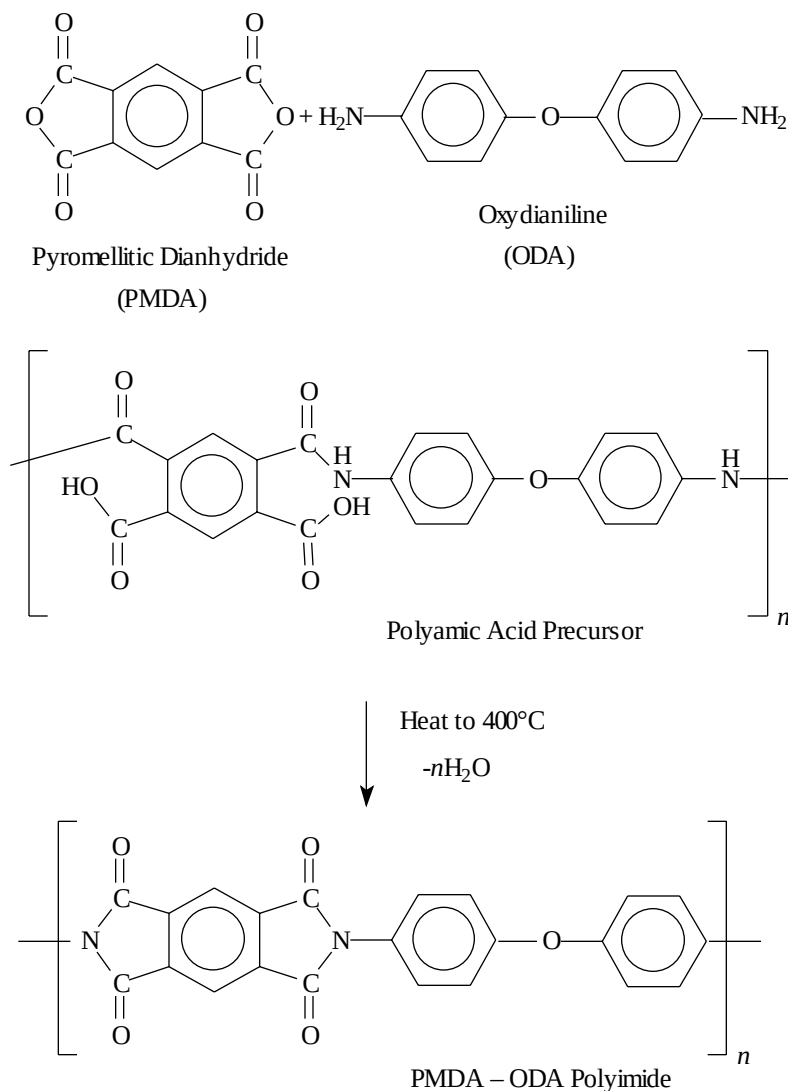


Figure 2.45. Synthesis of polyamic acid resin and condensation curing to form the polyimide.

*Pyralin[®] is a registered tradename of HD MicroSystems.

used polyimide in fabricating semiconductors, is based on the precursor formed from biphenyldianhydride and phenylenediamine.

The polyamic-ester precursors are reported to offer improved solubility and better viscosity control than the amide-acid precursors. Also, the alcohol that is released on curing is more easily volatilized and less corrosive to thin-film metals than the water released from the polyamic-acids.^[56] The properties of condensation-cured polyimides may be varied depending on the molecular structures of the two starting materials; for example, a Bisphenol A structure (See Sec. 2.6 “Epoxy”) can be integrated in the molecule to provide better flexibility and solubility (Fig. 2.46). Other variations of the dianhydride portion include: trimellitic anhydride, benzophenone dianhydride, and biphenyl dianhydride. Variations of the aromatic diamines include: m-phenylene diamine; 4,4'-oxydianiline; 4,4'-methylenedianiline; and 1,4-phenylenediamine.

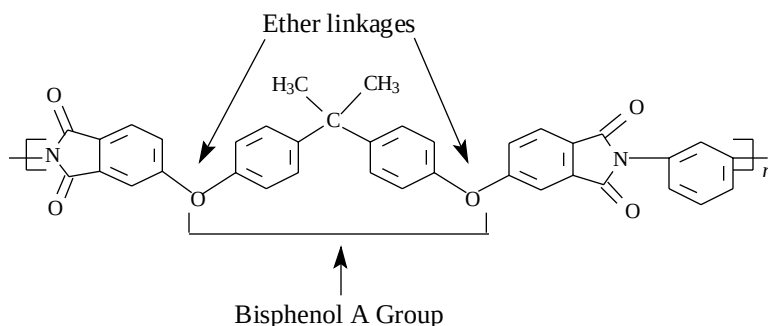


Figure 2.46. Bisphenol A-modified polyimide.

Condensation-cured polyimides may be purchased as pre-imidized polymers in a solvent solution or as the precursor polymer in a solvent solution, the latter being subsequently imidized after the coating has been applied to a part.

Other variations include pre-imidized polyimide-amide polymers (Fig. 2.47). Although theoretically high temperature curing is not required with pre-imidized coatings since cyclization is already complete, curing at 275° to 300°C is still recommended to completely remove the very polar solvent and attain optimum properties (Table 2.20).

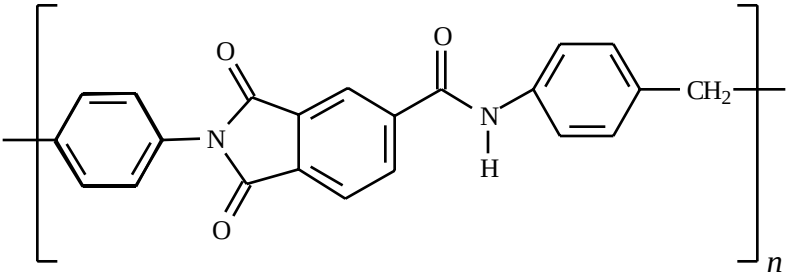


Figure 2.47. Structure for polyimide-amide polymer.

Table 2.20. Properties of a Polyimide-amide Coating: Durimide® 32 Series

Properties/Units	Measured
Physical	
Tensile Modulus (hardbake 2 hrs/350°C), GPa	3.3
Tensile Strength, MPa	184
Elongation, %	56
Refractive Index (633 nm)	1.72
Density, g/cm ³	1.33
Stress, MPa	26
Thermal	
Glass Transition Temperature, °C	300
Decomposition Temperature, °C	494
Coefficient of Thermal Expansion, ppm/°C	53
Electrical	
Dielectric Constant (24°C, 4%/50% RH)	3.5/3.8
Dissipation Factor (1 MHz, 4%/50% RH)	0.013/0.024
Dielectric Breakdown, V/μm	324
Adhesion	
90° Tape Peel Test, 72 hrs in boiling water (ASTM D-3359-83B)	5
*Durimide is a registered trademark of Arch Chemicals, Inc. (Courtesy Arch Chemicals, Inc.)	

Addition-cured Polyimides. A second class of polyimides cures by an addition polymerization mechanism. This class is based on low-molecular-weight polyimide precursors (oligomers) in which the imidization (ring closure) reaction has already been completed. The oligomers are terminated at each end with reactive acetylenic, ethylenic, or strained cyclic groups. On heating, these groups open up and join “head-to-tail” forming long-chain, high-molecular-weight polymers. A benefit of addition curing is that water or other potentially undesirable by-products are not eliminated during the cure. Acetylene-terminated polyimides were first synthesized by investigators at Hughes Aircraft^{[57][58]} and later licensed and marketed by National Starch and Chemical Company under the tradename Thermid. Although the Thermid polyimides had many benefits as interlayer dielectrics for multilayer circuits they were not widely implemented and are no longer commercially available.

Photocurable Polyimides. The first photosensitive polyimides were developed by Siemens^[59] in the mid-1970s, but only recently have they been modified and optimized to meet requirements for interlayer dielectrics and other microelectronic applications.^{[60]–[62]} Photocurable polyimides lend themselves to the batch fabrication of microvias of high aspect ratios (>1) for interconnect substrates (*cf.* Ch. 4 on “Applications”). Polyimide precursors may be synthesized and formulated to render them photosensitive and hardened by exposure to ultraviolet light, similar to photoresists. Thus, by coating an entire surface, drying to remove the solvent, and exposing to uv light through a mask, selective areas of the polyimide coating are cross linked, hardened, and rendered insoluble. The unexposed areas can then be removed by dissolving in an appropriate solvent. Subsequently, the coating is imidized at approximately 300°C with the simultaneous decomposition and volatilization of the cross-linking ester groups.

Most photodefinable polyimides are negative-acting, that is, they cross link and harden on exposure to ultraviolet light. In these compositions, the basic polyimide molecule has been altered to incorporate photoreactive unsaturated ester groups such as acrylates and photoinitiators. Figure 2.48 shows the structure for a typical photosensitive polyimide precursor while Fig. 2.49 depicts the cross-linking, imidization, and removal of the ester cross-linking groups. In the early formulations, the decomposition and removal of these ester appendages caused excessive shrinkage of the coating, as high as 60% in some cases, resulting in stresses and marginal via geometries.^[63] However, improved formulations and alternate photocuring mechanisms such as the use of ionic salt formations have been developed that reduce shrinkage. Both negative-acting and positive-acting

photoimageable polyimides are available, but positive-acting types have an advantage in being developed with aqueous solutions instead of organic solvents.

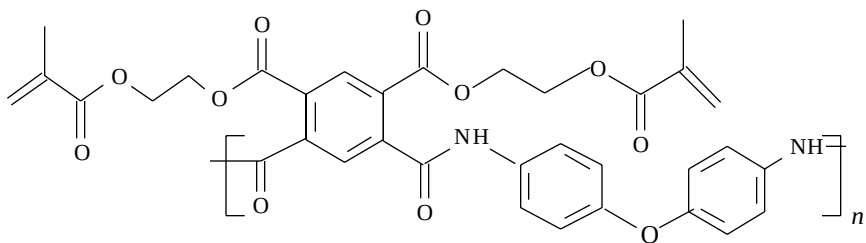


Figure 2.48. Typical structure for a photosensitive polyimide precursor.

2.9.2 Properties

Polyimides possess a highly aromatic ring structure and, as such, have exceptional thermal stability (as high as 500°C and even 600°C for short periods of time) and excellent radiation stability. Among their outstanding properties are:

- Wide temperature stability, ranging from -190° to 600°C
- Low weight loss in a thermal-vacuum environment
- Relatively low moisture absorption for some formulations and cure schedules
- Good dielectric properties
- High radiation resistance, up to 10⁸ rad total dose
- High wear resistance
- High chemical and solvent resistance
- Flame resistance (Polyimides will not support combustion in air and ignite only at temperatures above 400°C.)

The properties of polyimide films prepared from polyamic esters or polyamic acid precursors do not differ greatly (Table 2.21).

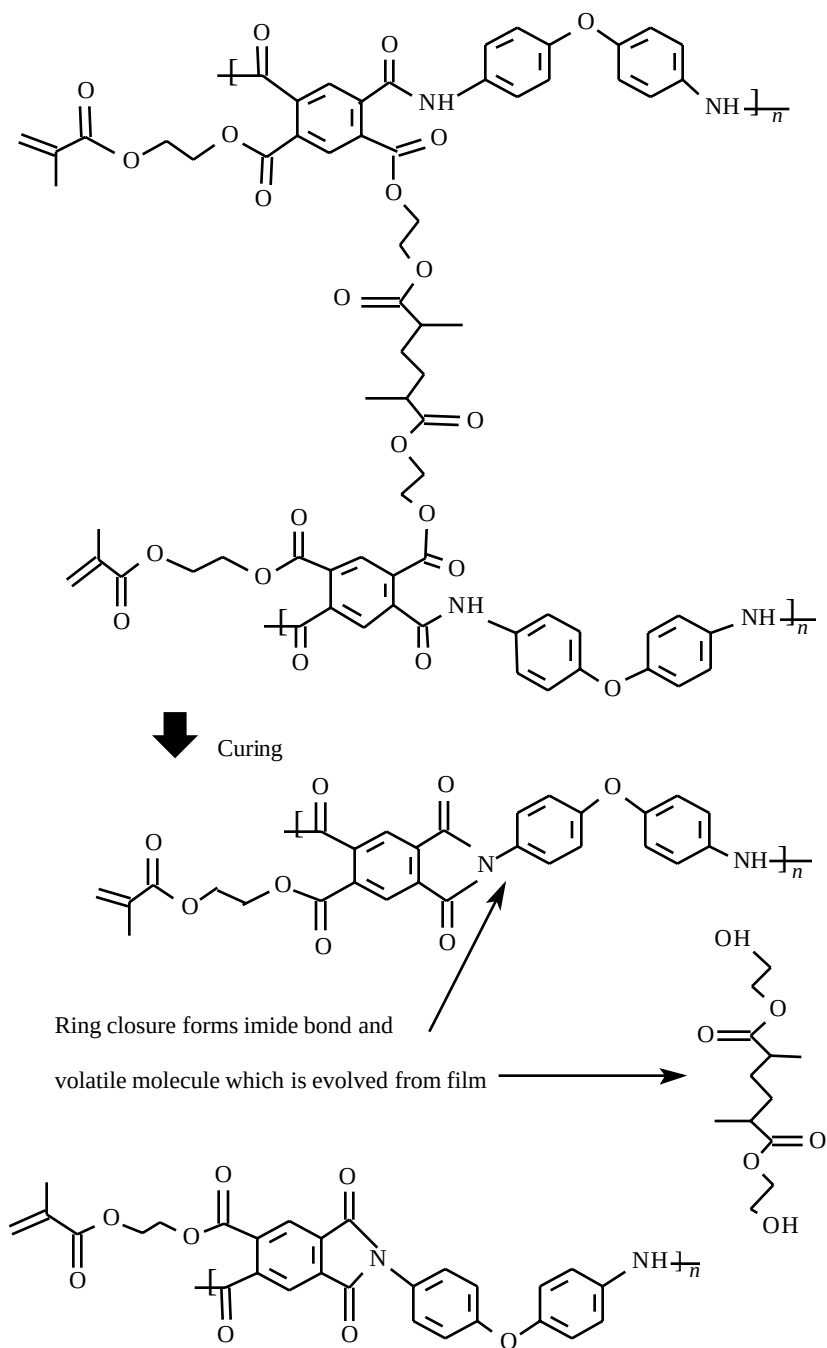


Figure 2.49. Steps in photocuring and imidizing polyimide.

Table 2.21. Properties of Polyimide Films Prepared from Polyamic Ester and Polyamic Acid Precursors^[64]

Material Property	Polyamic Ester Precursor	Polyamic Acid Precursor
Young's Modulus, GPa	3.1	3.3
Ultimate Strength, MPa	230	265
Elongation, %	115	80
CTE, ppm/°C	29	32
Coating Stress, MPa	21	20
Glass Transition Temp., °C	380	380
Dielectric Constant, 50% RH	3.3	3.4

Electrical and Physical Properties. Polyimides have been developed that meet the demanding requirements of interlayer dielectrics for multichip module interconnect substrates and for microwave hybrid circuits. Besides their low dielectric constants, ranging from 2.9 to 3.5, some fully-cured, low-stress polyimides have low CTEs, almost matching those of widely used substrate materials such as silicon, silicon nitride, and alumina^[65] (Table 2.22). These low CTE values mitigate stresses in a multilayer structure.

A high degree of imidization is important in obtaining optimum properties. The percent completion of the imidization reaction is a function of the curing temperature. The T_g , for example, increases linearly with an increase in imidization temperature, reaching approximately 400°C when cured at 400°–425°C (Fig. 2.50).^[66]

Although water absorptions for polyimides are generally high (1–3%), values for the low-stress formulations as low as 0.34% have been reported.^[65] The relatively high moisture absorption of polyimides results in increases in dielectric constant and capacitance that must be taken into consideration when they are used in an non-hermetic environment (Figs. 2.51 and 2.52).^{[67][68]} Table 2.23^[69] compares the electrical and physical properties of three widely used condensation cured polyimides while Table 2.24 presents properties of some photoimageable polyimides. Fully cured polyimides are highly resistant to solvents including ketones, cresols, alcohols, N-methyl-pyrrolidone, n-butyl acetate, and aliphatic hydrocarbons, but can be attacked by strong alkalis and acids.

Table 2.22. Comparison of Properties of Low-stress Polyimide with Other Polyimides^[65]

Property	Low-stress Polyimide	Other Polyimides
Dielectric Constant, 1 kHz, 25°C	2.9	3.1–3.6
Dissipation Factor, 1 kHz, 25°C	0.002	0.002
Dielectric Breakdown, V/mil	>5,000	>5,000
Volume Resistivity, ohm-cm	>10 ¹⁶	>10 ¹⁶
Coefficient of Thermal Expansion, ppm/°C	3.0	28–50
Water Absorption, % in 24 hr	0.34	0.73–4.2
Wafer Bow, 100 mm Si, 22 mils thick with 50 μm polyimide, mils/in	1.29	3.1–4.2
Decomposition Temperature	500°–600°C	500°–600°C
Glass Transition Temperature	>400°C	>400°C
Tensile Strength, kg/mm ²	35	10.5–13.5
Elongation, %	25	15–40
Weight Loss, 500°C 2 hr in air, %	1	2.9–3.6
Weight Loss, 400°C 7 hr in air, %	0.4	
Thermal Conductivity, cal/sec · cm °C	3.6 × 10 ⁻⁴	3.5–3.7 × 10 ⁻⁴
Thermal Conductivity, W/m·K	0.17	0.17
Radiation Resistance, total flux, rads	10 ⁸	10 ⁸

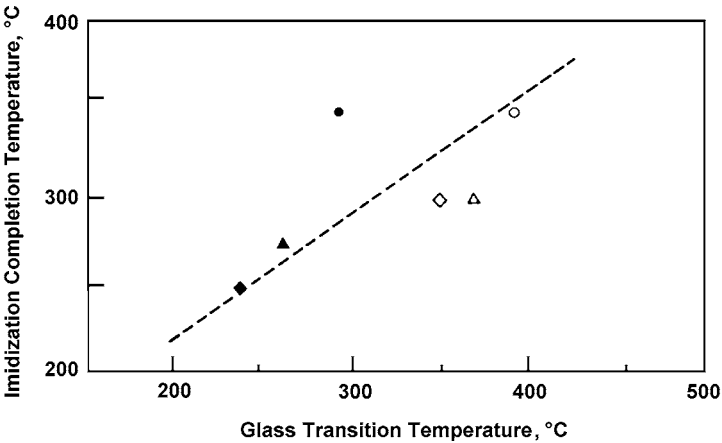


Figure 2.50. Glass transition temperature of polyimide as a function of cure temperature.^[66]

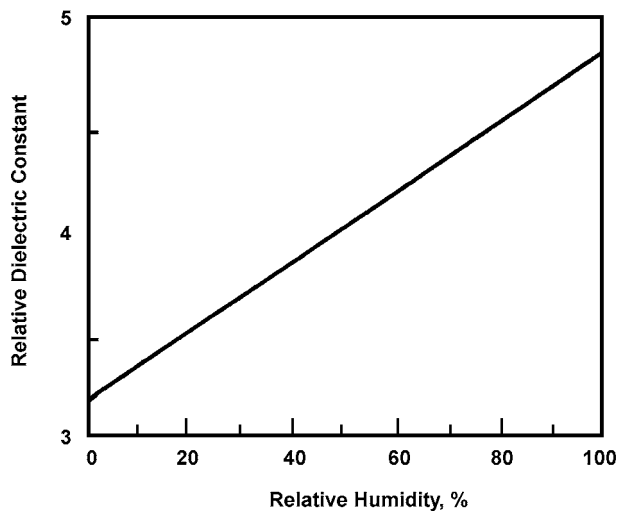


Figure 2.51. Effect of relative humidity on the dielectric constant of polyimide.^{[67][68]}

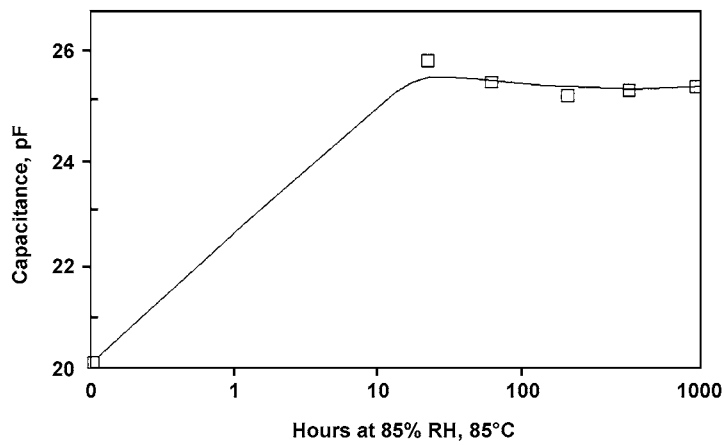


Figure 2.52. Degradation of the dielectric properties of polyimide on humidity/temperature exposure.^[70]

Table 2.23. Comparison of Pyralin LX with Other Pyralin Polyimides

Property	Units	PI2611	PI2540	PI2525
Tensile Strength	kg/mm ²	35	10.5	13.5
Elongation	%	25	40	15
Density	g/cm	1.40	1.42	1.39
Modulus	kg/mm ²	845	140	245
Moisture Uptake	%	0.5	2–3	2–3
Stress (10 μ m film)	MPa	2	16	37
Glass Transition Temperature	°C	>400	>400	>320
Melting Point	°C	none	none	none
Decomposition Temperature	°C	620	580	550
Weight Loss (500°C in air, 2 hrs)	%	1.0	3.6	2.9
Coefficient of Thermal Expansion	ppm/°C	3	20	40
Coefficient of Thermal Conductivity	cal/sec · cm °C	25×10^{-5}	37×10^{-5}	35×10^{-5}
Specific Heat	cal/g/°C	–	0.26	0.26
Dielectric Constant (@ 1 kHz, 50% RH)		2.9	3.5	3.3
Dissipation Factor (@ 1 kHz)		0.002	0.002	0.002
Dielectric Breakdown Field	V/cm	$>2 \times 10^6$	$>2 \times 10^6$	$>2 \times 10^6$
Volume Resistivity	Ω -cm	$>10^{16}$	$>10^{16}$	$>10^{16}$
Surface Resistivity	Ω	$>10^{15}$	$>10^{15}$	$>10^{15}$
Note: Stress was measured using a Tropel [®] Autosort Interferometer. (Courtesy HD MicroSystems.)				

Adhesion. Polyimides generally require a promoter or primer for optimum adhesion to surfaces such as silicon, silicon dioxide, silicon nitride, and metals. Adhesion promoters consisting of aqueous dilute solutions of amino organosilanes are spin coated onto the wafers, and dried or baked at 110°–130°C. The polyimide precursor solution is then spin coated and cured. Some polyimides are self-priming, that is, they have built-in adhesion promoters.

Table 2.24. Cured Film Properties of Photoimageable Polyimides, Durimide® Series

Property	7000 Series	7500 Series	7800 Series
Tensile Strength, MPa	170	215	215
Young’s Modulus, GPa	2.9	2.5	2.5
Tensile Elongation, %	73	85	85
Glass Transition Temp (T_g), °C	>350	285	285
Decomposition Temp, °C	>510	525	525
CTE, ppm/ °C	27	55	55
Coating Stress (100 Si), MPa	30	33	33
Dielectric Constant, 1 MHz, 0–50% RH	3.3	3.2–3.3	3.2–3.3
Dissipation Factor, MHz, 0–50% RH	0.007	0.003–0.008	0.003–0.008
Dielectric Strength, V/μm	340	345	345
Moisture Absorption @ 50% RH, %	1.3	1.08	1.08
Density, g/cc	1.39	1.39	1.39
Refractive Index	na	1.69	1.69
Note: Values are typical, not to be used for specification purposes without contacting the manufacturer. Durimide® is a registered trademark of Arch Chemicals, Inc. (Courtesy Arch Chemicals, Inc.)			

2.10 P-POLYXYLYLENES (PARYLENES)

Parylene (p-polyxylylene) coatings represent a unique class in their ability to be polymerized and deposited by vapor deposition onto surfaces maintained at room temperature. Extremely thin, pinhole-free, high purity coatings are deposited that fulfill many of the requirements of advanced microelectronics. As such, they continue to find new applications in space, medical, and other high-reliability electronics.

2.10.1 Chemistry

Poly-p-xylylene films were first synthesized by the pyrolytic dehydrogenation of gaseous p-xylene. In this rather drastic process, p-xylene was subjected to very high cracking temperatures of 700°–1100°C at a reduced pressure of 1–5 torr, whereupon it lost a molecule of hydrogen and converted to an unstable quinoid compound. On quenching, this quinoid structure polymerized rapidly to yield the desired poly-p-xylylene film.^{[71]–[73]} This process found little practical use because of the high temperatures that were required. Furthermore, the resulting films were infusible and intractable (Fig. 2.53). In 1965, a simplified process for preparing a series of poly-p-xylylenes that were completely linear polymers was developed by Gorham at Union Carbide.^{[74]–[75]} Parylenes, Union Carbide's tradename for their high-purity p-polyxylylenes, were introduced for commercial applications in 1966.

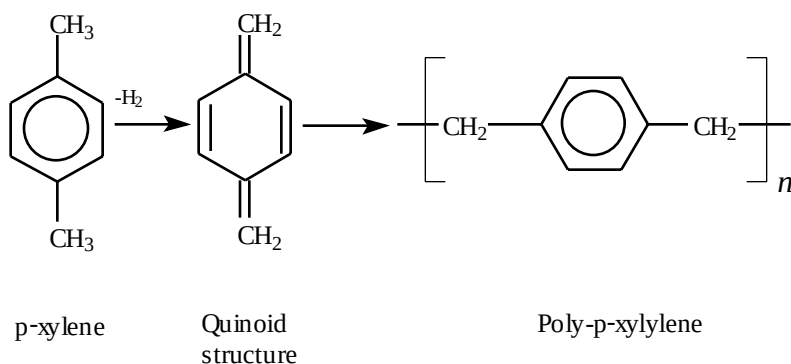


Figure 2.53. Early synthesis of poly-p-xylylene.

Parylenes have the distinction of being the only polymer coatings that can be vapor deposited on a commercial scale by the thermal decomposition of a solid dimer. The first step in the process consists of heating the solid dimer (di-p-xylene) at approximately 150°C and 1 torr whereupon it sublimates. The gaseous dimer then passes through a heated tube at 650°–680°C and a vacuum of 0.1–0.5 torr whereupon it dissociates into gaseous diradicals (Fig. 2.54). These diradicals immediately polymerize

on any surface they contact by combining “head-to-tail,” forming long-chain, high-molecular-weight linear polymers. Items to be coated are generally maintained at room temperature in a separate chamber so that the

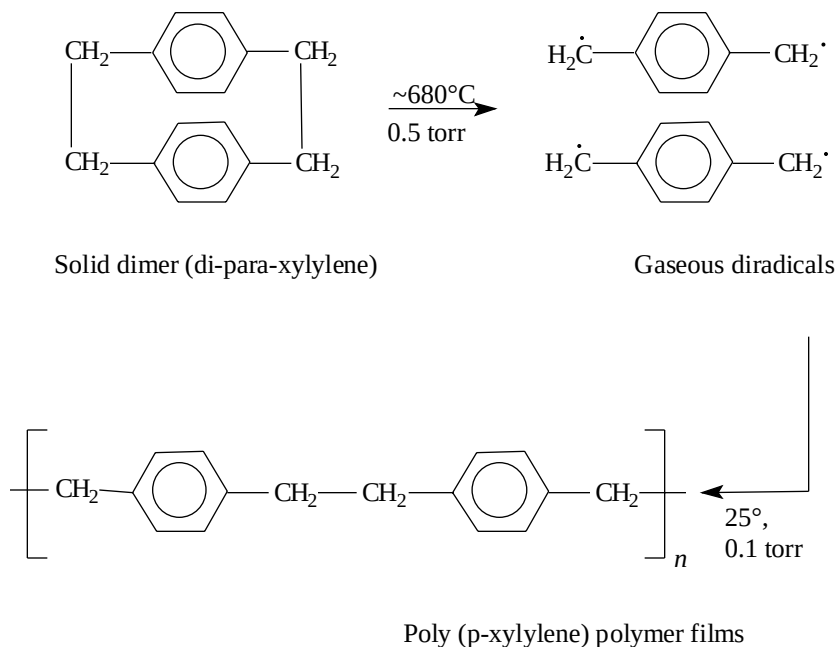


Figure 2.54. Commercial polymerization mechanism for Parylene N.

process becomes especially suitable for coating temperature-sensitive devices.

Three parylene types, differing only in the number of chlorine atoms that each phenyl group contains, were initially introduced by Union Carbide. Parylene N contains no chlorine atoms, while Parylene C contains one chlorine atom per phenyl group and Parylene D contains two chlorine atoms per phenyl group. A fourth type, Parylene E, containing fluorine atoms in the phenyl group, was also introduced, but is no longer available. Recently, a fifth type, Parylene HT, tradenamed NOVA HT[®], was introduced by Specialty Coating Systems (a division of Cookson Electronics). It contains fluorine atoms in lieu of hydrogen atoms in the aliphatic portion of the molecule thus rendering it highly resistant to thermal oxidation. Parylenes N and C have the longest history of use. All patents for the original Union Carbide parylenes were issued in the mid-1960s^{[76]–[78]} and have since expired. There are now

several firms that provide services for coating parts with parylene. The solid dimer starting material is also commercially available, and, with the proper deposition equipment, any firm can apply its own coating.

The adhesion of parylene is enhanced if the part is first primed using either a liquid aqueous/alcohol primer (A-174) or a proprietary dry primer developed by Specialty Coatings Systems.

2.10.2 Properties of Parylene Coatings

The inherent properties of parylene films and their compatibility with bare field effect transistors (FET) were extensively studied by Lee and Licari.^[79] Bachman,^[80] at the AT&T Laboratories, studied stresses, dielectric constant, and thermal stability and found compressive stresses to be 50% lower for parylene than for polyimide. She also reported on the excellent electrical properties of parylenes even after extensive humidity exposure.

In summary, the parylenes have many benefits for advanced microelectronics packaging, among which are:

- Parylene is deposited at room temperature by vapor phase polymerization.
- Vapor phase deposition results in complete coverage even beneath and around closely spaced wires and chips.
- The coating envelops and reinforces fragile wire bonds.
- Parylene has excellent adhesion to most surfaces.
- Parylene is among the best coatings for moisture impermeability.
- Parylene polymerizes as it deposits from a gaseous diradical state to a solid state. It does not require a hardener or catalyst nor subsequent heat curing.
- Parylene is a pure hydrocarbon having a low dielectric constant, low dissipation factor, and high electrical insulation resistance. No by-products are released during polymerization, as with epoxies and silicones.

Table 2.25 summarizes the major benefits and limitations of using parylene coatings. The coefficients of friction for parylene coatings are low ranging from 0.25 to 0.33 so that their lubricity is close to that of Teflon which, together with its other properties, make parylenes good candidates for use in micro-electromechanical systems (MEMS).

Table 2.25. Benefits and Limitations of Parylene Coatings

Parameter	Benefits	Limitations
Stress	50–54% lower than PI, CTE = 35 ppm/°C, compressive stress	
Cure	Not applicable, vapor deposited, room temp.	
Outgassing	Low, no by-products, catalysts, hardeners, or fillers; passes NASA outgassing requirements	
Thermal Stability	80°C long term in air 115°C short term in air	Poor in air @ 125°C 8% wt loss in 8 hr @ 225°C, 13% wt loss in 16 hr @ 225°C
Chemical Resistance	Highly resistant to all organic solvents, alkalis, and acids	Cannot be removed with normal solvents and chemicals for rework
Coefficient of Friction	Low coefficient of friction (0.25 to 0.33); high lubricity	
MVTR* (g-mil/m ² 24hr) 37°C, 90% RH	7.75 (Teledyne, NASA) 15.5 (Union Carbide)	
Water Absorption, 24 hr	Very low: 0.01%	
Purity	Excellent: no possibility of Na ⁺ , K ⁺ , or Cl ⁻ , no by-products	
Dielectric Constant	2.95–3.1, not sensitive to humidity, unchanged at 100% RH	
Masking		Difficult for small areas
Demasking		Can leave residues
Rework		Difficult to remove, insoluble in all solvents, can be plasma etched in oxygen, removed by excimer laser, or abraded
*Moisture Vapor Transmission Rate for Parylene C		

Moisture Permeability and Water Absorption. The moisture vapor transmission rates (MVTR) of the parylenes are among the lowest of polymers. Furthermore, since the parylenes are of high purity, any moisture that permeates or becomes absorbed will not degrade its electrical properties or contribute to chemical corrosion. Provided that the coating adheres well to the surface, moisture will breathe in and out and not become trapped beneath the coating. However, if adhesion is not adequate, moisture condenses and becomes trapped in voids at the interface. Both the MVTR and water absorption for Parylene C are better than for Parylene N. The MVTR for Parylene C is about one-third that for the N version. Water absorption after 24-hours immersion in water was only 0.01% by weight for a 19-mil-thick film of Parylene C and 0.06% for a 29-mil-thick sample of

Parylene	Gas Permeability cc-mil/100 in ² 24 hr-atm (23°C)						Moisture Vapor Transmission Rate g-mil/100 in ² 24 hr (37°C, 90% RH)
	N ₂	O ₂	CO ₂	H ₂ S	SO ₂	Cl ₂	
N	7.7	39.2	214	795	1,890	74	1.6
C	1.0	7.2	7.7	13	11	0.35	0.5
D	4.5	32	13	1.45	4.75	0.55	0.25

(Courtesy of Specialty Coating Systems.)

Parylene N. Values for MVTRs and gas permeation rates for the three parylene types are given in Table 2.26.

Electrical Properties. The electrical properties of the parylenes are among those of the best polymers (Table 2.27). The dielectric breakdown voltage for a one-mil-thick film of Parylene C is 5,600 volts while that for Parylene N is 7,000 volts. Figure 2.55 gives breakdown voltage as a

Table 2.27. Electrical Properties of Parylene Coatings*

Property	Parylene N	Parylene C	Parylene D
Dielectric Strength short time, V/mil (1-mil thick)	7,000	5,600	5,500
Volume Resistivity 23°C, 50% RH, ohm-cm	1×10^{17}	6×10^{16}	2×10^{16}
Surface Resistivity 23°C, 50% RH, ohms	10^{13}	10^{14}	5×10^{16}
Dielectric Constant			
60 Hz	2.65	3.15	2.84
1 kHz	2.65	3.10	2.82
1 MHz	2.65	2.95	2.80
Dissipation Factor			
60 Hz	0.0002	0.02	0.004
1 kHz	0.0002	0.019	0.003
1 MHz	0.0006	0.013	0.002
*Measurements made using ASTM methods. (Courtesy Specialty Coating Systems.)			

function of film thickness. It is anticipated that moisture will have an effect on the breakdown voltage, but data are not available.

The insulation resistance of Parylene C in 10-day humidity/temperature cycling drops from almost 10^{14} ohms to 10^{10} ohms, but is still well above the MIL-I-46058 specification requirement of 1×10^9 . Some epoxies under the same conditions are reported to drop to 10^8 ohms or lower, largely due to ion impurities.^[81] The test was performed with a polarizing voltage of 100 volts dc (Fig. 2.56). In general, the electrical properties of Parylene N are better and more stable over a temperature range than for Parylene C

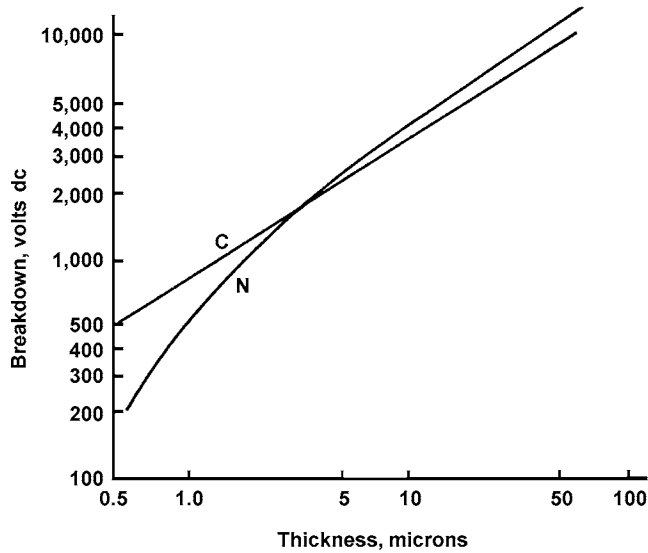


Figure 2.55. Breakdown voltage of Parylenes C and N vs film thickness.^[81]

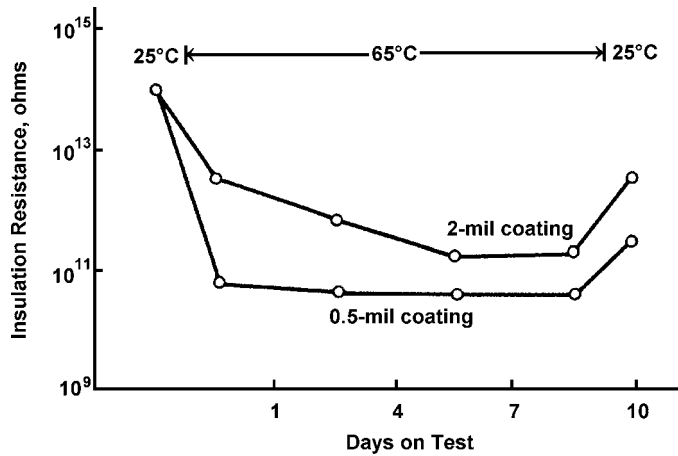


Figure 2.56. Insulation resistance of Y-Patterns on G-10 boards coated with Parylene C during 10-day humidity exposure per MIL-STD-202, Method 302B.^[81]

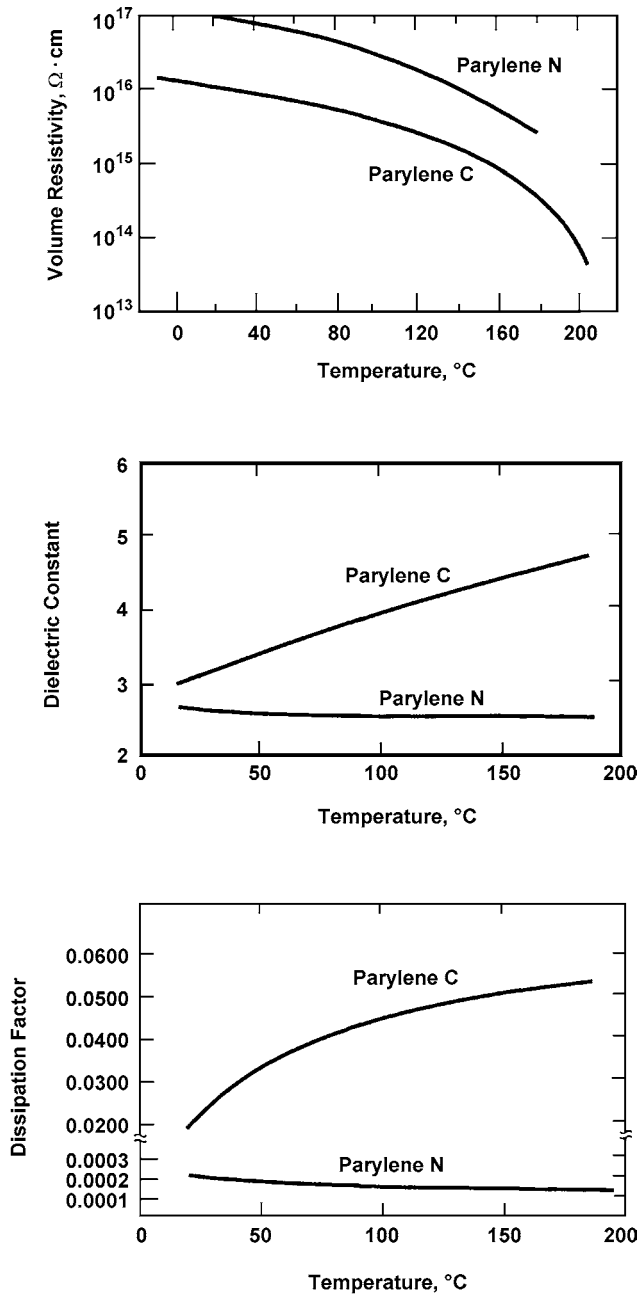


Figure 2.57. Electrical properties of Parylene C and N vs temperature at 1 kHz.

(Fig. 2.57). Nevertheless, Parylene C is more widely used commercially because its deposition rate is much greater.

Thermal and Mechanical Properties. Parylenes N, C, and D are noted for their long-term thermal stabilities in vacuum or in inert atmospheres up to 200°C, but their stabilities are limited in air to temperatures below 115°C. At temperatures of approximately 115°–125°C in air, the parylenes

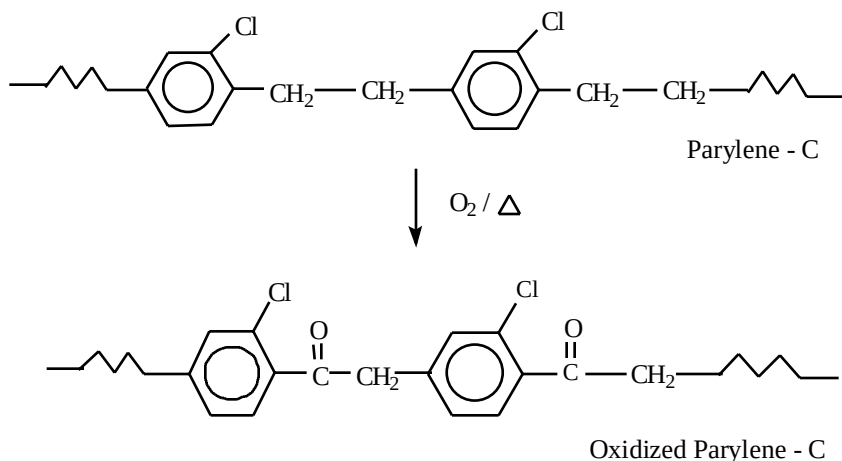


Figure 2.58. Initial oxidation stage for Parylene C.

begin to undergo oxidative degradation starting at their weakest linkages: the aliphatic ($-\text{CH}_2-\text{CH}_2-$) connections between the aromatic groups (Fig. 2.58).

Although not visible at first, the oxidation can be detected by infrared spectroscopy by the appearance of a carbonyl absorption band at 1695 cm^{-1} . With extended aging in air at elevated temperatures, this absorption band intensifies and the progress of the oxidation can be followed quantitatively. Figure 2.59 shows the FTIR spectra for Parylene C, as deposited and after aging for 24 hours at 170°C.^[82]

The different parylenes begin to oxidize at different temperatures and the failure time is a logarithmic curve based on temperature. For example, Parylene N at 60°C will fail in ten years, at 80°C in one year, and at 120°C in 24 hours. Parylenes C and D follow similar curves, but failures

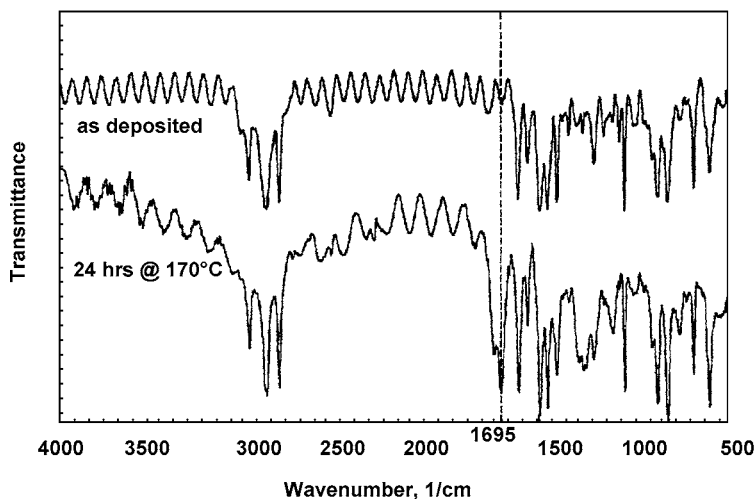


Figure 2.59. FTIR spectra of Parylene C, before and after thermal aging in air.^[82]

occur at higher temperatures^[83] (Fig. 2.60). Failures resulted in 50% loss in tensile strength.

On extended thermal exposure in air, parylene films ultimately discolor, become brittle, and decompose. However, when aged in an inert ambient or in a vacuum, all the parylenes exhibit very high thermal stabilities. Figure 2.61 shows that ten-year projections exceed 200°C for parylenes in a high vacuum environment. This, together with their other properties, makes parylene coatings especially suitable and reliable for deep-space applications.

The thermal oxidative instabilities of the parylenes were recently found to be minimized or completely eliminated by overcoating with thin inorganic coatings such as silicon dioxide, silicon nitride, or aluminum oxide.^[82] The newly introduced Parylene F (NOVA HT*) also obviates this

*Nova HT® is a registered tradename of Specialty Coating Systems.

oxidation mechanism because the hydrogen atoms in the aliphatic portion of the molecule have been substituted for fluorine atoms. Hence, the NOVA HT coatings are thermally stable both in air and inert atmospheres at very

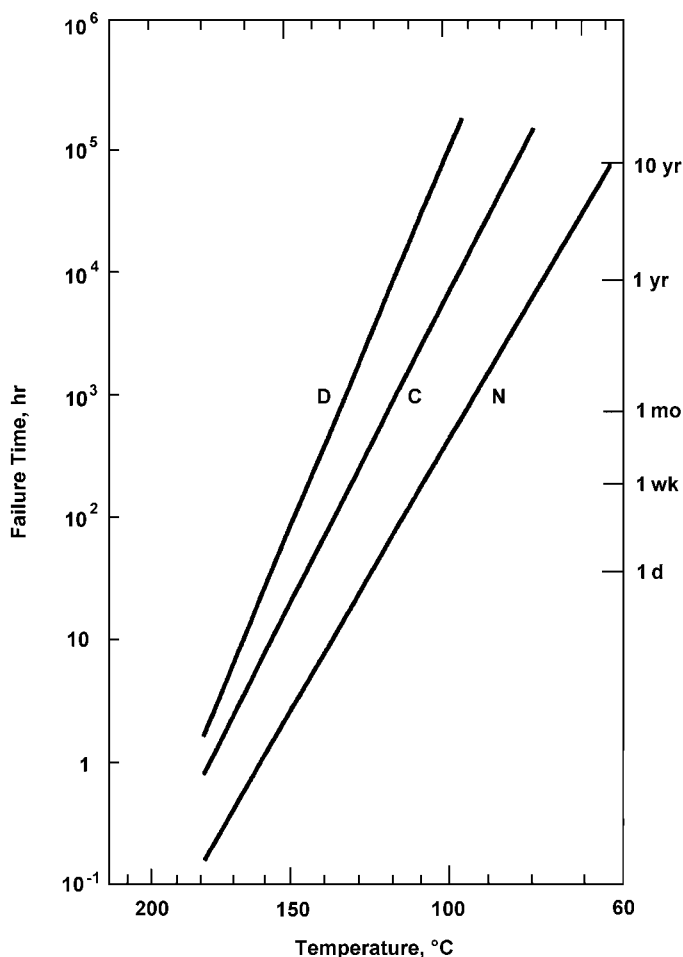


Figure 2.60. Useful life expectancies of parylenes as a function of temperature in air. (Failure equals a 50% loss in tensile strength.)

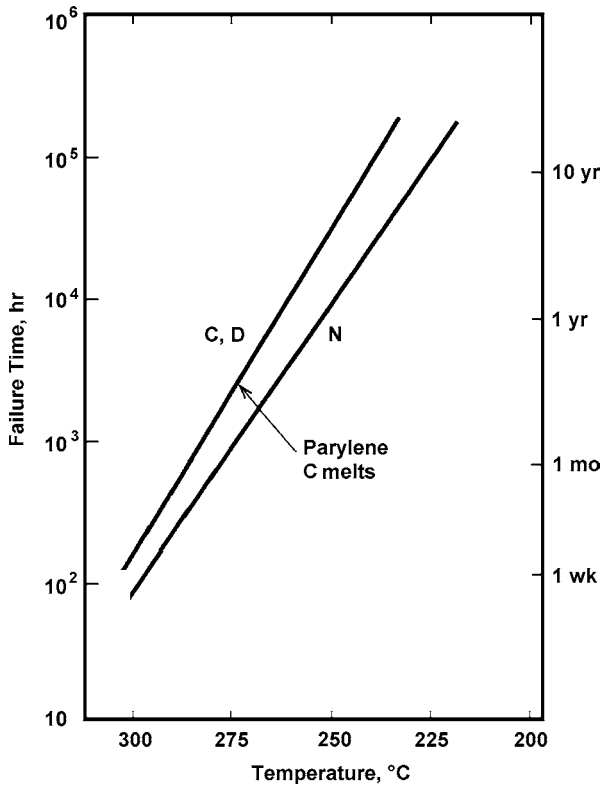


Figure 2.61. Useful life expectancies of parylenes as a function of temperature in vacuum. (Failure equals a 50% loss in tensile strength.)

high temperatures. The thermal and mechanical properties of the parylene coatings are summarized in Table 2.28.

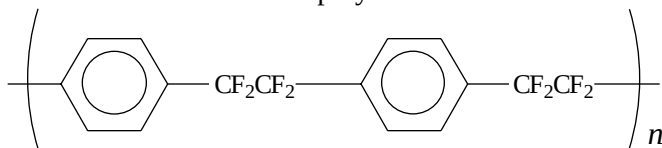
Chemical Resistance. The parylenes are highly resistant to all organic solvents and chemicals such as acids and alkalis. This is a benefit in protecting electronics from solvents and chemicals that may be used during subsequent processing or that may be encountered in field use, but also a detriment in its ability to be removed for rework and repair. As an example of the extreme resistance to corrosive solvents, PWAs coated with parylene have withstood a highly caustic solvent DS-2 for eight hours without degradation while a similar PWA coated with epoxy showed

Table 2.28. Thermal and Mechanical Properties of Parylene Coatings*

Property	Parylene N	Parylene C	Parylene D
Tensile Strength, psi	6,500	10,000	11,000
Yield Strength, psi	6,100	8,000	9,000
Elongation to Break, %	30	200	10
Yield Elongation, %	2.5	2.9	3
Density, gram/cm ³	1.11	1.289	1.418
Coefficient of Friction			
Static	0.25	0.29	0.33
Dynamic	0.25	0.29	0.31
Water Absorption in 24 hr, %	0.06 (0.029 in)	0.01 (0.019 in)	-
Refractive Index @ 23°C	1.661	1.639	1.669
Melting or Heat Distortion Temp., °C	405	280	>350
Coefficient of Thermal Expansion, ppm/ °C	69	35	-
Thermal Conductivity, W/m.K	0.126	-	-
*Measurements made using ASTM methods. (Courtesy Specialty Coating Systems.)			

extensive corrosion to solder, damage to components, and loss of adhesion.^[84]

Parylene F (NOVA HT). Parylene F ($\alpha,\alpha,\alpha',\alpha'$ -tetrafluoro-p-xylylene) is an analog of Parylene N in which the aliphatic hydrogens have been replaced with fluorine atoms, thus obviating the thermal oxidation problem associated with the other parylenes.



Because of its resistance to thermal oxidation, NOVA HT is characterized by very high temperature resistance (>450°C), low dielectric constant, low

Table 2.29. Preliminary Properties of Parylene NOVA HT

Property	Value
Dielectric Constant	2.28
Dissipation Factor	<0.001
Breakdown Voltage @ 1 μ m	750
Modulus, GPa	2.7
Elongation to Break	>20%
Tensile Strength, MPa	45
Water Absorption	<0.1%
Thermal Stability, <1% wt. loss/hr	>450°C
Crystalline Melting Point	>500°C
Volume Resistivity, Ω -cm	5.3×10^{16}
Surface Resistivity, Ω	1.3×10^{14}
Density, g/cm ³	1.58
Thermal Expansion, ppm/ °C	35
Coefficient of Friction	0.20
<i>(Courtesy of Specialty Coating Systems.)</i>	

moisture absorption, and good uv stability. Preliminary properties for NOVA HT are given in Table 2.29.

As with Cyclotene, NOVA HT was introduced primarily as an interlayer dielectric for IC wafer fabrication.^[85] However, as a moisture barrier, a brief evaluation on a few Sandia National Laboratories' ATC-01 test chips showed no improvement over Parylene C.^[86]

2.11 BENZOCYCLOBUTENE, CYCLOTENE®

The polymers of bis-benzocyclobutene, also known as BCB, comprise a relatively new class of high-performance dielectric coatings that are now used for high-density microelectronic circuits. Bis-benzocyclobutene polymer coatings are competing with polyimide for many high-density microelectronic applications such as multilayer interconnect substrates,

gallium arsenide ICs, and other high-speed, high-frequency devices. Initial patents were granted to Dow Chemical Company in 1985–89^{[87][88]} and Dow has been at the forefront of developing and marketing these coatings. Commercial interest in BCB polymer coatings for microelectronics is due to:

- Ease of processing by thermal polymerization, requiring no catalysts or hardeners, and producing no water or other by-products.
- Low dielectric constant (2.7) and low dissipation factor (0.0008) and stability of these electrical properties over a wide temperature and frequency range, rendering them useful for very high frequency applications.
- A high degree of planarization (>90%) obtained in one step when spin coated on circuit surfaces.

One member of the BCB series, a divinylsiloxane bis-benzocyclobutene (DVS-BCB) has been commercialized by Dow Chemical under the tradename Cyclotene*. Over the past ten years, an extensive database and experience with these coatings have been generated.^{[89]–[91]}

2.11.1 Chemistry

Bis-benzocyclobutene polymers are derived from the monomers having structure (a) (Fig. 2.62) in which the R portion may be varied. On heating to 200°C or higher, the cyclobutene portion of the molecule rearranges, at first to form a transient intermediate, o-quinodimethane (structure (b), Fig. 2.62) which, because of its highly reactive double bonds, then reacts with similar molecules or with other unsaturated groups to form a highly cross-linked, high-molecular-weight polymer.

In Cyclotene, the R group is a tetramethyl divinyl siloxane (DVS) as in structure (c) of Fig. 2.62. The polymerization process is purely addition type, thus, unlike polyimides, no water or other by-products are produced. Bis-benzocyclobutene coatings are sold as solutions of BCB oligomers (partially polymerized B-staged) in mesitylene or xylene solvent. Upon

*Cyclotene® is a registered tradename of Dow Chemical Co.

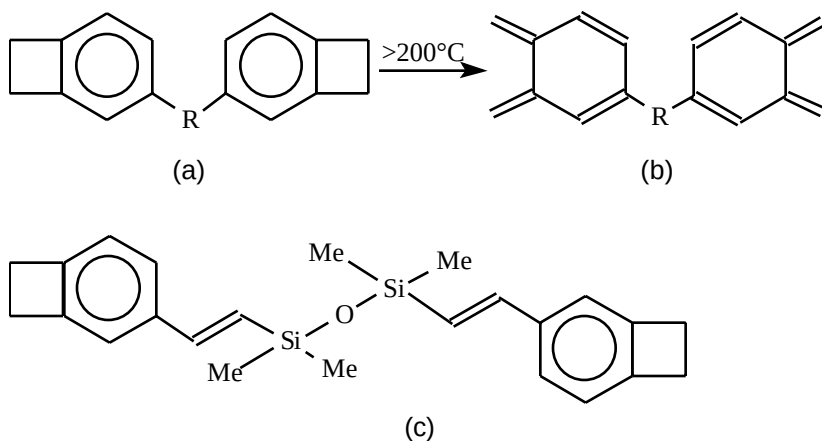


Figure 2.62. Molecular structures for BCB monomers, (a) BCB monomer, (b) o-Quinodimethane intermediate, and (c) DVS-BCB monomer.

evaporation of the solvent and heating in a nitrogen ambient to 200–250°C, the B-staged material continues to polymerize.

An optimum cure schedule is one hour at 250°C at which the Cyclotene achieves 95% polymerization and results in a hard transparent coating. It is important that Cyclotene be cured in a dry nitrogen or vacuum ambient. If cured in air, it oxidizes, forming anhydride and/or carbonyl groups and turns yellowish-brown in appearance.^[89] Oxidation has also been shown by absorption bands appearing in the 1700–1850 cm^{-1} region of the FTIR spectrum.^[86]

The curing temperatures for BCB resins are approximately half those for polyimides, but, even so, are much too high for either BCB or polyimides to be used as conformal coatings over assembled modules. Temperatures above 200°C degrade epoxy die-attach adhesives and accelerate intermetallic growth in gold-to-aluminum wire bonds. Both coatings are, therefore, better suited as dielectric layers in the fabrication of multilayer interconnect substrates and IC devices at the wafer stage.

Cyclotene is also available as a photocurable composition^[92] thus reducing the number of processing steps in forming vias for multilayer interconnections. The photocurable version is a negative-acting formulation based on DVS-BCB and a bisarylazide photo-cross-linking agent. High-resolution conductor lines and spacings of 16 μm from a 5.6- μm -thick film have been reported.^[93]

2.11.2 Properties

A combination of electrical, thermal, and physical properties render BCB coatings particularly suitable as dielectrics for high-speed, high-frequency devices, circuits, and high-density multilayer interconnect substrates. Bis-benzocyclobutene Cyclotene coatings have become key competitors to polyimides for many of these applications.

Physical Properties. Cyclotene may be purchased as BCB solution coatings of various solids contents from 35% to 63%, thus thicknesses of the deposited films can be controlled as a function of viscosity and spin speed.^[94] Coatings ranging from 1.0 μm to 26.0 μm are achievable in a single spin-coat application (Table 2.30). A key attribute of BCB coatings is their high degree of planarization (DOP). Degrees of planarization of 90–

Table 2.30. Film Thicknesses of Dry-etch Cyclotenes

Product	Film Thickness Range (μm) spin coated @ 1000–5000 rpm
Cyclotene 3022–35	1.0–2.4
Cyclotene 3022–46	2.4–5.8
Cyclotene 3022–57	5.7–15.6
Cyclotene 3022–63	9.5–26
(Courtesy Dow Chemical Co.)	

95% are reported for Cyclotene while typical DOPs for polyimide dielectrics are reported to be between 18 and 30%.^[95]

Electrical Properties. Cyclotenes’ very low dielectric constant and dissipation factor, over a wide frequency and temperature range, make them attractive as both coatings and interlayer dielectrics for high-frequency, high-speed circuits. Dielectric constants range from 2.6 to 2.8 and are relatively flat even in the high GHz region and at temperatures up to 200°C. Measurements have been made at 10 GHz,^[96] 35 GHz, and even at 1500 GHz.^[97] Dissipation factors are also low (0.0008 to 0.002) and stable over the same frequency range. Figure 2.63 compares these properties with those

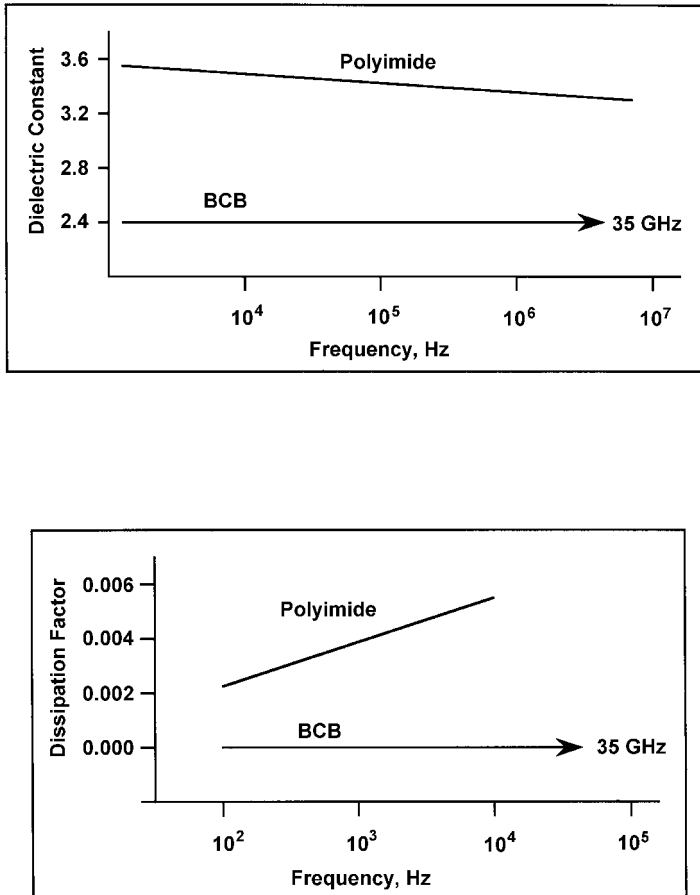


Figure 2.63. Electrical properties of BCB (Cyclotene) and polyimide as a function of frequency.

of polyimide. Other electrical properties reported are volume resistivity of 1×10^{19} ohm-cm and breakdown voltage of 3.0×10^6 V/cm.^[98]

Moisture Absorption. Another beneficial property of Cyclotene for electronic applications is its low moisture absorption^[99] (Fig. 2.64 and Table 2.31^[100]). Unlike most polyimides, the excellent electrical properties

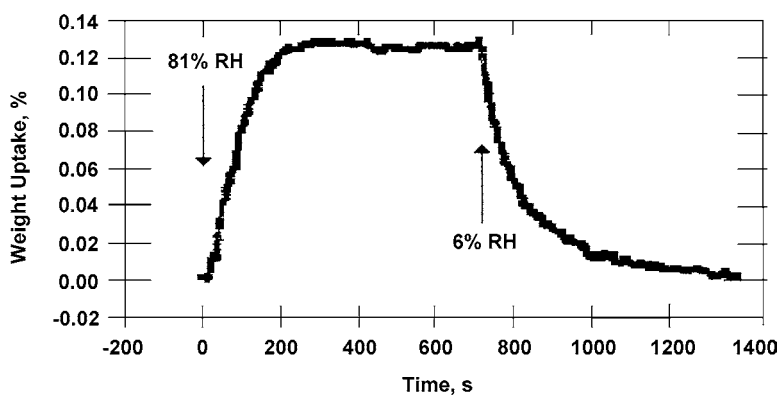


Figure 2.64. Moisture absorption/desorption for Cyclotene 3022 resin.^[99] (Courtesy Dow Chemical Co.)

Table 2.31. Moisture Absorption for Cyclotene 4000 Series Resin Photo-products^[100]

Cyclotene Resin	Film Thickness, μm	Relative Humidity, %		
		30	54	84
4024	5	0.061	0.075	0.14
4026	10	0.058	0.077	0.14
4026	20	0.050	0.082	0.14

(Courtesy Dow Chemical Co.)

of Cyclotene are preserved under humid conditions because of its low water absorption and the hydrophobic nature of its siloxane structure.^[101]

Thermal Properties. The Cyclotenes show no weight losses at temperatures as high as 400°C in an inert ambient (Fig. 2.65). A TGA curve shows no weight loss in nitrogen up to 400°C^[89] (Fig. 2.66). However, Cyclotene films, like parylene films, oxidize when heated in air at temperatures above 150°C. Cyclotene's thermal stability in air is reported to be 150°C for extended periods of time which is adequate for most of its current

uses. Thermal oxidative stability can be improved by the addition of an antioxidant. Cyclotene has a proven history of reliability in its use as a dielectric for GaAs chips and bumped devices with hundreds of millions of GaAs chips in the field without any problems associated with the coating.^[102] A summary of the mechanical and electrical properties of Cyclotene films is given in Table 2.32.

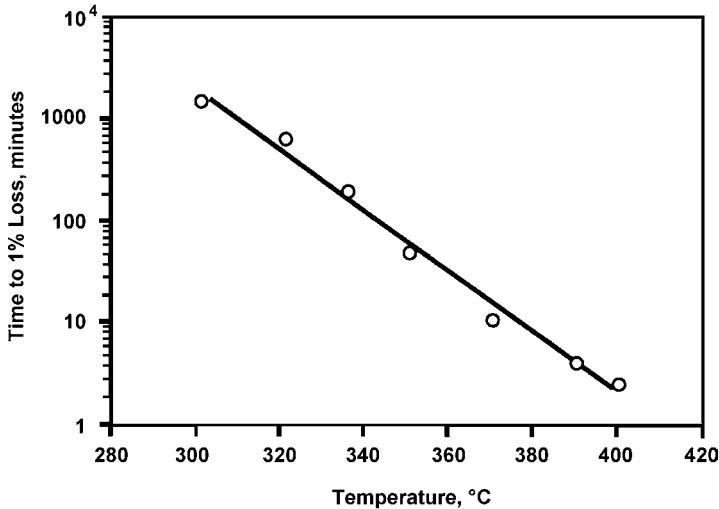


Figure 2.65. Weight loss of a 2- μm -thick Cyclotene film on wafer in helium. (Courtesy Dow Chemical Co.)

2.12 FLUOROCARBONS AND FLUORINATED POLYMERS

The accidental synthesis of polytetrafluoroethylene (Teflon) in 1938 by DuPont researcher Dr. Roy Plunkett was the basis for a whole series of fluorinated polymers with properties that before were not possible. High purity and chemical and thermal inertness of the fluoropolymers are indispensable today in the manufacture of semiconductor devices. As electronics move toward high-speed, high-frequency applications, fluoropolymers are critical to electrical functions because of their very low dielectric constants and dissipation factors.

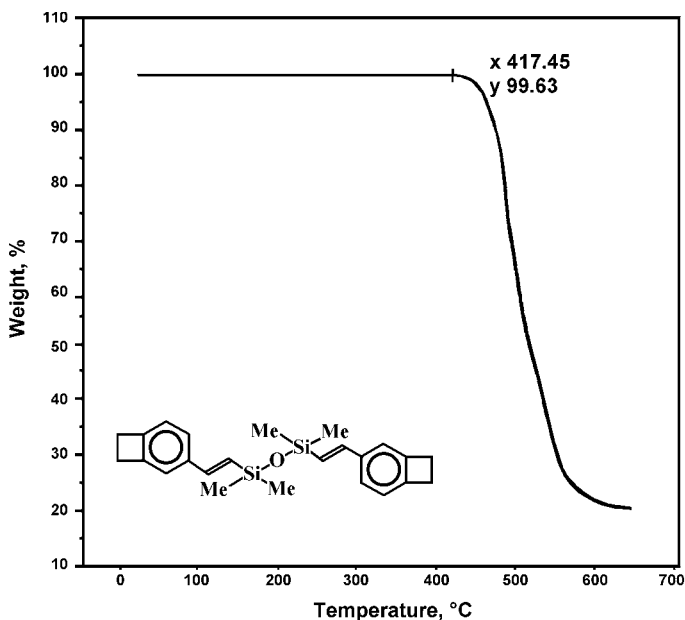


Figure 2.66. Thermal gravimetric analysis (TGA) curve for DVS-BCB. (Courtesy Dow Chemical Co.)

2.12.1 Chemistry

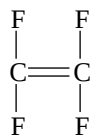
The basic fluorocarbon polymers, originally developed by DuPont, are prepared by the addition polymerization of fluorinated ethylene, alkoxyfluorinated ethylene, or by copolymerization of fluorinated ethylene with other fluorinated ethylenic monomers. Teflon PTFE (polytetrafluoroethylene), the best known of this group, is synthesized by the addition polymerization of tetrafluoroethylene (TFE), a gaseous monomer. Teflon FEP (fluorinated ethylene propylene) is formed by the copolymerization of tetrafluoroethylene with hexafluoropropylene (Fig. 2.67). Teflon ETFE (ethylenetetrafluoroethylene) also known as Tefzel ETFE, a relatively new member of the Teflon family, is a copolymer of TFE and ethylene. Other fluorocarbon resins include polychlorotrifluoroethylene (CTFE), polyvinyl fluoride (PVF), and polyvinylidene fluoride (discussed in Sec. 2.3 under “Vinyl Polymers”).

Table 2.32. Mechanical and Electrical Properties of Cyclotene* Films

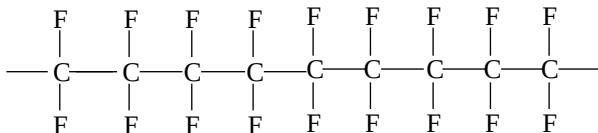
Property	Measured Value
Dielectric Constant, 1 kHz	2.65
Dielectric Constant, 35 GHz	2.4
Dissipation Factor, 1 kHz	0.0008
Dissipation Factor, 35 GHz	0.0003
Breakdown Voltage, V/cm	3×10^6
Volume Resistivity, ohm-cm	1×10^{19}
CTE, ppm/°C	52
Glass Transition Temperature, °C	>350
Tensile Modulus, GPa	2.9
Tensile Strength, MPa	87
Elongation, %	8
Stress, MPa	28
Moisture Absorption @ 85% RH	0.14%
Refractive Index, photocured	1.561–1.543**
Refractive Index, heat cured	1.552–1.535**
Poisson's Ratio	0.34
Shrinkage during Cure	<5%
*Cyclotene is a registered tradename of Dow Chemical Co. Compiled from Dow Chemical Co. brochures and articles. **Measured from 0.6 to 1.55 μm .	

Fluorocarbon Dispersion Coatings. Teflon coatings, both Teflon PTFE and FEP, are available as one-part, water-based dispersions. They consist of colloidal suspensions of hydrophobic negatively-charged particles (average size is 0.2 μm) in water. Dispersions contain from 32 to 62% by weight of resin and may be stabilized with an immiscible oil, non-ionic wetting agents, or mixtures of ionic and non-ionic wetting agents. After spraying or dipping and evaporating off the water at approximately 120°C, the fluorocarbon particles must be melted and fused at temperatures of 360° to 400°C, depending on the composition. Both sintering temperature and time are critical in obtaining optimum coating properties. It is reported that exposures of 5 minutes at 370°C provide the best mechanical and electrical

Polymerization of TFE Resins
TFE (Tetrafluoroethylene)



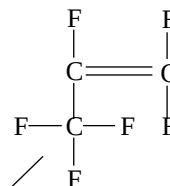
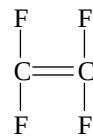
Several TFE molecules join
to form PTFE
(Polytetrafluoroethylene)



Polymerization of FEP Resins

TFE (Tetrafluoroethylene)

HFP (Hexafluoropropylene)



Join to form FEP
(Fluorinated Ethylene Propylene)

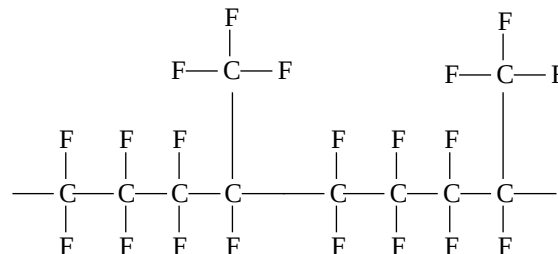


Figure 2.67. Polymerization reactions for fluorocarbon polymers.

properties and that these properties are equivalent to those obtained from molded Teflon.^[103] In addition to fusing the Teflon particles, the high temperatures are necessary to decompose and volatilize the wetting agent. Some discoloration may be evident after sintering, owing to incomplete removal of carbonized residues from the wetting agent. Sintering cycles of 8 to 10 minutes are recommended for obtaining high-purity coherent films of one-mil thickness. The maximum thickness deposited in a single application should be kept at 0.5 mil; thicker coatings tend to crack or craze although thicker films may be built up sequentially by multiple coating and baking steps without crazing.

On completing the sintering, the coatings may be cooled rapidly by quenching in water to increase their toughness, or they may be cooled slowly to impart better wettability for succeeding steps. For multiple coatings, it is important to cool the films slowly after each step except for the last one, which may be quenched rapidly.^[104]

The cure temperatures for most fluorocarbon coatings are too high to be used as conformal coatings for assembled circuits. Therefore, using Teflon coatings for electronics applications is restricted to parts that can withstand the high cure/fusion temperatures.

In addition to spray or dip application from colloidal dispersions, Teflon coatings may be applied by extrusion, fluidized-bed, or electrostatic spraying. In all cases, Teflon FEP is somewhat easier to process than Teflon PTFE because of its lower melt temperature.

Other Fluorinated Polymers. Fluorinated acrylates, fluoroparylene (refer to Sec. 2.10 on Parylenes), fluorinated benzoxazole, and other fluorinated polymers are also useful as coatings for electronics. They are easier to process than the Teflon coatings, requiring much lower temperatures, and, thus, are more compatible with assembled electronic components and circuits, yet preserve excellent electrical properties.

Fluorinated Benzoxazole Polymers. Research and development is underway at the Air Force Research Laboratories to develop dielectric coatings for very high-speed integrated electronic circuits.^{[105][106]}

The research focus is on synthesizing polymers having low dielectric constants and dissipation factors, high temperature stabilities, and ease of processing. A series of fluorinated benzoxazole polymers has been synthesized, one of which is depicted in Fig. 2.68. Typical dielectric constants were 2.1 to 2.5 at 1 MHz. Boiling water absorption, even after several days, was 0.2%, and thermal stabilities ranged from 350° to 400°C.

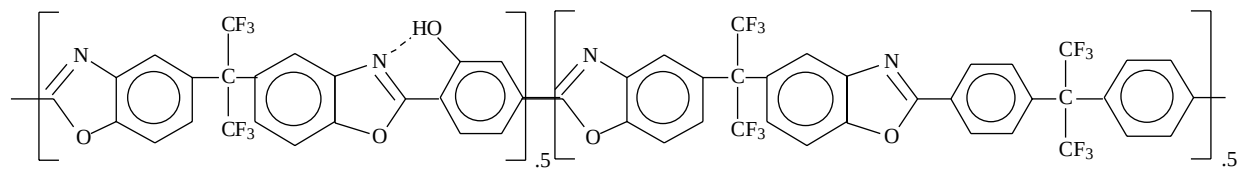


Figure 2.68. Fluorinated benzoxazole copolymer.

Fluoroacrylates.A recently developed fluoroacrylate, 3M’s Novec* EGC-1700, applied by dipping, gives a thin 1-μm-thick coating that is highly repellent to moisture, lubricating oils, heptane, toluene, silicones, and photoresist solutions used in manufacturing semiconductors. In addition, it is non-flammable and thermally stable to 175°C. Typical properties are shown in Table 2.33.

Table 2.33. Typical Properties of Novec EGC-1700 Fluoroacrylate Coating

Properties	Novec Coating EGC-1700
Appearance	Clear, colorless to light-colored liquid solution
Solids	2%
Specific Gravity @ 25°C	1.5
Solvent	3M Engineered Fluid HFE-7100DL
Boiling Point of Solvent	61°C
Flash Point	None
Thermal Stability of Dry Film	Repellent to chlorinated silicone oil after 24 hrs at 175°C
Surface Energy of Dry Film (dynes/cm)	11–12
Volume Resistivity @ 30% RH, 25°C (40 V dc)	4.6×10^{12} ohm-cm
Dielectric Constant @ 30% RH, 25°C @ 1 kHz	3.1
Coating Thickness (dip coated)	~1 micron
Dissipation Factor @ 30% RH, 25°C @ 1 kHz	0.0089
Dielectric Strength @ 35% RH, 25°C	1.0 kV/25.4 microns
Refractive Index	1.38
*3M is a registered trademarks of Minnesota Mining and Manufacturing (3M Co.). Note: Values are typical, not to be used for specification purposes. Contact 3M Co. for additional data. (Courtesy of 3M Specialty Materials.)	

*Novec® is a registered tradename of Minnesota Mining and Manufacturing (3M Co.).

2.12.2 Properties

Fluorocarbons are used as dielectric coatings on ceramic or metal interconnect substrates; insulation for wire and cable; capacitor insulation; impregnants for motors, generators, and transformers; and protective coatings for electronic chassis. Their low dielectric constants and dissipation factors have made them especially useful for high frequency microwave interconnect substrates and printed wiring boards. The key beneficial attributes of fluorocarbon coatings are:

- High and low temperature stability. Most types can operate continuously at 260°C and intermittently at 325°C. Some fluorocarbon polymers can withstand cryogenic temperatures lower than -185°C.
- Excellent electrical properties. Their dielectric properties make them especially suited to high-frequency microwave circuits.
- Excellent mechanical properties. They combine high abrasion resistance with very low coefficients of friction.
- Extreme inertness to solvents and chemicals. Fluorocarbons are unaffected by acids, alkalis, corrosive salt solutions, and organic solvents, except for molten alkalis and reactive fluorinating agents.
- Excellent moisture resistance. The water absorption and MVTR are among the lowest of known polymers. The MVTR for Teflon FEP, for example, is 6.2 g/m²/24 hr/mil. Water absorptions after 24 hours immersion range from less than 0.01% to 0.03%.
- High purity. Because the synthesis of fluorocarbons involves addition polymerization, no by-products are formed and the polymers are inherently pure. Further, the polymers consist of highly stable non-polar C–F bonds that impart high thermal stability, low moisture absorption, and excellent electrical characteristics.

These unique properties may be attributed to the fluorocarbon polymer structure. The molecules consist of closely packed long linear chains of carbon atoms protected by a tightly bound sheath of fluorine atoms. Since the carbon-to-fluorine covalent bond strength is among the strongest

of atom combinations, fluorocarbon polymers are inert to both chemical attack and high-temperature exposure.

Thermal Properties. Teflon PTFE has a continuous service temperature of 260°C and may be used for short periods of time at temperatures as high as 316°C. Specimens have been heat aged at 300°C for six months with no change in dielectric constant. Teflon FEP has a lower continuous service temperature of 204°C and intermittently up to 232°C. Specimens have been heat aged at 260°C without any change in dielectric constant. Although the maximum service temperature for Teflon FEP is lower than that for PTFE, Teflon FEP is considerably easier to process. Weight loss of Teflon PTFE at temperatures up to 315°C is low, then increases due to the onset of decomposition^[107] (Table 2.34).

Table 2.34. Weight Loss Rate Data for Teflon PTFE^[107]

Temperature, °C	Weight Loss, %/hr
205	0.0002*
260	0.0002*
315	0.0002*
360	0.001**
390	0.006**
420	0.09**
*Test on granular molding powder. **Test on molded sheet.	

Fluorocarbon polymers are also useful at cryogenic temperatures. Their strength actually increases at low temperatures and a degree of elongation and resilience is retained. Teflon PTFE parts have been successfully used at temperatures as low as -270°C.

Electrical Properties. Of all known polymers, Teflon PTFE and FEP have the best electrical properties and best retention of properties at continuous temperatures up to 260°C for Teflon PTFE and 204°C for Teflon FEP. Dielectric constants range from 2.1 to 2.6. Dielectric constants and

dissipation factors for these fluorocarbons are among the lowest of all known polymers and remain low and fairly constant over a broad frequency range from 100 Hz to 3 GHz (Fig. 2.69).

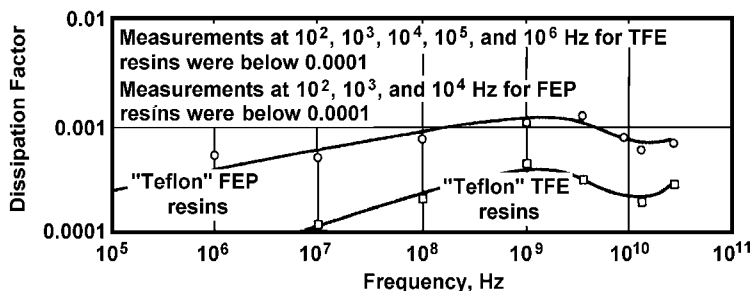


Figure 2.69. Dissipation factor vs frequency for Teflon resins (at 23°C) per ASTM D150. (Courtesy DuPont.)

Fluorocarbons also exhibit one of the lowest dielectric power losses over the same temperature and frequency ranges. Surface and volume resistivities are high for all the Teflon coatings. Surface resistivities, measured according to ASTM D257, are greater than 10^{15} ohm/sq while volume resistivities, by the same procedure, are greater than 10^{17} ohm-cm. Other electrical properties are given in Table 2.35.

Mechanical Properties. The outstanding mechanical properties of Teflon coatings include their low coefficients of friction—the lowest for any known plastic materials—and their high abrasion resistance. The coefficients of friction of Teflon and Teflon-like polymers are in the range of 0.05 to 0.3 and thus produce non-wetting surfaces. Fluorocarbon surfaces are both oleophobic and hydrophobic. They are, therefore, used as mold release coatings and maskants. Adhesion to Teflon surfaces is difficult and requires modification of the surface to render it polar and wettable. The friction and abrasion resistance properties of Teflons are, in fact, so good that they are often used as fillers in other plastics to lower their coefficients of friction and improve their wear properties. Some experimental values are given in Tables 2.36 and 2.37. Other physical and thermal properties are given in Table 2.38.

Table 2.35. Typical Electrical Properties of Teflon Fluorocarbons*

Property	Teflon PTFE	Teflon FEP	Teflon PFA	Teflon ETFE
Dielectric Constant, 1 MHz	2.1	2.1	2.1	2.6
Dissipation Factor, 1 MHz	<0.0001	0.0006	0.0001	0.007
Dielectric Strength, ¹ V/μm	18	53	80	79
Arc Resistance, ² sec	>300	300	>180	122
Volume Resistivity, ohm-cm	>10 ¹⁸	>10 ¹⁸	>10 ¹⁸	>10 ¹⁷
Surface Resistivity, ohm/sq	>10 ¹⁸	>10 ¹⁶	>10 ¹⁷	>10 ¹⁵
Note: Values are averages, not intended for specification purposes. Contact DuPont for further information. ¹ 100 μm film. ² per ASTM D-495. *Copyright© 2002. E. I. duPont de Nemours & Co., used under permission of DuPont. Teflon is a registered trademark of DuPont for its fluoropolymer resins. (Tables of Teflon fluorocarbon resins provided courtesy of DuPont.)				

Table 2.36. Coefficient of Friction for Teflon FEP (against steel at 23°C)

Load, psi	Static Coefficient	Dynamic Coefficient, 25 ft/min
1	0.14	0.425
10	0.11	0.415
100	0.08	0.350

Table 2.37. Abrasion Resistance of Teflon PTFE and FEP Coatings

Test Method	Weight Loss, PTFE	Weight Loss, FEP
Armstrong (200 cycles, ASTM D1242-56, g/in ²)	0.337	0.174
Taber (1000g load, CS-17F Calibrase Wheel, mg)		
1000 cycles	8.9	7.5
2000 cycles	13.4	13.2

Table 2.38. Typical Physical and Thermal Properties of Teflon Fluorocarbons*

Property	Teflon PTFE	Teflon FEP	Teflon PFA	Teflon ETFE
Specific Gravity, g/cm ³	2.15	2.15	2.15	1.76
Tensile Strength, psi	3,000–5,000	3,400	3,600	5,800–6,700
Elongation, %	300–500	325	300	150–300
Hardness, Shore D	50–65	56	60	72
Taber Abrasion, ¹ mg/1000 cycles	12	14.8	-	-
Coefficient of Friction Static Dynamic	0.12–0.15 0.05–0.10	0.12–0.20 0.08–0.3	0.2 -	0.24–0.5 0.3–0.4
Contact Angle, water, degrees	104–111	95–105	104–111	90–100
Melting Point, °C	327	260	306	267
Cure Temperature, °C	379–429	360–385	379–399	302–323
Max. Use Temp., °C Continuous Intermittent	260 316	204 232	260 288	149 199
Thermal Conductivity, W/m.K	0.25	0.20	0.19	0.24
Thermal Expansion, ppm/°C	100			
Water Absorption, % in 24 hr	<0.01	<0.01	<0.03	< 0.03
MVTR, g/100 sq in./24 hr/mil	-	0.40	-	-
Note: Values are averages, not intended for specification purposes. Contact DuPont for further information. ¹CS 17 wheel, 1 kg load. *Copyright© 2002. E. I. duPont de Nemours & Co., used under permission of DuPont. Teflon is a registered trademark of DuPont for its fluoropolymer resins. (<i>Tables of Teflon fluorocarbon resins provided courtesy of DuPont.</i>)				

Chemical and Solvent Resistance. Fluorocarbon polymers are resistant to the widest variety of organic and inorganic acids and bases, solvents, and gases. They provide excellent corrosion protection for metals. In fact, the only chemicals to which they are not resistant are molten alkali metals, such as sodium or potassium, fluorine gas, and fluorine precursors such as oxygen difluoride and chlorine trifluoride at elevated temperatures. Even when there are weight increases and slight absorption of chemicals, no significant loss of physical or electrical properties occurs.

Limitations. Among limitations in using fluorocarbons in electronics are the following:

- High processing temperatures of 300° to 400°C required to melt and fuse the particles together into a coherent film. This limits their use to substrates and parts that can withstand these high temperatures.
- Susceptibility to cold flow and low cut-through resistance.
- Poor resistance to radiation, especially for PTFE Teflon in an air ambient. However, the Tefzel fluorocarbon type has far better radiation resistance than PTFE Teflon and has been used in many space environments.

2.13 POLYSULFONES

Polysulfones, due to their highly aromatic structures, have high melting points and low solubilities, thus rendering them more suited to extrusion or molding processes than to liquid coating. As extruded coatings, polysulfones find applications as high-temperature-stable, moisture-resistant insulation for wire and cable.

2.13.1 Chemistry

Organic polymers that contain the repeating sulfone unit are known as polysulfones. Important members of this class are the polyarylsulfones (PAS) which consist of aryl (phenyl, biphenyl, or Bisphenol A) groups linked by ether and sulfone groups. A basic polymer structure is depicted in Fig. 2.70.

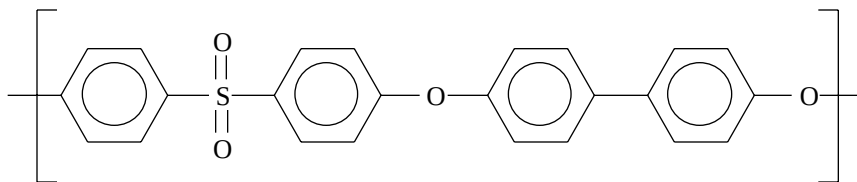


Figure 2.70. Molecular structure for a basic polyarylsulfone (PAS).

Other variations of this basic structure involve modifications of the aryl units, for example, substitute groups for the hydrogens of the phenyl ring or inclusion of the isopropylidene group may be used. The latter is synthesized from the sodium salt of Bisphenol A and *p*, *p'*-dichlorodiphenylsulfone.^[108] Such modifications reduce the melting temperature, enhance the solubilities, and improve processibility, albeit at some expense to thermal resistance. Polyarylsulfones are semicrystalline thermoplastic solids having a melt temperature of 254°C and can be molded or extruded. Their poor solubilities in organic solvents obviates their use as solution coatings. As extruded coatings, they have found their greatest application for high-temperature wire insulation.

2.13.2 Properties

Polyarylsulfones are noted for their heat resistance, resistance to oxidation, and hydrolytic stability. Extensive thermal, physical, and electrical properties are given by Lee, Stoffey, and Neville.^[108]

2.14 POLYARYLETHETHERKETONE, PEEK

PEEK belongs to a class of ketone polymers in which aryl ketone groups alternate with aryl ether groups. The ether linkages impart flexibility while the aromatic keto groups impart strong thermal and chemical stability. Like the polyarylsulfones, PEEK is a linear thermoplastic, semicrystalline

polymer, but it has a higher melting point (340°C) than that of PAS (254°C) and greater thermal resistance. It has short-term thermal stability at 315°C and long-term stability at 250°C. Its CTE is 26 ppm from 0° to 290°F and 60 ppm from 290° to 500°F.

PEEK's highly aromatic structure (Fig. 2.71) also renders it very resistant to radiation damage and outgassing. It is reported that no significant reduction of mechanical properties occurs on exposure to 1×10^9 rads total flux of gamma radiation.

Electrical properties are reported to be excellent with a dielectric constant of 3.2 under ambient conditions at 60 Hz, a dissipation factor of 0.003 under the same conditions, a dielectric strength of 480 V/mil, and volume resistivity of 4.9×10^{16} ohm-cm.^[109]

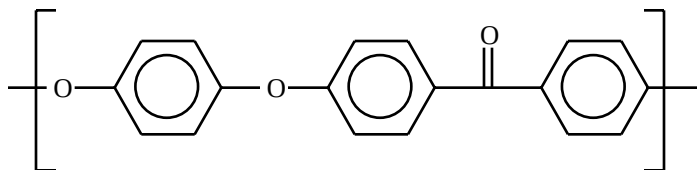


Figure 2.71. Structure for polyaryletheretherketone (PEEK) polymer.

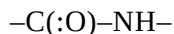
Like PAS, PEEK has limited solubility in all organic solvents and is best applied by extrusion. As a coating for electronic applications, it has found its greatest use as insulation for wire and cable.

2.15 POLYAMIDES

Polyamides such as nylon, like polysulfones, are generally processed by extrusion or molding and used primarily for wire and cable insulation for commercial applications. As coatings, polyamides are employed as hardeners to cure epoxy resins improving flexibility, reducing stresses, and improving other mechanical properties of epoxies. Polyamide hardeners are based on a different chemistry than the nylon polyamides. (See Sec. 2.6.2.)

2.15.1 Chemistry

Polyamide resins are characterized by the presence of the repeating amide group along the polymer chain



They are formed by the condensation of di- or polyamines with dibasic or polybasic acids and may be classified according to three main types:

- Thermosetting fatty-acid polyamides
- Thermoplastic fatty-acid polyamides
- Nylon polyamides

Of these, the thermosetting polyamides are most widely used as coatings. They are derived from dimerized fatty acids and trifunctional amines. For example, diethylenetriamine, DETA, ($\text{H}_2\text{NCH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{NH}_2$) reacts with dimer acid (a mixture of dicarboxylic and polycarboxylic acids derived from linoleic acid) to yield a series of liquid resins. These resins may be used as such, but, more often, are co-reacted with epoxies. The high concentration of amino groups along the polyamide chain readily react with the epoxy rings resulting in extensive cross-linking. Epoxy-polyamide coatings thus formed are reported to possess greater adhesion, higher flexibility, greater ability to wet surfaces, and better corrosion and chemical resistance than either epoxies or polyamides alone.^{[110][111]} In addition to their high reactivity with epoxy resins, polyamide resins co-react with phenolics and with other resins to yield highly cross-linked thermosetting coatings.^[112]

Thermoplastic polyamides are prepared by the condensation of dimerized fatty acids with short-chain diamines, such as ethylenediamine ($\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$). They are quite soluble in many solvents and are compatible with plasticizers and other resins. As such, they may be formulated as solution coatings, as aqueous dispersions, or as hot-melt coatings. Both the thermosetting and thermoplastic polyamides may be applied by conventional spray, dip, or brush methods. The thermoplastic types may also be applied by fluidized-bed, electrostatic spray, or hot-melt methods.

Nylons, originally developed by DuPont, are also polyamides, but their structure, aside from containing amide groups, is rather different from the other polyamides just described. Nylon polyamides consist of linear polymers derived from the condensation of aliphatic diamines with aliphatic

dicarboxylic acids, the most common and well-known of which is Nylon 6,6, prepared from hexamethylenediamine and adipic acid as shown in Fig. 2.72. Nylon polyamides, such as Zytel*, have found their greatest use as molding compounds. The nylon polyamides have had only limited use as coatings for electronics because of difficulties in formulating and applying them as coatings. Because of their low solubility and high softening temperatures, coatings are difficult to prepare. Of the various nylons, however, Nylon 6 has been formulated both as a solution coating and a dispersion coating for use as a wire insulation.^[112]

2.15.2 Properties

Polyamide coatings, as such, are not widely used as insulation for electronic or electrical equipment because of their marginal electrical properties, especially in the presence of moisture. Compared with other polymer types, polyamides absorb above-average amounts of water. In a 24-hour period, they may absorb 1.5 to 2%, and as much as 6% in an 8-day period when immersed in water.^[113] High performance polyamides such as Zytel HTN, were introduced by DuPont in 1994 and have moisture absorptions as low as 0.4%. Polyamide-epoxy combinations, however, are widely used as coatings, adhesives, filleting compounds, and encapsulants for many electronic applications.

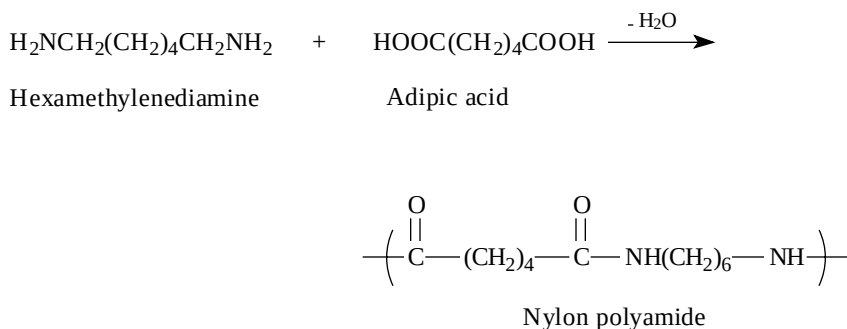


Figure 2.72. Synthesis of nylon polyamide.

*Zytel® is a registered tradename of DuPont.

2.16 PHENOLICS

Phenolic resins, developed in 1909 by L. H. Baekeland, are the oldest completely synthetic polymers. They have found their greatest applications as molding compounds and laminates for commercial products. Phenolics were among the first synthetic polymers to be used in electronic applications, but were later supplanted by higher performance polymers such as epoxies. Phenolic coatings are still used for electrical insulation, impregnating varnishes, and chemical-resistant coatings.

2.16.1 Chemistry

Phenolic resins are formed by the chemical reaction of phenols with aldehydes, in the presence of either an acid or a base catalyst. The simplest, most widely used phenolic resin is based on the condensation of phenol with formaldehyde (Fig. 2.73).

Phenolic resins may be liquid or solid, depending on their structure and molecular weight. Hardening or curing is achieved by heating them either alone or with hexamethylenetetramine, which acts both as a catalyst and a source of methylene groups.^{[114][115]} In this manner, cross-linking of the resin molecules occurs opposite the hydroxyl groups (Fig. 2.74).

Phenolic varnishes are formulated from substituted phenols such as the p-phenyl or p-tertiary butyl derivatives by reacting them with tung, linseed, or other oils. Although these varnishes may be air dried, baking is recommended to achieve optimum chemical and environmental resistance.

2.16.2 Properties

Phenolic coatings are available as solution coatings that may be applied by spraying, roller coating, or dipping. After a short air-drying period to allow evaporation of the solvents, they are baked at temperatures as high as 205°C to complete the polymerization and attain optimum properties.

Phenolic coatings have four outstanding properties: high thermal stability, high chemical resistance, good adhesion, and low cost. Some formulations are reported to withstand 205° to 260°C continuously with little loss of mechanical or electrical properties. Mineral fillers are normally incorporated to achieve these high thermal stabilities. Fillers are also added

to improve electrical properties; for instance, fillers increase arc resistance and dielectric strength and lower dissipation factors.

Nevertheless, phenolic coatings are losing ground to epoxies for high-reliability electronic applications. For example, there are many reports that phenolic plastics have caused corrosion of copper and other metals due to the acidic or alkaline nature of the catalysts used in their cure.

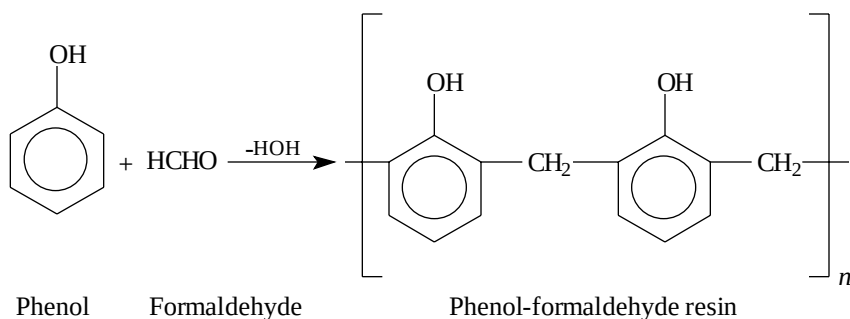


Figure 2.73. Synthesis of simplest phenolic resin.

2.17 POLYSULFIDES

Polysulfides are being treated last in this section and are included primarily for reference since they are not used as coatings or dielectrics for microelectronic applications. Their main uses are as sealants and caulking compounds largely for commercial applications.

2.17.1 Chemistry

Polysulfides are aliphatic polymers that contain two or more consecutive sulfur atoms in the form of disulfide ($-\text{S}-\text{S}-$) repeating linkages. Polymerization occurs through the mercaptan or thiol ($-\text{SH}$) end-groups in their structure. A generalized structure may be represented as follows



Liquid polysulfide resins of molecular weight 3,000 to 4,000 may be further polymerized to produce solid rubbery coatings. Polymerization occurs by an oxidative free-radical mechanism through the terminal thiol groups. Consequently, they require the addition of a free-radical-initiating curing agent such as dicumene hydroperoxide or other organic peroxide.^[116] Polysulfides can also be co-cured with various polymers to yield a variety of elastomeric or plastic properties based on the ratio of ingredients used. For example, polysulfides have been reported to co-cure with epoxy resins mixed with aliphatic or aromatic amines.^[117]

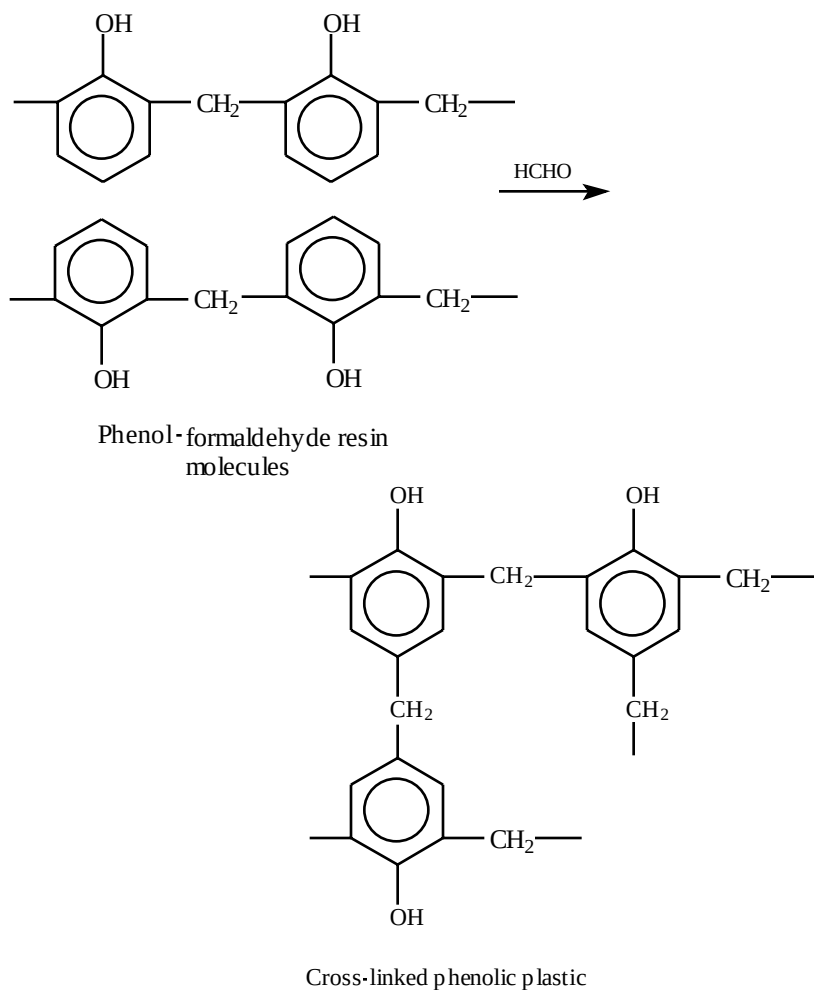


Figure 2.74. Polymerization of phenolic resins.

2.17.2 Properties

Cured liquid polysulfides provide flexible, rubbery coatings that have excellent adhesion to many surfaces and are excellent as sealers for water, moisture, oil, fuel, ozone, and oxidation.^[118] Their electrical properties are good, but not exceptional. Dielectric constants are high and may range from 5.5 to 8 and insulation resistance, though initially high, can deteriorate rapidly and irreversibly on exposure to humidity, temperature, and applied bias. The choice of curing agent may improve electrical properties, for instance using lead dioxide instead of cumene hydroperoxide. The intermediate electrical properties of polysulfides are valuable for many low-cost electrical applications, principally for transformer and connector potting and sealing. Polysulfides are seldom used for printed circuit assembly protection or for microelectronic insulation. The application of a voltage potential across polysulfide-coated conductor patterns under humid conditions invariably lowers the insulation resistance values to less than 10^8 ohms and results in decomposition of the coating. The electrical properties of polysulfides may be altered by the addition of fillers, but, in general, they are poor compared with epoxies, silicones, and other polymers.

REFERENCES

1. Korshak, V. V., and Vinogradova, S. V., *Polyesters*, (translated from the Russian edition by B. J. Hazzard), Pergamon, New York (1965)
2. Lawrence, J. R., *Polyester Resins*, Plastics Application Series, Reinhold, New York (1960)
3. Bjorksten, J., *Polyesters and Their Applications*, Reinhold, New York (1956)
4. Beavers, E. M., Applications for Alkyds and Polyesters, *Ind. Eng. Chem.*, 41:738 (1949)
5. Smith, V. M., *Vinyl Resins*, Plastic Application Series, Reinhold, New York (1961)
6. Materials Selector Issue, *Materials Design Engineering* (Oct. 1963)
7. Struber, V. R., *Theory and Practice of Vinyl Compounding*, Argus Chemical Corp., New York (1968)
8. Raech, H., *Allylic Resins and Monomers*, Plastics Application Series, Reinhold, New York (1965)

9. Lee, H., and Neville, K., *Handbook of Epoxy Resins*, McGraw-Hill, New York (1967)
10. Skeist, I., *Epoxy Resins*, Plastics Application Series, Reinhold, New York (1962)
11. Erich, W., *Literature Survey on the Synthesis of Epoxy Resins from Bisphenols*, Picatinny Arsenal TN-12, AD158199 (Mar. 1958)
12. Batog, A. E., Pet'ko, I. P., and Penczek, P., Aliphatic-Cycloaliphatic Epoxy Compounds and Polymers, *Advances in Polymer Science*, Vol. 144 (1999)
13. Wear, R. L., St. Paul, W., and Bowman, R. L., Heat Curing Epoxy Resin Composition, U. S. Patent 3052650 (Sep. 1962)
14. Floyd, D. E., *Polyamide Resins*, Plastics Application Series, Reinhold, New York (1962)
15. Saunders, T. F., Levy, M. F., and Serino, J. F., A Mechanistic Study of the Dicyandiamide Epoxy Curing Process, *Proc. Am. Chem. Soc., Div. of Organic Coatings Plastics*, 26(1) (Mar. 1966)
16. Crivello, J. V., The Discovery and Development of Onium Salt Cationic Photoinitiation, *J. Polymer Sci., Part A: Polymer Chemistry*, 37(23):4241–4254 (Dec. 1, 1999)
17. Greenlee, S. O., Synthetic Drying Compositions, U. S. Patent 2456408 (Dec. 14, 1948)
18. Pauling, L., *Nature of the Chemical Bond*, Cornell U. Press, Ithaca (1960)
19. Licari, J. J., High Temperature Adhesives, *Prod. Eng.* (Dec. 1964)
20. Dittman, D. O., Licari, J. J., and Glovak, M., Ablative Thermal Insulation Composition of a Silicone, Epoxy Resin, Cork, and Curing Agent, U. S. Patent 3380941 (Apr. 30, 1968)
21. Epocast Tech. Bull., Furane Plastics (now Vantico).
22. Quant, A Low-Density Potting Compound, Sandia National Laboratory, Preprint SCR-417 (1961)
23. Graves, H. K., and Pizzino, M. A., Effects of High Humidity on Dielectric Properties of Casting Resins, *Elec. Mfg.* (Apr. 1956)
24. Applegath, D. D., Helmreich, R. F., and Sweeney, G. A., Epoxy Novolacs, *SPE J.* (Jan. 1959)
25. Union Carbide Tech. Bull., Comparative Properties of Filled Epoxy Electrical Potting Compounds (Aug. 1959)
26. Stringfellow, A. E., and Reighter, D. H., Circuit Interrupter Having Track-resistant Coating Thereon, U. S. Patent 3192347 (Jun. 1965)
27. Radley, G. R., Electrical Apparatus with a Thermal and Electrical Insulating Coating, U. S. Patent 2862838 (Dec. 1958)

28. Torossian, K. A., and Jones, S. L., A Study of Polymers Applicable to Insulation Systems, *17th Ann. Tech. Conf. SPE*, Washington, DC (Jan. 1961)
29. Ehlers, G. F. L., Thermal Gravimetric Analysis of Polymers, TD Report, ASD-TR-61-622 (1961)
30. Conley, R. T., (ed.), *Thermal Stability of Polymers*, Marcel Dekker, NY (1970)
31. Kline, G. M., Plastics in Germany, 1939–1945, *Modern Plastics*, 23:152A-P (1945)
32. Farmer, E. H., and Sutton, D. A., *J. Chem. Soc.*, p. 139 (1942)
33. Saunders, J. H., and Frisch, K. C., *Polyurethanes: Chemistry and Technology Part II*, Interscience, NY (1964)
34. Patton, T. C., Fundamentals and Advances in Urethane Coating Technology, *J. Paint Tech.*, 39(512), (Sep. 1967)
35. Wells, E. R., Hudson, G. A., Saunders, J. H., and Hardy, E. E., The Properties and Applications of Urethane Coatings, *Official Digest*, Fed. Soc. Paint Tech., 31(416) (Sep. 1959)
36. Hostettler, F., and Cox, E. F., *Ind. Eng. Chem.*, 52:609 (1960)
37. Patton, T. C., *Official Digest*, 34(446):342 (1962)
38. A New Approach to the Old Problem of Preventive Maintenance, Product Info. Bulletin, Mobay Chemical Co.
39. Stanton, J. M., and Rohalt, D. M., Oil-Modified Urethanes in Industrial and Maintenance Finishes, *Paint Ind. Mag.* (Jul. 1961)
40. Stark, F. O., et al., *Silicones*, *Comprehensive Organometallic Chemistry*, 2:305, Pergamon Press (1982)
41. Noll, W., *Chemistry and Technology of Silicones*, Academic Press (1968)
42. Rochow, E. G., *Silicon and Silicones*, Springer-Verlag, Berlin (1987)
43. Lockhart, F. J., The Role of Silicone Packaging Materials in the Semiconductor Industry, *Proc. Nat. Electronic Pkg Prod. Conf.*, Long Beach, CA (Jan. 1967)
44. *Silicone, Chemistry and Technology*, CRC Press, Boca Raton, FL (1991)
45. Clarson, S., (ed.), *Silicones and Silicone-modified Materials*, Oxford U. Press (2001)
46. Colas, A., Silicone Chemistry Overview, *Chimie Nouvelle*, 8(30):847 (1990)
47. McGregor, R. R., *Silicones and Their Uses*, McGraw-Hill, New York (1954)
48. Rochow, E. G., Halogenated Aryl Silicones, U. S. Patent 2258219 (Oct. 1941)
49. Clarson, S. J., (ed.), *Silicones and Silicone-Modified Materials*, ACS Symposium Series No. 729

50. Meals, R. N., and Lewis, F. M., *Silicones*, Plastics Application Series, Reinhold, NY (1961)
51. Dow Corning Technical Bulletin 07-103 (Dec. 1963)
52. Balde, J. W., The Effectiveness of Silicone Gels for Corrosion Prevention of Silicon Circuits, *Final Report: IEEE Computer Society Computer Packaging Committee Special Task Force*, IEEE Trans. Components, Hybrids, and Manufacturing Technology, 14:352 (1991)
53. Clegg, D., Reliability without Hermeticity (RwoH) Phase 1 Summary, Organic Coatings on Wire Bonded Devices, *11th Nat. IEPS Conf. Proc.* (1991)
54. David, R. F., and Bakhit, G., Block Copolymer Coating of Hybrid Microcircuits, *Proc. Electronic Components Conf.*, Orlando, FL (1983)
55. King, J., Qualification of Dow Corning Q3-6527 as a Particle Getter, Singer Internal Report YS57A834 (1985) and Use of Silicone Gel Particle Getters For Microcircuits Packaging, *Proc. ISHM* (1985)
56. Weber, W. D., Hopla, R. H., Roza, A. J., and Maw, T., Polyamic Esters, *Advanced Packaging* (Summer 1993)
57. Bilow, N., et al., Acetylene-substituted Polyimide Adhesives, *SAMPE Journal* (Jan./Feb., 1982)
58. Bilow, N., Acetylene-substituted Polyimides as Potential High-Temperature Coatings, ACS Symposium on Organic Coatings, *177th Am. Chem. Soc. Meeting*, Honolulu, HI (1979)
59. Rubner, R., Siemens Forsch-u Entwickl-Ber., 5:235 (1976)
60. Ahne, H., Kruger, H., Pammer, E., and Rubner, R., *Polyimides*, (K. L. Mittal, ed.), Plenum Press, New York (1984)
61. Licari, J. J., *Multichip Module Design, Fabrication, and Testing*, McGraw-Hill (1995)
62. Chakravorty, K. K., et al., High Density Interconnection Using Photosensitive Polyimide and Electroplated Copper Conductor Lines, *IEEE Trans. Components, Hybrids, and Manufacturing Technology*, Vol. 13 (1990)
63. Chakravorty, K. K., and Cech, J. M., Photosensitive Polyimide as a Dielectric in High Density Thin Film Copper Polyimide Interconnect Structures, *J. Electrochem. Soc.*, 137(3) (1990)
64. Weber, W. D., et al., Polyamic Esters, *Advanced Packaging*, (Summer 1993)
65. Himmel, R. P., and Licari, J. J., Fabrication of Large-area, Thin-film Multilayer Substrates, *ISHM Multichip Module Symp.*, Denver (1989)
66. Numata, S., and Kinjo, N., Studies on Thermal Cyclization of Polyamic Acids, *Polyimides*, (K. L. Mittal, ed.), Vol. 1, Kluwer Academic/Plenum Publishers, NY (1984)

67. Jensen, R. J., *IEEE Trans. Components, Hybrids, and Manufacturing Technology*, CHMT-7, (4):384 (1984)
68. Brown, R., *Materials and Processes for Microwave Hybrids*, Monograph, ISHM (1991)
69. HD MicroSystems, Pyralin Polyimide Coatings for Electronics, PI2610 Series-Product Information and Process Guidelines (Jul. 1998)
70. Bachman, B. J., Poly-p-xylylene as a Dielectric Material, *Proc. 1st Int. SAMPE Electronics Conf.* (Jun. 1987)
71. Sorenson, W. R., and Campbell, T. W., *Preparative Methods of Polymer Chemistry*, Interscience, NY (1961)
72. Szwarc, M. J., *J. Polymer Science*, 6:319 (1951)
73. Szwarc, M. J., *J. Chem. Physics*, 16:128 (1948)
74. Gorham, W. F., A New General Synthetic Method for the Preparation of Linear Poly-p-xylylene, *J. Polymer Science*, 4:3027–3039 (1966)
75. Gorham, W. F., Halogenated Di-paraxylylenes, U. S. Patent 3221068 (Nov. 30, 1965)
76. Gorham, W. F., Halogenated Di-paraxylylenes, U. S. Patent 3221068 (Nov. 30, 1965)
77. Gorham, W. F., Para-xylylene Polymers, U. S. Patent 3342754 (Sep. 19, 1967)
78. Gorham, W. F., Para -xylylene Copolymers, U. S. Patent 3288728, (Nov. 29, 1966); U. S. Patent 3472795
79. Lee, S. M., Licari, J. J., and Litant, I., Reliability of Parylene Films, *Proc. Met. Soc. Tech. Conf. Defects Electronic Mater. and Devices* (1970)
80. Bachman, B. J., Poly-p-xylylene as a Dielectric Material, *Proc. 1st Int. SAMPE Electronics Conf.* (Jun. 1987)
81. Loeb, W. E., and White, C. E., Parylene for Conformal Insulation, *Proc. Natl. Electronics Packaging Convention*, Long Beach, CA (Jan. 1968)
82. Licari, J. J., and Jones, E., Reliable, Low-Cost, Low-Weight, Non-Hermetic Coatings for MCM Applications, *IMAPS/JPL Conf.* (Jun. 1999)
83. E-mail communication with Andrew Brooks, Specialty Coating Systems (Mar. 2002)
84. Specialty Coating Systems Advertisement, *Circuits Assembly* (Apr. 1995)
85. Gaynor, J., and Ralston, A., AF-4 Parylene F as a VLSI Interconnect Material, *Semiconductor Int.* (Dec. 1997)
86. Licari, J. J., and Jones, E., *A Non-Hermetic Packaging Technology For Low-Cost Low-Weight Multichip Modules*, Air Force Contract F29601-97-0028, Final Report (1999)
87. Kirchoff, R. A., U. S. Patent 4540763 (Sep. 10, 1985)

88. Schrock, A. K., U. S. Patent 4812588 (Mar. 14, 1989)
89. Burdeaux, D., Townsend, P., Carr, J., and Garrou, P., Benzocyclobutene (BCB) Dielectrics for the Fabrication of High-Density, Thin-Film Multichip Modules, *J. Electronic Mater.*, 19(12) and references therein (1990)
90. Garrou, P., Polymer Dielectrics For Multichip Module Packaging, *Proc. IEEE*, 80(2) (Dec. 1992)
91. Stokich, T. M., et al., Planarization with Cyclotene 3022 Polymer Coatings, *Proc. MRS Symp.*, Vol. 308, San Francisco (Apr. 1993)
92. Foster, R., Photoimageable BCB Technology Lowers Costs For MCMs, *Solid State Technology* (Jun. 1995)
93. Rutter, E. W., et al., A Photodefinable Benzocyclobutene Resin for Thin Film Microelectronic Applications, *Proc. Int. Conf. on Multichip Modules*, Denver, CO (1992)
94. Cyclotene Processing Procedures, Dow Chemical Co. Brochure (1997)
95. Merriman, B., et al., *Proc. 39th ECC* (1989)
96. Smith, J., and Hensen, D., *Solid State Technology* (Nov. 1986)
97. Nagel, M., and Heiliger, H. M., *Institute for Semiconductor Tech. II*, Aachen, Germany.
98. www.dow.com/cyclotene
99. Denton, D. D., and Pranjoto, H., Moisture Uptake of Bisbenzocyclobutene Films for Electronic Packaging Applications, *Proc. MRS*, Vol. 203 (1991)
100. Chakrabarti, A., et al., On the Mechanical Reliability of Photo-BCB Thin-Film Dielectric Polymer for Microelectronic Applications, *Proc. Workshop on Mechanical Reliability of Polymeric Materials and Plastic Packages of IC Devices*, EEP, Vol. 25, Paris (1998)
101. Heistand, R. H., BCB: Planar and Simple, *Materials Engineering* (Mar. 1992)
102. Personal communication with Dr. P. Garrou, Dow Chemical Co. (Apr. 2002)
103. Renfrew, M. M., and Lewis, E. E., *Ind. Eng. Chem.*, 38:870 (1946)
104. Lontz, J. F., and Happoldt, W. B., Teflon Tetrafluoroethylene Resin Dispersion, *Ind. Eng. Chem.*, Vol. 44 (Aug. 1952)
105. Dang, T. D., Arnold, F. E., Alexander, M. D., and Spry, R. J., Low Dielectric Constant Polymers Developed for High-Speed Integrated Circuits, *Tech. Horizons*, 2(2) (Jun. 2001)
106. Dang, T. D., et al., Synthesis and Characterization of Fluorinated Benzoxazole Polymers with High T_g and Low Dielectric Constant, *J. Polymer Sci.*, 38:1991–2003 (2000)
107. Brenner, W., Lum, D., and Riley, M. W., *High Temperature Plastics*, Reinhold, New York (1962)

108. Lee, H., Stoffey, D., and Neville, K., *New Linear Polymers*, McGraw-Hill (1967)
109. San Diego Plastics, www.sdplastics.com/peek.html
110. Glaser, D., Floyd, D. E., and Wittcoff, H., Coatings Based on Blends of Polyamide and Epoxy Resins, *Official Digest*, 29:159–169 (1957)
111. Floyd, D. E., Peerman, D. E., and Wittcoff, H., Characteristics of Polyamide-Epoxy Resin System, *J. Applied Chem.*, 7:250–260 (1957)
112. Roberts, A. G., Organic Coatings, Properties, Selection, and Use, *Building Sci.*, Ser. 7 (Feb. 1968)
113. Designing with Zytel® Nylon Resin, DuPont Technical Bulletin (1969)
114. Martino, C. F., and Keutgen, W. A., Phenolics, *Modern Plastics Encyclopedia*, Vol. 45, McGraw-Hill, New York (1968); and Vol. 64 (1988)
115. Jost, H. D., Phenolic Resins, *Modern Plastics Encyclopedia*, Vol. 45, McGraw-Hill, New York, (1968); and Vol. 64 (1988)
116. Hockenberger, L., Preparation and Application of Solid and Liquid Organic Polysulfide Polymers, *Chemie-Ing. Technol.*, Vol. 36 (1964)
117. Morton Thiokol Product Bulletin LP (Feb. 1985)
118. Lee, T. C. P., Properties and Applications of Elastomeric Polysulfides, *Rapra Review Reports*, 9:(10), Report 106 (1999)

3

Manufacturing Technology

The manufacturing steps involved in coating an electronic part or assembly are numerous; each is essential to the performance and reliability of the end product. Among these steps are:

- Masking (if necessary)
- Cleaning
- Surface preparation
- Preparation of the coating
- Application of the coating
- Drying and curing
- Mask removal
- Inspection
- Rework (if necessary)

Numerous choices are possible for each process step and trade-offs must be made based on the part to be coated, the expected performance of the coated part, yield and cost, and equipment available. The manufacturing engineer must be concerned not only with the traditional process variables such as yield, cost, and equipment, but also with the many local, state, federal, and even global regulations concerning volatile organics, toxicity, and flammability.

3.1 MASKING

Often, not all the components of an assembly require a coating; in fact, some surfaces must be left uncoated, for example, surfaces where electrical connections are subsequently to be made. Masking can be a tedious and labor-intensive operation especially for small areas and non-flat surfaces. Adhesive-backed tape or a temporary coating, one that will not dissolve or be attacked during application of the permanent coating, can be applied manually. The maskant should be easily removable, preferably with water or a solvent that is compatible with the final coating. Maskants, such as solder maskants, are generally left permanently on printed circuit boards. Solder maskants based on epoxy resins are widely used to protect large areas of a printed circuit board from solder bridging between conductor lines. They must possess many of the electrical insulation attributes of a conformal coating and also be able to withstand solder reflow temperatures of 183° to 235°C. With the introduction of lead-free solders, even higher reflow temperatures may be needed.

Another approach to masking involves special tooling that presses against areas to be left uncoated and that can accommodate the coating of hundreds of parts simultaneously. For high production runs, dispensing a liquid maskant in selected areas using a computer-programmed dispenser is becoming more widely used.

3.1.1 Types of Maskants

Temporary maskants used to shield certain portions of an electronic module or printed circuit generally consist of liquid latex formulations in either an aqueous or an organic solvent medium. Latex maskants are solutions of natural latex rubber in water, stabilized by an alkaline compound such as ammonium hydroxide. Several precautions are indicated in using this type of maskant. The alkaline portion can inhibit the cure of some coatings that cure by a catalytic mechanism or can cause corrosion of metallization, such as copper, if allowed to remain in contact as a liquid for a prolonged time.

Synthetic polymer latexes as water solutions are also available and used where the natural latexes inhibit the curing of coatings. Heating either type of maskant will speed up the cure, but temperatures above 70–80°C

should be avoided since the mask begins to degrade above these temperatures making it difficult to completely remove.

3.1.2 Masking During Parylene Coating

Masking of vapor-deposited parylene coatings is among the most difficult of all polymer coatings because the monomer vapor has a tendency to penetrate and polymerize beneath the maskant. Pressure-sensitive tape has been used to mask off the leads of a hybrid package or edge connectors of a circuit board, but considerable time is necessary to firmly apply the tape without damaging fragile leads. Subsequent to coating, the removal of the tape also requires care not to damage the leads. Depending on the tape used, residues from the adhesive may also be left behind and must be removed by special cleaning. An alternate masking method employs a strippable liquid latex maskant. The maskant is also difficult to apply in controlled amounts in selected areas, and its removal is tedious in that the parylene overcoating grips and tenaciously adheres to the maskant. For production coating, the best technique employs special tooling designed so that a rubber or foam gasket is pressed tightly against the surface to be protected during deposition. One example of tooling designed to mask off the seal areas and pins of a hybrid microcircuit is shown in Fig. 3.1. The tooling consists of two metal plates, a bottom one that may be flat or contain cavities into which the assemblies are placed, and an upper metal plate with apertures corresponding to the cavities in the bottom plate. Two thin sheets of foam or elastomer, such as RTV silicone, also with apertures, are then inserted between the plates so that the assemblies are sandwiched between the two rubber sheets and plates and the seal areas and pins are thus protected.

3.2 CLEANING

Cleaning and preparing a substrate or an assembly prior to coating are extremely important steps, but, unfortunately, are often inadequately performed or not performed at all. Efficient cleaning and surface preparation are critical to the immediate and long-term performance of both the coating and the assembly. Residual contaminants such as ions, salts, fluxes, oils, and particulates result in poor coating adhesion and subsequent moisture absorption, corrosion, and electrical failures.

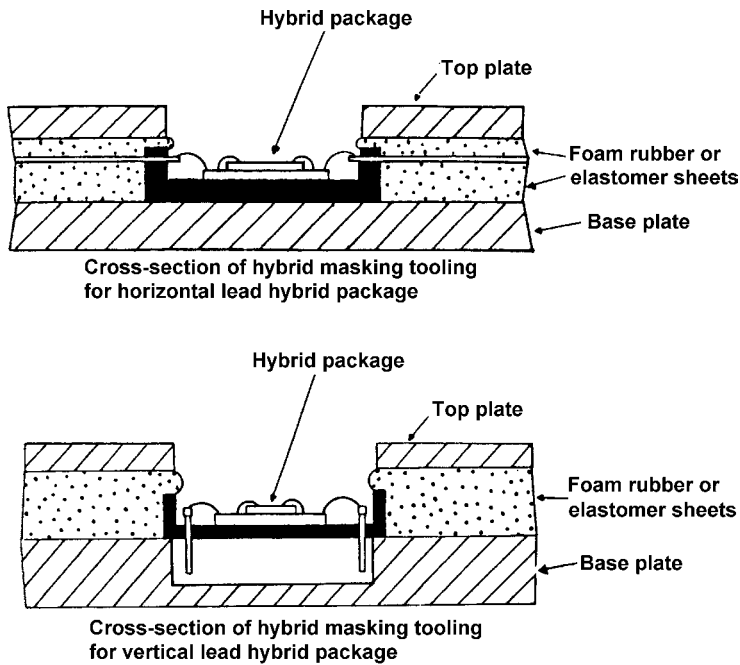


Figure 3.1. Masking tools for parylene coating.

3.2.1 Contamination Control

Although it is difficult to completely avoid contaminants during the processing and handling of electronic assemblies, contaminants can be minimized by conducting the coating operations in clean areas, such as Class 10,000 clean rooms, or better, and Class 100 laminar-flow work stations. It is also best to conduct the drying or curing operations in laminar-flow ovens. The clean room classifications are defined in Fed-Std-209*; the class number is the maximum number of particles 0.5 μm or larger that are allowed in one cubic foot of air. For example, for a Class 100 clean area, there should be no more than 100 particles that are at least 0.5 μm in size. Clean room facilities are achieved by the continuous laminar flow of room air through HEPA filters arranged either vertically or horizontally. Before, during, and

*Fed-Std-209 has been cancelled and superceded by ISO-14644-1 (Classification of Air Cleanliness) and ISO-14644-2 (Cleanroom Testing and Compliance).

after assembly, parts should be stored in dry nitrogen-purged cabinets. Pure, filtered solvents and chemicals are also necessary to assure cleanliness. Filtering solvents and coatings through 0.2 to 0.5 μm membrane filters at the point of dispensing has been found effective and useful for the more critical applications. Fingerprints, saliva, hair, and fibers, originating from assembly personnel, are among the more pervasive contaminants encountered in an electronics assembly facility. They can be prevented from getting onto circuits by having operators wear finger cots or gloves, face masks, head caps, and smocks and by the use of protective shields at the inspection stations. The segregation of particle- and oil-generating equipment, as used for machining, grinding, and polishing, from the clean room environment is extremely important. For many consumer/commercial applications, these precautions may be sufficient and only minimal cleaning prior to coating will be necessary.

3.2.2 The Nature and Effects of Contaminants

Contaminants have always been a serious problem in the manufacture and operation of electronic devices and assemblies. The control of contaminants in the manufacture of integrated circuits where dimensions are now in the submicron range is well established through the use of ultra-clean room facilities and practices. Such tightly controlled clean room facilities, however, are not necessary at the next level of assembly (die attach, wire bonding, or solder surface mounting), but cleaning and handling are, nonetheless, important. Low yields and electrical failures are not encountered immediately as with integrated circuits processing, but contaminants left on the board cause long-term corrosion or electrical failures. Contaminants most often found on electronic assemblies are categorized in Table 3.1.

Many of these contaminants are not visible or detectable until after their separation and magnification as, for example, the fiber and particles flushed from a printed wiring board shown in the photomicrograph (Fig. 3.2). Ion residues are also not readily visible, and are detectable only after extracting them with an alcohol-deionized water solution and measuring the electrical resistivity of the extracts. The lower the resistivity value, the greater the ionic concentration, usually calculated and expressed as micrograms of sodium chloride per square centimeter (see Ch. 5). The exact nature of the ions may be identified using instrumental analysis such as ion chromatography, atomic absorption spectroscopy, or flame photometry.

Identification of the particles and subsequently their source can also be made by flushing the part with a solvent, filtering, and comparing the filtered particles with photomicrographs of known particles as published in the literature.^[1]

Table 3.1. Typical Contaminants Found on Electronic Assemblies and their Sources

Contaminant	Possible Source
Fibers (nylon, cellulose, etc.)	Clothing, paper towels, other paper products
Silicates	Soil, sand, rocks, fly ash
Oxides and Scale	Oxidation products from some metals, for example, tin or silver, chips from ceramic substrates or components
Oils and Greases	From machining, fingerprints, body greases, hair sprays, tonics, lotions, and ointments
Silicones	Hair sprays, shaving creams, hand lotions, mold releases, adhesives, potting compounds, encapsulants
Metals	Slivers and powder from grinding, machining, and fabricating metal parts, solder balls and solder splatter, pieces of aluminum or gold wire, silver epoxy die attach, silicon chips from die, nickel plating residues, tin or silver from metal migration
Ionic Residues	Perspiration (ammonium compounds), fingerprints (sodium chloride), plating and etching solutions, cleaning solutions containing ionic detergents, certain fluxes such as glutamic acid hydrochloride
Non-ionic Residues	Rosin fluxes, non-ionic detergents, organic processing materials such as photoresists, adhesives
Solvent Residues	Commercial grade cleaning solvents and solutions, glycols
Ceramic and Glass	Chips of alumina or beryllia from substrates, thick film resistors, dielectrics



Figure 3.2. Photomicrograph of contaminants removed from an electronic assembly, showing a long fiber and numerous metallic and nonmetallic particles ($\times 100$).

The presence of metal particles on electronic assemblies, even in trace quantities, is especially serious. A single metal particle wedged between two closely spaced conductors can result in catastrophic failure; an electrical short immediately or, in time, corrosion and the formation of ionic species. Besides metal particles remaining from processing, as from wire bonding or solder attachment, metal particles have been detected in several commercial-grade cleaning solvents, probably introduced from storage cans or in transferring solvent from one container to another. Other non-metallic particles, such as synthetic fibers, greases, and soil minerals, most likely generated by assembly personnel, have also been isolated and identified.

3.2.3 Cleaning Solvents and Methods

Cleaning printed circuit boards during various stages in their fabrication has been treated extensively in the literature.^[2] Cleaning processes treated in this section focus mainly on those required after a printed wiring board or an electronic module has been assembled. Since solder maskants and resists are considered coatings, cleaning and surface preparation prior to their application will also be included.

Adequate preparation, cleaning, and drying of surfaces are critical to adhesion of the coating initially and during the life of the product. A proven cleaning procedure for an application should always be specified in a drawing or process specification. To establish a scientific basis for selecting a cleaning method, the coatings engineer first needs to answer the following questions:

1. What contaminants are likely to remain on the surface from previous processing and handling steps?
2. What damage can these residues cause, if not removed?
3. How can they be removed?
4. What threshold of contaminants may be allowed to remain without affecting reliability?
5. What tests can be used to measure the amounts of residues remaining and assure their removal?

These are not easy questions to answer or quantify. Elaborate studies may be required at the beginning to assure that a cleaning process, once selected and under control, will provide a reliable product. A discussion of some of the materials, procedures, and equipment used for cleaning interconnect substrates and electronic assemblies is given below.

The Nature of Solvents. Solvents may be classified as *polar* or *non-polar*, depending on whether the molecule has a dipole moment or not. A high dipole moment exists when one end of the molecule is electronegative relative to the opposite end. Water is a highly polar molecule because of the highly negative electron cloud surrounding the oxygen nucleus and its non-linear structure. Other polar solvents include alcohols, ketones, and aldehydes. In non-polar compounds, the dipole moment is zero. This may be due to the cancellation of individual dipole moments due to the symmetry of the molecule as in perfluoroethane, other fluorinated hydrocarbons, benzene, hexane, and heptane. Generally polar solvents are *hydrophilic* and completely miscible with water while non-polar solvents are *hydrophobic*

(immiscible in water). Hence, for optimum solvency, polar solvents should be used to remove polar residues, such as ionic residues, and non-polar solvents used to remove non-polar residues such as greases and oils. Cleaning solvents may thus be categorized into three groups as in Table 3.2.

Table 3.2. Solvent Types and Examples

Chemical Type	Examples
Hydrophobic	
Organic Solvents	Naphthas, xylene, toluene
Fluorocarbons	Freon TF, Freon TMC
Chlorinated Hydrocarbons	1,1,1-Trichloroethane, perchloroethylene, trichloroethylene
Hydrophilic	
Organic Solvents	Acetone, methylethyl ketone (MEK), methanol, ethanol, isopropanol
Ionic	Alkaline, acid, and some detergent-water solutions
Non-ionic	Some detergent-water solutions
Water	Tap, deionize, or distilled
Hydrophobic-hydrophilic	
	Alcohol naphtha (50:50 mixture), DuPont TWD-602 (a Freon-water emulsion containing a surfactant), Freon TA (an azeotrope of Freon TF and acetone), Freon T-E35 (a blend of Freon TF and ethyl alcohol)

Azeotrope solvents are effective since they consist of two or more solvents that form a constant boiling mixture. Their key feature is that they distill at a constant boiling temperature that is lower than either of the constituents without fractionating or changing in composition. Because azeotropes often combine polar and non-polar solvents, they are particularly efficient solvents when used in a vapor degreaser to remove a wide range of contaminants in one step. These solvents are particularly adapted for the removal of water-soluble and solvent-soluble solder fluxes.

A dramatic example of what can happen if only one type of solvent is used is shown in Fig. 3.3. When only the hydrophobic solvent was used in cleaning a printed wiring board prior to coating (Fig. 3.3a), considerable blistering of the coating occurred after humidity exposure. When both hydrophobic and hydrophilic (aqueous solution) solvents were used, no blistering occurred (Fig. 3.3b).

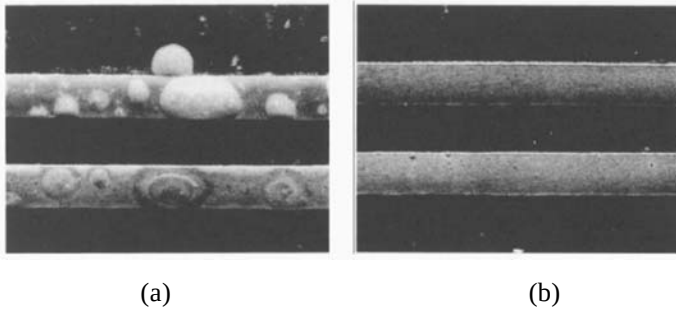


Figure 3.3. The effect of aqueous cleaning of a printed circuit board prior to coating; (a) test board prepared without aqueous cleaning, (b) cleaned with aqueous solvent.

Environmentally Friendly Solvents. Many organic solvents previously used to remove organic residues from electronic assemblies are now prohibited or restricted by OSHA and EPA because of emissions that can cause ozone depletion and warming of the atmosphere or because of toxicity. Unfortunately, some of the best solvents for cleaning electronic assemblies fall into these categories. Among these are the aromatic hydrocarbons such as xylene and toluene, chlorocarbons such as perchloroethylene, chlorohydrocarbons such as methyl chloroform, chlorofluorocarbons (CFC), and fluorocarbons such as the Freons. Actually, all organic solvents are being scrutinized for toxicity, volatiles, and ozone depletion effects. Numerous county, state, and federal regulations are in effect requiring compliance for ODP (Ozone Depletion Potential), GWP (Global Warming Potential), VOC (Volatile Organic Compounds), and HAP (Hazardous Air Pollutants). Among currently acceptable cleaning solvents are: deionized water, isopropanol, ethanol, aqueous and semi-aqueous cleaners,

methylethyl ketone, Axarel* 32, Axarel 2200, and Axarel 6100, and azeotrope mixtures such as n-propylbromide with isopropanol that remove both polar and non-polar residues. The Axarel solvents, supplied by Petroferm[®], but originally developed by DuPont, and the dichloropentafluoropropanes (hydrochlorofluorocarbons), such as AGA Chemicals AK-225 are now widely used as alternatives to CFC-113. The Axarels are semi-aqueous hydrocarbon cleaners/degreasers that dissolve and remove flux residues, lubricants, oils, and ions from printed wiring assemblies. To clean hybrid microcircuits and bare-chip microelectronic assemblies, where Freon and Freon azeotropes can no longer be used, a class of solvents based on hydrochlorofluorocarbons such as AGA Chemicals' AK-225, and azeotropes with alcohols are effective and also meet the new regulations. These newer cleaning solvents are non-ozone-depleting solvents that have high flash points.

Cleaning Mechanisms. There are essentially five mechanisms for removing contaminants from a surface:

1. *Dissolution.* This involves selecting a solvent that completely dissolves the contaminants; for example, water dissolves ionic salt residues such as sodium chloride while organic solvents dissolve oils and greases. In cleaning assemblies where components have been solder attached, it is important to know the type of flux that was used in order to choose the appropriate solvent. A rosin-based flux, for example, is best removed with organic solvents while a water-based flux requires water or water-isopropanol for effective removal.
2. *Chemical Reaction.* By this method, the contaminant reacts with a chemical solution and is transformed into soluble compounds that can then be washed away. Examples include the removal of metal oxides and scale by reacting with acids or alkalis. Chemical reactions may also be of a dry nature such as the oxidation of organic residues by ozone and atomic oxygen generated by exposure to ultraviolet light in air or oxygen.
3. *Physical.* Physical dislodging of particles involves use of a pressurized liquid or inert gas, or mechanical scrubbing,

*Axarel[®] is a registered tradename of Petroferm, Inc.

abrasion, or brushing. Examples include the removal of metal or fiber particles by a jet spray, by ultrasonic energy, or by brushing. A relatively new variation consists of jet spray cleaning with carbon dioxide in which solid carbon dioxide snow and gaseous carbon dioxide impinge on the part to dislodge and sweep away particulate contaminants.

4. *Plasma Exposure.* Subjecting the parts to an argon or oxygen plasma is an effective method of removing thin organic residues. In using a mixture of oxygen and argon, the mechanism is physical-chemical since it combines bombardment with energized atoms with oxidation of the organic residues.
5. *Vacuum Baking.* Vacuum baking removes volatile residues such as low-molecular-weight polymer species, absorbed or adsorbed processing solvents, chemicals, and moisture.

In practice, cleaning methods that employ combinations of these mechanisms are the most efficient. The basic cleaning processes based on these mechanisms may be classified as follows:

1. Aqueous and semi-aqueous immersion and spray
2. Solvent immersion and spray
3. Vapor degreasing
4. Ultrasonic immersion
5. Integrated in-line cleaning
6. Brushing, scrubbing, or swabbing
7. Plasma cleaning
8. Ultraviolet light/ozone exposure
9. Carbon dioxide jet spray

Aqueous and Semi-aqueous Cleaning. For circuit boards and other electronic assemblies, the cleanliness of the board and its assembled components before coating is essential for long-term reliability. Where solder is used to mount components, as in SMT printed wiring boards, the type of solder flux used generally defines the cleaning solvent and method that must be used since some flux residues are water soluble while others are soluble only in organic solvents or in semi-aqueous solvents.^{[3]–[5]}

Water, generally containing 5–15% of surfactants or saponifiers, is widely used and preferred for cleaning printed wiring boards and assemblies. Surfactants lower the surface tension of the water allowing it to penetrate and wet surfaces better, especially in removing flux residues from beneath flip-chip and ball-grid array devices and packages.^[6] Semi-aqueous cleaning involves the use of a mixture of water and an organic solvent such as a terpene or an aliphatic hydrocarbon and is effective in removing both organic and ionic residues. Cleaning assembled PWBs after solder attaching components and prior to conformal coating is essential when rosin-based fluxes such as RMA and RA are used. In all cases, a final rinse with deionized water should be used. Aqueous cleaning methods are among the simplest, least expensive, and safest cleaning methods, but they must often be employed with a more aggressive method. Automated pressurized spraying of aqueous, semi-aqueous, or organic solvents at different angles is used to clean printed wiring boards on many production lines (Fig. 3.4). Directing the cleaning liquid along the plane of a circuit board has been found very effective in removing residues that become trapped beneath BGA parts. Automatic spray rinsing of printed circuit boards is used by most production firms as a final step, often after the boards have been cleaned by more rigorous processes. Deionized or distilled water having a high resistivity is used to remove ionic salt-like residues. A continuous recirculation and repurification system should be used to keep the water free of organic contaminants and particulates. The water should have a resistivity of 15 to 18 megohms.

With the introduction of “no-clean” fluxes (fluxes containing low solids and leaving low residues), some PWA manufacturers have shown results equivalent to those obtained when using RMA fluxes, but without the need for aqueous cleaning. Conformal coatings applied to these boards were reported to have sufficient adhesion after 21 days at 85°C and 50% RH.^[7] Others, however, report that cleaning is still necessary even when no-clean fluxes are used.

When spray cleaning assemblies that contain fragile wire, wire bonds, and bare-chip devices, such as hybrid microcircuits or multichip modules, the spray pressure must be adjusted and controlled to avoid damaging these components. The use of water to clean circuits having bare chip devices and thin-film metallizations has always been discouraged because of the absorption of water which is later difficult to remove prior to hermetic sealing. Thus, cleaning using organic solvents or azeotropic mixtures has been the mainstay for hybrid circuits.^[8]

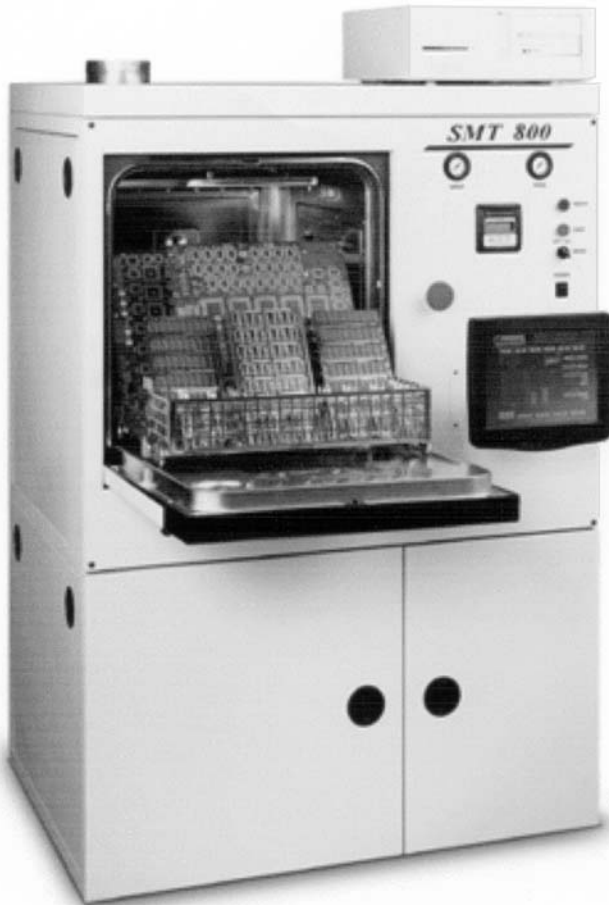


Figure 3.4. Aqueous spray cleaning system, Model SMT800. (Courtesy Aqueous Technologies.)

Spray cleaning with solvent from a squirt bottle or from an aerosol can or brushing with a solvent is used primarily after touch up or minor rework on assemblies that had originally undergone thorough cleaning. Solvent spraying with a hygroscopic organic solvent such as dry isopropanol can be used as a final drying operation to remove moisture from boards that had previously been cleaned with aqueous solutions.

Solvent Immersion Cleaning. Like spray cleaning, solvent immersion is a simple low-cost method and, for effectiveness, may be assisted by mechanical or ultrasonic agitation or be complemented by another cleaning method such as vapor degreasing. Immersion in a cascade system is an effective rinsing process. Cascade cleaning consists of successive rinses in ultrapure water (18 megohms) or in water-alcohol solutions until the resistivity of the rinse solvent stabilizes at a high value of at least 15 megohms.

Water and water-alcohol mixtures are preferred for immersion cleaning because most purely organic solvents are flammable, do not meet air pollution standards for VOC, and are expensive. However, some organic solvents are available that are non-flammable, meet VOC standards, and can be used in tightly controlled immersion equipment that minimizes loss of solvent.

Vapor Degreasing. Vapor degreasing is a widely used, effective, and benign method for cleaning electronic parts. In vapor degreasing, the part is suspended in a specially-designed chamber (commercially available) that allows vapors of a heated solvent to condense on the part's surface and flush it clean. The condensed solvent, carrying the dissolved contaminants, drips back into the pot and the process is repeated with the evaporation of fresh solvent. When the part reaches a temperature where the solvent vapors cease to condense, cleaning stops and the part is then removed. The part is washed with freshly distilled solvent as opposed to solvent immersion or other manual cleaning methods where the solvent is stagnant and soon becomes contaminated. Cooling coils surround the upper portion of the chamber to prevent solvent vapor from escaping into the atmosphere. Vapor degreasers must now comply with strict EPA regulations pertaining to both the vapor degreasers and the use of organic solvents. The National Emissions Standards for Hazardous Air Pollutants (NESHAP) requires that batch vapor solvent cleaning machines and in-line vapor degreasers meet emission standards implementing Sec. 112 of the Clean Air Act.^[9] Halogenated solvents such as methylene chloride, perchloroethylene, trichloroethylene, chloroform, and carbon tetrachloride are among 189 that have been identified as hazardous air pollutants (HAP).

Several variations of vapor degreasing exist. The basic method utilizes the vapor zone alone and is efficient only when small amounts of oil or grease residues are present. A more efficient variation alternates vapor degreasing with a liquid spray (Fig. 3.5). The part to be cleaned is suspended in the solvent vapors until condensation ceases, then is sprayed with fresh solvent for approximately 30 seconds and returned to the vapor. Azeotropes,

constant temperature boiling mixtures of a hydrophobic and hydrophilic solvent, are popular because they are capable of removing both the salt-like and grease-like contaminants in a single step. Detailed instructions for vapor degreasing using a particular solvent may be obtained from the solvent supplier. Special attention is being paid to reducing the amount of solvent that is lost through evaporation. Secondary or subzero cooling coils in the upper portion of the chamber and the use of automated equipment reduce emissions.

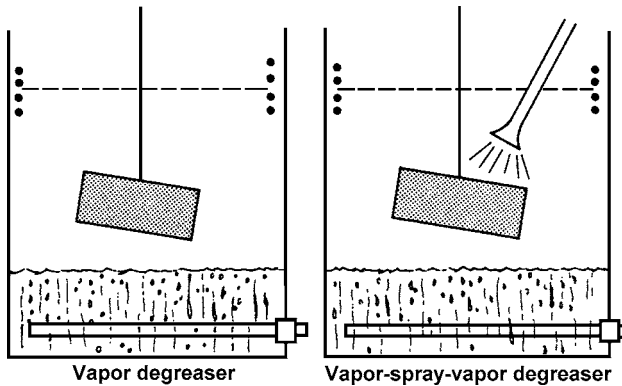


Figure 3.5. Diagrams of two types of commonly used vapor degreasers.

The most widely used solvents for vapor degreasing have been 1,1,1-trichloroethane (methyl chloroform), Freon TF, and azeotropes of chlorofluorocarbons, but these solvents are being rapidly replaced because of concerns about emissions and ozone depletion. Some alternate acceptable solvents include AK-225* (pentafluorotrichloropropane), azeotropes of AK-225* with ethanol (AK-225 AES), azeotrope of AK-225 with cyclohexane and ethanol (AK-225-T), and an azeotrope of n-propylbromide with isopropyl alcohol (Lenium ES**). As with other cleaning solutions, the compatibility of these new solvents with the electronic assemblies should be verified before specifying them for production use.

*AK-225, AK-225 AES, and AK-225-T are tradenames of AGA Chemicals, Inc.

**Lenium ES is a registered trademark of Petroferm, Inc.

Ultrasonic Immersion. One of the most effective cleaning methods entails immersion of the part in an ultrasonically agitated solvent bath. The basic equipment consists of an ultrasonic transducer, an ultrasonic power supply or generator, and a solvent tank. The generator converts electrical energy from an ac line at 50–60 Hz to electrical energy at the desired ultrasonic frequency while the transducer converts the electrical energy into mechanical vibrations. The transducer expands and contracts at the same frequency generating the desired ultrasonic vibration. Piezoelectric or magnetostrictive transducers are employed to generate the ultrasonic energy. Sound vibrations at frequencies greater than 20 kHz (usually 20 to 50 kHz) cause *cavitation*—the rapid formation and sudden collapse of thousands of microscopic bubbles in the solvent or cleaning solution. The transfer of this energy to the part results in a very strong scrubbing action.^[10] Because of the high energy imparted to the solvent, contaminants are rapidly and easily dislodged even from crevices and difficult-to-reach areas.

Ultrasonic cleaning is a very rapid process, requiring only a few minutes per part and lends itself well to automated procedures. Almost any solvent or solution may be used for the ultrasonic bath. Many solvents and cleaning solutions are commercially available and others have been formulated for the removal of specific contaminants. The choice of solvents is limited only by their toxicity, flammability, and vibration damping characteristics. Some liquids damp ultrasonic vibrations more than others. Concentrated detergent solutions and acetone, for example, have high damping characteristics and are not as effective as the Freons. For the most efficient operation, the solvents (especially organic solvents) should be maintained at about 40°C. Cooling may be necessary because ultrasonic agitation heats the solvent after several hours of continuous operation.^[11] Aqueous detergent solutions or alkaline solutions are more effective at temperatures of 40° to 60°C in which cases the heat generated by the bath itself will be sufficient to maintain these temperatures.

Although ultrasonic cleaning is one of the most effective cleaning methods, it has several limitations that should be recognized. Because of its high efficiency, the bath becomes contaminated and the solvent must be filtered or purified frequently and replaced periodically. Second, the ultrasonic vibration forms standing waves in the cleaning solvent. This phenomenon causes areas of concentrated energy called “hot spots” and areas of low energy called “cold spots.” The consequences are erratic cleaning and possible part damage. To avoid this, some manufacturers of ultrasonic equipment use either multiple transducer elements or an electronic sweep that produces random harmonics thereby eliminating the hot and cold spots.

Finally, precautions should be taken when ultrasonically cleaning circuits that contain fragile components. Glass diodes and other glass-sealed semiconductor devices may fail mechanically or electrically due to cracking of the glass or separation of the leads. Other potential failures involve distortion or breakage of fine one-mil-diameter wires and separation or weakening of wire bonds in hybrid microcircuits and damage to glass-to-metal seals in hermetically-sealed packages, rendering them non-hermetic. In these cases, even if failures do not occur immediately, there is always the risk of long-term effects due to the ultrasonic stresses.

Integrated In-line Cleaning. For more effective cleaning, several cleaning methods may be used in sequence. One sequence consists of vapor degreasing, immersing in a heated ultrasonic solvent, and lastly spray rinsing with fresh solvent and drying. Ultrasonic vapor degreasing is performed in an integrated multiple-compartment system consisting of boiling solvent sumps and ultrasonic rinse sumps. This process is easily automated by employing a robotic arm controlled by a microprocessor (Fig. 3.6). To prevent contamination of parts due to particles, the ultrasonic vapor degreaser continuously filters the solvent. The degreaser may also be equipped with water separators to remove water that is dragged into the tank. Water separators are particularly important when using azeotropes of hydrophobic-hydrophilic solvents that tend to absorb moisture from the air. The integrated system may also include cleanliness testing equipment such as the Omega-meter[®].

Brushing and Scrubbing. Brushing or scrubbing with aqueous or semi-aqueous solutions should be used only for cleaning substrates and printed circuit boards prior to assembly, or assembled printed circuit boards that are considered rugged enough to withstand the scrubbing action. Conveyorized automated scrubbing is usually used for printed circuit boards at various stages prior to applying solder maskants. A variety of contaminants; ionic, organic, and particulates, can remain on the PCB prior to the application of a solder maskant. Some particulates can become embedded either in the laminate or in the metallization and be difficult to remove. Abrasion and vigorous scrubbing are used to dislodge these particles. Among commonly used effective cleaning methods are pumice scrubbing, bristle brush scrubbing, and applying an abrasive slurry by a pressurized spray. It should be noted, however, that such aggressive cleaning can only be used on PCBs prior to solder maskant application and prior to component assembly. Pumice scrubbing leaves a copper surface clean of oxides and sufficiently roughened to promote good solder mask adhesion, but adequate

rinsing is required since pumice residues can cause subsequent peeling or blistering of the solder maskant.

To remove ionic salt residues remaining from acid or alkaline plating and etching processes, aggressive water rinsing and drying are necessary. Manual brushing or swabbing with organic solvents is often used after touch up or rework.

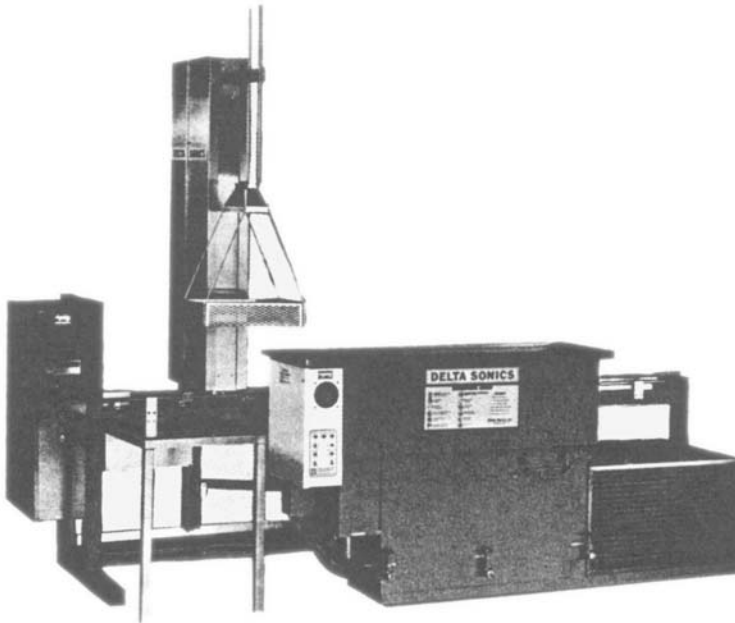


Figure 3.6. Ultrasonic vapor degreaser with robotic conveyor system. (Courtesy DeltaSonics, Inc., now Branson Ultrasonics Corp.)

Plasma Cleaning. Cleaning and surface preparation by exposing a part to a gaseous plasma is a proven process that has been used in the electronics industry for over twenty years. Plasma cleaning is especially effective in removing thin residues of tenacious organic materials such as silicones, mold releases, oils and greases from ceramic, metal, or plastic surfaces. Plasma cleaning is a dry process in which a gas or mixtures of gases, primarily argon and oxygen, are energized by powering with a RF generator at 13.56 MHz and several hundred watts. A key benefit of plasma

cleaning over conventional cleaning is the absence of solvents, thus avoiding environmental concerns about the handling and disposal of organic solvents. The effectiveness of removing grease-like residues from a variety of surfaces has been demonstrated by reduction in the contact angle of a water-drop. After plasma cleaning, the contact angle for water on a copper surface was reduced from 88° to 31.7° , on aluminum from 64.5° to 32° , and on an epoxy surface from 85° to 22° .^[12]

In the assembly of hybrid microcircuits, plasma cleaning is often used after die attachment and prior to wire bonding to remove bleed-out that may occur from the epoxy die-attach adhesive during its cure.^[13] Plasma can be used as the final cleaning step to enhance the adhesion of coatings and adhesives. Other applications involve improving the wettability of metal surfaces for better solderability, stripping of organic films such as photore-sists, and removal of organic coatings for rework. The most commonly used plasmas are those generated from argon, oxygen, or mixtures of oxygen and argon, but other oxidizing gases such as tetrafluoromethane and sulfur hexafluoride can also be used. An oxygen plasma works by forming ozone which, in turn, forms high-energy monatomic oxygen.^[14] The reactive oxygen oxidizes organic residues such as hydrocarbons converting them to volatile products primarily water and carbon dioxide. Tetrafluoromethane works on the same principle; the high-energy plasma consists of CF_3 and fluorine free-radicals that react with the organic residue decomposing and converting it into gaseous species. An argon plasma, although about 50% slower than an oxygen plasma, is more benign, physically breaking up organic molecules by impingement. Argon is also inert making it safer for sensitive electronic devices and plastic substrates. Although very effective in removing organic residues, plasma cleaning is not as effective in removing inorganic or salt-like residues. On the contrary, plasma may embed these contaminants further into the substrate. Salt-like and ionic residues are still best removed by aqueous or semi-aqueous spray or immersion methods.

Because of the wide variety, functions, and sensitivities of semiconductor devices, plasma cleaning should first be tested to assure that devices are not damaged electrically or physically. However, equipment is available that is capable of generating downstream electron-free plasma that avoids electron damage even to sensitive CMOS devices. Equipment is available that ranges from small laboratory models with 6-inch-diameter chambers to large capacity production units (Fig. 3.7).



Figure 3.7. Plasma cleaner. (Courtesy Glen Technologies, Div. of Yield Engineering Systems.)

Ultraviolet Light/Ozone Exposure. Surfaces can be cleaned by irradiating them with ultraviolet light in the presence of air or oxygen. A low pressure quartz-mercury vapor lamp that generates ultraviolet radiation at the 254 and 185 nm wavelengths is used. Organic residues absorb at these

wavelengths, become excited, and dissociate. Simultaneously, the uv radiation excites and converts the oxygen into ozone and monatomic oxygen. These highly reactive species quickly react, oxidize, and volatilize traces of organic contaminants such as greases, oils, silicones, photoresist, and rosin fluxes. The oxidation products are volatile gases primarily carbon dioxide, carbon monoxide, nitrogen, and water. Ultraviolet/ozone cleaning is a simple, inexpensive, and fast method of obtaining ultra-clean surfaces, especially as a final cleaning step following a more traditional cleaning process. A further benefit for electronics is that the cleaning process takes place at room temperature in a matter of a few minutes. In cleaning residues from a plastic surface, as from a solder maskant, the exposure time to uv/ozone is critical since extended time will degrade the plastic surface.^[15]

Carbon Dioxide Jet Spray Cleaning. In carbon dioxide (CO_2) jet spray cleaning, also known as “snow cleaning,” a jet spray of solid carbon dioxide “snow” and gaseous carbon dioxide impinge on the part and dislodge and sweep away particulate contaminants. The snow is generated from liquid pressurized CO_2 as it expands rapidly through specially designed nozzles. The CO_2 is constrained to pass through a triple point where solid, liquid, and gas co-exist. At the triple point, the aerosol turns into solid CO_2 , creating “snowflakes.” The velocity, density, and size of the snowflakes can be controlled to provide aggressive, moderate, or benign cleaning conditions. For example, high-velocity snowflakes, approximately 1–2 μm diameter, provide aggressive cleaning while low-velocity flakes 0.5 μm in diameter are used for benign cleaning of precision parts such as optics or hybrid microcircuits containing fine wire bonds.^[16] Snow cleaning is a relatively new process developed as an alternative to using CFC and other organic solvents that are environmentally damaging, for example, ozone depleting. Other advantages of snow cleaning are:

- Leaves no residues, essentially a dry process
- Removes submicron particles
- Can remove thin films of greases and oils
- Cleans rapidly in seconds rather than minutes or hours
- Can be used on very sensitive surfaces

One precaution, however, is that ambient moisture will condense on the cleaned surfaces because the parts cool during cleaning. To prevent this condensation, inert ambient enclosures may be used.

The equipment for snow cleaning is relatively simple and inexpensive. Cylinders of pressurized CO₂ and one of a variety of hand-held or automated spray guns are commercially available.^{[17]–[19]}

3.3 SURFACE PREPARATION

Subsequent to cleaning, other processes may be required to prepare the surface for coating. Among these are thorough drying to remove any residual water or organic solvents used in cleaning and vacuum baking to remove potential outgassing, especially from plastic substrates. Other surfaces may have to be primed or chemically etched to achieve the best adhesion of the coating.

3.3.1 Drying

Drying the parts after cleaning is important in assuring adhesion of the coating. Parts that have been subjected to aqueous cleaning, especially plastic parts, absorb water which, if not removed, results in poor adhesion and blistering of subsequently applied coatings. Drying may be performed using forced dry air or nitrogen, oven baking for several hours at temperatures up to 95°C or by vacuum baking at lower temperatures. Other drying methods involve gettering the moisture by final spraying or rinsing with a desiccating organic solvent such as dry isopropanol or storing the parts over a desiccant.

3.3.2 Vacuum Baking

Besides being a method of drying, vacuum baking is also effective in removing low-molecular-weight compounds, unreacted constituents, and other volatile species, thus stabilizing the surface and avoiding outgassing after the coating has been deposited and cured. Vacuum baking is commonly used to remove moisture from hybrid microcircuits and multichip modules prior to hermetic sealing in order to meet the 5,000 ppm residual moisture requirement of MIL-PRF-38534. Vacuum baking is also effective in

removing moisture from plastic-coated or encapsulated integrated circuits prior to exposure to high-temperature solder reflow, thus preventing the sudden evaporation and expulsion of water which generates internal stresses and cracking,^{[20][21]} a phenomenon referred to as “popcorning.”

3.3.3 Priming

Many coatings can be applied directly to a cleaned surface and provide adequate adhesion. Others require a separate primer or an internal primer to promote adhesion to a diversity of surfaces. Primers are generally not necessary for epoxy coatings because of their high polarity and affinity for most surfaces. In fact, solvent-thinned epoxies have been used as primers for other polymer coating types. Primers are often required for one-part and two-part RTV silicone coatings. Primers are generally low-solids content, solvent-based, and air drying and can be applied by spraying, dipping, spin coating, or brushing. To be most effective, primers should be applied in very thin layers. Flammable hydrocarbon solvents are used in many primers and safety measures should be taken to prevent ignition.

3.3.4 Surface Etching

Some surfaces have traditionally been difficult to adhere to regardless of the coating used. Notorious among these are Teflon, other fluorocarbons, gold, and other noble metals. It has been necessary to chemically etch Teflon substrates or Teflon-insulated wire to increase its wettability and adhesion. Organic solvent solutions of sodium naphthalene complex or of metallic sodium are Teflon etchants that are effective and commercially available.* Adequate adhesion to gold, besides using primers, may require abrasion to roughen the surface.

3.3.5 Chemical Surface Preparation

The formation of oxides on metal surfaces may either be beneficial or detrimental to adhesion. As an example, for the outer copper conductor

*For example, Tetra-Etch[®], a tradename of W. L. Gore Associates.

surfaces, it is desirable to have a highly reactive oxide-free surface to obtain the best solder wettability. Surface copper oxide can react with and be dissolved in solutions of hydrogen-peroxide-sulfuric acid, cupric chloride, or ammonium-potassium persulfate. In other cases, an oxide is desirable, especially in enhancing the adhesion to an epoxy laminate or to a solder maskant.

3.4 COATING PREPARATION

Besides cleaning and preparing surfaces prior to coating, several issues related to the preparation and condition of the coating material itself are critical to the reliability of the final coated part. Among these are the shelf life of one-part systems and the pot life after mixing of two-part systems. Conditions of mixing and deaerating of two-part coatings, chemical and viscosity changes during storage or application, and contamination occurring during transfer of the coating also affect the performance of the coated part.

3.4.1 Shelf Life and Pot Life

Shelf life is the length of time that a coating can be stored in an unopened container and still be usable and meet all engineering and reliability requirements. As a general rule, manufacturers recommend a shelf life of one year at room temperature or lower. Storage conditions, especially high temperatures, may dictate shorter shelf lives.

Pot life is an even more critical manufacturing issue than shelf life. The pot life of a coating is the length of time a coating can be used after a container has been opened or after a two-part system has been mixed. The pot lives of two-part systems such as many epoxies, once mixed, can be extremely short—hours or even minutes. In such cases, rapid automatic mixing and dispensing equipment must be used. Once the can is opened, it is best to use up all the coating within a short period of time since changes such as premature polymerization, increases in viscosity due to solvent evaporation, air inhibition or moisture inhibition begin to occur. A short pot life can lead to a rapid increase in viscosity and substantial material waste.

3.4.2 One-part versus Two-part Systems

Mixing two-part systems requires care in removing air entrapped during the mixing process. A commonly used procedure involves deaerating by subjecting the mixture to a moderate vacuum (up to 28 in. Hg) in a vessel that has at least four times the volume of the mixture. The vacuum is maintained until air bubbles are no longer visible. The vacuum may be broken and reapplied several times to assure complete removal of air bubbles. One-part systems are more desirable from a manufacturing standpoint because no weighing, mixing, or deaerating are required, and pot life is generally not an issue.

3.4.3 Filtering

Besides particles that are generated by personnel and equipment in an assembly room, cleaning solvents and solutions may contain particles that can cause pinholes in the coating. If so, most particles can be removed by filtering, for example, through a microporous membrane filter, at the point of dispensing.

3.4.4 Storage

Ultraviolet-light-sensitive coatings such as photoresists and photodefineable dielectrics should be stored in brown bottles and processed under yellow light. Application and processing of these coatings are best done under clean-room conditions or in a laminar-flow enclosure. Thin coatings are susceptible to pinholes due to specks of dirt or ambient particles.

3.5 APPLICATION METHODS

Because of the wide variety and complexity of electrical and electronic parts, numerous coating application methods are now in use. Coating application processes range from the simplest and most common, low-cost spraying and dipping methods, to the unique higher-cost vapor deposition and selective dispensing methods. The coating of micron-size semiconductor junctions or the application of ultrathin continuous dielectric

layers on the foil wrap of a capacitor, on one extreme, to the impregnation of huge motor rotors and stators or the coating of thousands of feet of wire, at the other, has necessitated the development of a wide variety of deposition and curing techniques. Spraying, dipping, brushing, flow coating, fluidized bed, vapor deposition, and selective dispensing are used to coat complex and irregular-shaped parts while screen printing, spin coating, extrusion coating, curtain coating, meniscus coating, and roller coating are used to coat large flat panels prior to assembling components. In addition, within each category, there are several variations. Some of these processes, their advantages, limitations, and typical applications are summarized in Table 3.3 and discussed below.

3.5.1 Spray Coating

Spray coating is the most widely used method for applying organic coatings to electronic parts. Spraying includes not only the commonly used compressed-air vaporization method, but also airless pressure spray, hot flame spray, hot vapor impelled spray, electrostatic spray, dry powder resin spray, and even the ubiquitous aerosol can spray.

A variety of air-pressure spray equipment is commercially available, but, in their use, each coating application must be customized by careful adjustment of the spray equipment and viscosity of the coating. Diluting the coating is often necessary for optimum spray characteristics. To avoid backstreaming of oil and to assure a supply of clean dry air, an oil trap should be utilized on the compressed air lines.

If the part to be sprayed has a high density of components, it may be necessary to spray the coating on several different planes to ensure complete coverage both over and under the components. One pass may be sprayed across the entire surface of the part holding the spray gun at an angle of 45° to the part. The part is then rotated 90° after each pass, and spraying repeated in all four directions. If coverage under the components is still inadequate, it may be necessary to dip coat the unit with a highly diluted coating (50% or more) prior to spraying. The viscosity of the diluted coating should be low enough to prevent filleting or bridging of the components which can induce stresses. With most coatings, it is difficult to avoid pinholes or other imperfections in the coating in the first pass. Pinholes or pores that penetrate through the coating can be eliminated or minimized by applying multiple coats of the same coating, reducing the probability that a single

Table 3.3. Comparison of Application Methods

Method	Advantages	Limitations	Typical Uses
Spray	Fast, adaptable to various shapes and sizes, low cost	Material loss from overspray; Difficult to obtain complete coverage on complex parts and to obtain uniform thickness; solvent emissions	Printed circuit assemblies, electronic modules, components, electronic enclosures, and chassis
Dip	Low cost; good coverage even on complex parts	Viscosity and pot life of coating bath must be controlled, bath can become contaminated, rate of withdrawal is critical; masking; solvent emissions	Ceramic and plastic printed circuits, fungus and moisture protection, wire insulation
Screen Print	Deposits coating in select areas through a mesh screen; good pattern definition and thickness control	Requires flat smooth surface; requires specially formulated thixotropic paste coatings	Solder maskants and etching maskants for circuit boards, interlayer dielectric, overglaze, markings
Spin Coat	Reproducible, ultra-thin coatings, uniform thickness	Requires flat smooth surfaces, limit on size and shape of substrate; high material loss	Photoresists for semiconductor and thin-film circuit fabrication; interlayer dielectric for multilayer thin film circuits; flat panel displays
Vacuum Impregnate	Complete coverage of intricate, closely spaced parts; seals fine leaks and pores	Requires vacuum or pressure cycling or both	Coils, transformers, other magnetics, sealing porous structures; metal castings

(cont'd.)

Table 3.3. (cont'd.)

Method	Advantages	Limitations	Typical Uses
Fluidized Bed	Thick coatings can be applied in one dip; uniform coating thickness; use of dry powder materials saves cost of solvent and solvent emissions	Requires preheating the parts above the fusion temperature of the coating; temp. may be too high for some electronic parts	Motor stators, heavy-duty electrical insulation on castings; insulation on metal substrates for circuit boards and heat sinks
Vapor Deposition	Ultra-thin pinhole-free films; excellent coverage over complex, high-density modules; high purity	Specific for parylene series of coatings; masking and rework are difficult; requires special deposition equipment	Printed circuit boards, immobilizes loose particles in hybrid microcircuits, moisture barrier, dielectric, and insulator
Extrusion	Low material waste compared to spin coating; uniform thicknesses	Requires special equipment; requires flat smooth surfaces	Photoresists for semiconductor fabrication and thin-film microcircuits, flat panel displays, interlayer polyimide dielectrics for multichip modules
Automated Selective Dispensing	Automated for high throughput; coats selective areas; avoids waste	Special equipment; high cost	Printed wiring boards and assemblies
Electrostatic Spraying	Efficient coverage and use of coating on complex parts; can be automated	Cannot be used on ESD-sensitive components	Heat sinks, electronic enclosures, open-work grills, and complex parts
Brushing	Very simple	Labor intensive; not for high reliability or production parts	Used primarily for touch up before or after rework or to selectively apply protective coatings to markings

pinhole will form a moisture path from the ambient to the surface of the part. A second coat also provides better coverage over solder spikes. Figures 3.8a and 3.8b illustrate, on an exaggerated scale, the formation of pinholes and the stretching of the coating over sharp edges and protrusions after a single coating application; Fig. 3.8c illustrates a substantial reduction in the number of contiguous pinholes after a second coating; and Fig. 3.8d shows the same component after three coats with no pinholes protruding to the surface.

Epoxy and polyurethane coatings provide a high degree of chemical and solvent resistance, but have heretofore been difficult to apply in production because they are generally two-part systems and have relatively short pot lives. However, spray equipment is now available that facilitates the application of these two-part systems. The equipment proportions and mixes the resin and hardener continuously and feeds the mixture to the sprayhead or extrusion nozzle.

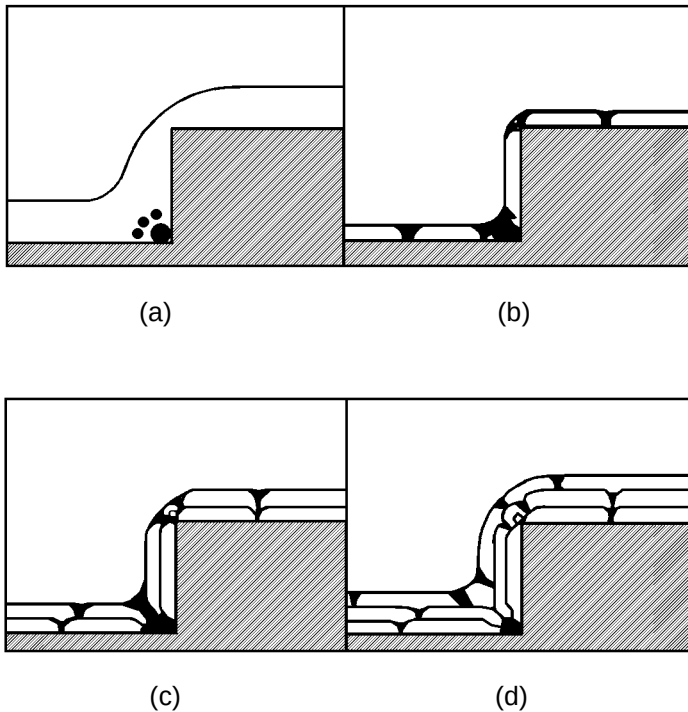


Figure 3.8. Reduction of pinholes by using multiple coats; (a) wet coat, (b) dry coat, (c) two dry coats, (d) three dry coats.

3.5.2 Pressurized Liquid Spray

Most spray methods are based on the principle of atomizing the coating into a fine mist that is then directed to the part to be coated. Atomization is accomplished by using compressed air, pressurized volatile solvents, or a high velocity jetstream. With the proper technique, a thin continuous wet layer of coating may be deposited without drips, sags, “curtains,” “orange peel,” or other imperfections. A skilled spray operator can apply a uniform coating and inspect and touch up defective areas during the process. In coating substrates, such as circuit boards, that have discrete components, the desired thickness can be achieved by spraying from four different directions to cover both the top and all sides of the components and force the coating beneath the components. Avoiding pinholes, skips, and voids should be a major consideration in applying environmental protective coatings. Turntables, either hand or power rotated, are useful in orienting the work for directional spraying. Conveyors may be utilized to move parts past automatic sprayheads, as in fully-mechanized spray lines. All spray coating should be done in a well-ventilated spray booth that exhausts the overspray and solvent vapors, preferably to a fume or solvent trap system. Fumes may be noxious, flammable, and even toxic after prolonged inhalation.

3.5.3 Airless Spray

A disadvantage of pressurized spraying is the tendency for the blown cloud of atomized coating to be swirled out of recesses, holes, and corners by the accompanying air stream, leaving these areas lightly coated or bare. Airless spray equipment avoids this problem since it does not depend on atomization by high-velocity air, but produces a spray by forcing the material under high pressure through tiny-orifice nozzles. The coating is circulated continuously in the storage system and may be heated to reduce its viscosity and volatilize the solvents more rapidly. Airless spraying is highly efficient, especially for coating parts having numerous recesses, cavities, or projections.

3.5.4 Aerosol Spray

The aerosol spray can is a convenient way to package and dispense coatings, and almost every conventional paint, varnish, enamel, or one-part

coating has been successfully packaged in an aerosol can. Automatic packaging equipment capable of packaging over 100 cans per minute has greatly reduced the price per can. Aerosol spraying is most economical for touchup and for priming or coating a few parts. For high-volume production, automated spray and dipping are the most economical methods. A limitation of aerosol packaged coatings for electronics is that two-part systems, as are most epoxies and polyurethanes, cannot be packaged. At present, the aerosol method is useful only for one-part coatings such as acrylics, vinyls, some silicones, epoxy-acrylics, oil-modified polyurethanes, and some moisture-cured polyurethanes.

3.5.5 Electrostatic Spray Coating

Several modifications of the spray method have been developed and are commercially available. Of these, the electrostatic spray process, originally developed by Ransburg ElectroCoating Company (now ITW Ransburg), is used extensively to coat parts that have intricate shapes or a high proportion of open areas. Electrostatic spray coating, also known as powder coating, consists of depositing negatively-charged polymer particles onto a metal surface. The powder particles are rendered electrostatic as they are propelled through a diffuser at the front of the spray gun and are then rapidly attracted to the part that is grounded (Fig. 3.9). Subsequent curing or fusion of the coating is performed in as little as 20–60 seconds at 205°C or at lower temperatures for longer periods of time. Some coatings may be cured by uv irradiation. Well over 95% of thermosetting powder coatings are applied by electrostatic spraying.

Powder coatings, that may be epoxies, polyesters, epoxy-polyesters, or acrylics, are applied with an electrostatic spray gun. The power supply operates at 110 volts, 60 cycles, with single-phase voltage and power consumption of approximately 71 watts. The electric current is 210 microamps from the exposed voltage contact when it is grounded. The power output voltage does not exceed 90,000 volts dc when the gun is actuated. Air used to propel the powder is first passed through a drying bed to remove moisture. The powder is emitted from the nozzle by a rotating diffuser driven by a small air motor located in the handle. Adequate safety features are incorporated into the equipment to protect the operator from electrical shock. Coatings ranging in thickness from 1 mil to over 50 mils may be applied, depending on the plastic powder selected. In general, the same

proprietary powder coatings used for fluidized bed or powder spray applications can be used for electrostatic spray. Some coating types and their properties are given in Table 3.4.^[22]

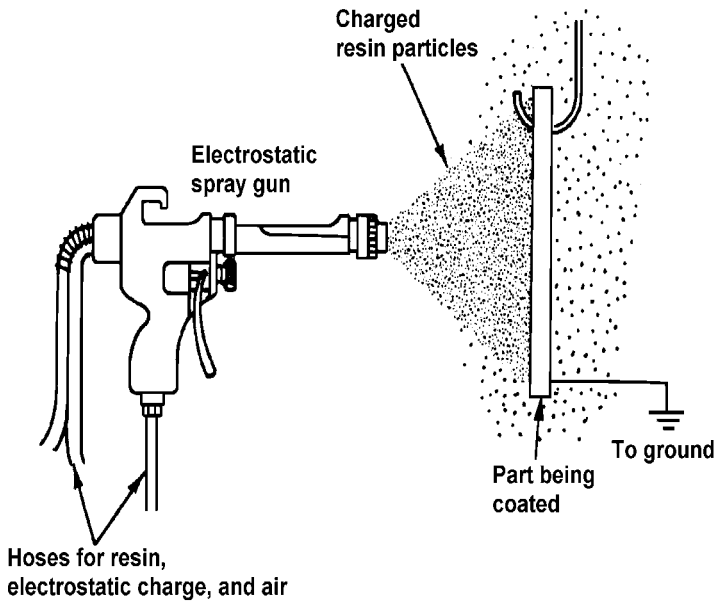


Figure 3.9. Electrostatic spray coating.

The advantages of the electrostatic spray process over other spray processes include high deposition efficiency (very little material is lost from overspray) and the high film buildup that is achievable in one application, reducing both time and cost. Coating material savings of 25–50% over conventional spraying are not uncommon. The process is also adaptable to automated production, hence less susceptible to human errors.

Electrostatic spraying lends itself well to coating a wide variety of metal articles, especially for commercial use. In the electronics industry, it may be used for electrical insulation and corrosion protection of heat dissipators (Fig. 3.10), metal brackets, black-box chassis, circuit board housings, and motor windings. Electrostatic spraying is not recommended for coating assembled electronic circuits because of the potential for damage due to the electrically charged particles and the high temperatures required to cure or fuse the particles.

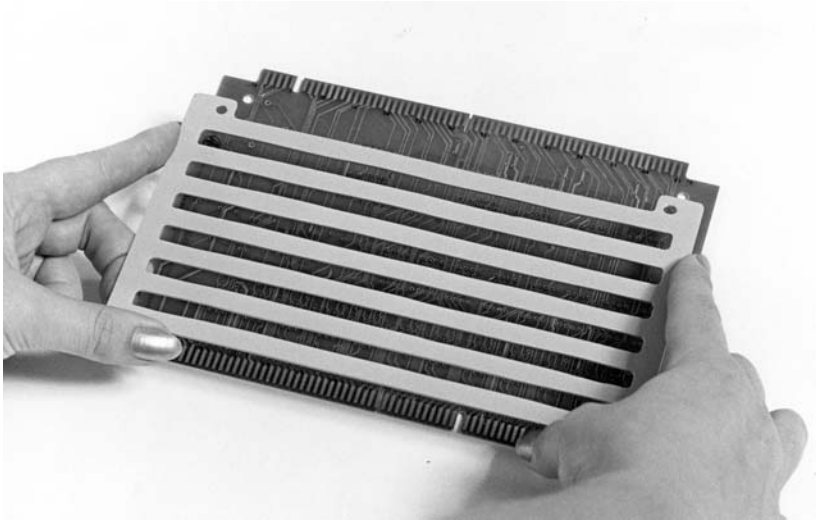


Figure 3.10. Heat-sink rail, insulated with electrostatically-coated epoxy.

3.5.6 Hot-melt Flame Spraying

In hot-melt flame spraying, a cloud of powdered resin suspended in air is introduced into a special spray gun and is melted by being blown through a flame-shrouded nozzle of the spray gun. The melted plastic solidifies immediately on contact with the object being coated. This technique is limited to plastics that are stable above their melt temperatures. The applied coatings are generally thermoplastic types such as polyethylenes, polypropylenes, and polytetrafluoroethylenes. Techniques have also been developed for spraying some unstable polymers that have sufficiently long induction periods before decomposition occurs.^[23]

3.5.7 Dip Coating

Dip coating is an effective low-cost production method for coating electronic parts or assemblies that are not too bulky or irregular in shape (Fig. 3.11). The parts are immersed into a dip tank containing the liquid coating, then withdrawn at a controlled rate and cured. In production equipment, the parts are conveyORIZED and automatically dipped into the coating then passed through an in-line infrared radiation or convection oven for curing. Dip

coating has an advantage over spray coating in assuring coverage of all surfaces and crevices. It is most suitable for one-part polymer coatings that have sufficiently long pot lives. Its use in the electronics industry can be limited because most high-reliability coatings are two-part systems and their pot lives after mixing, in some cases, are only fractions of an hour. Even in systems with long pot lives, polymerization and/or evaporation of solvent results in continual viscosity changes that cause variations in thickness and adhesion of the subsequently cured coating. Techniques used to maintain a stable two-part dip bath include replenishing solvents lost by evaporation to maintain constant viscosity and refrigerating the dip bath to extend its pot life.

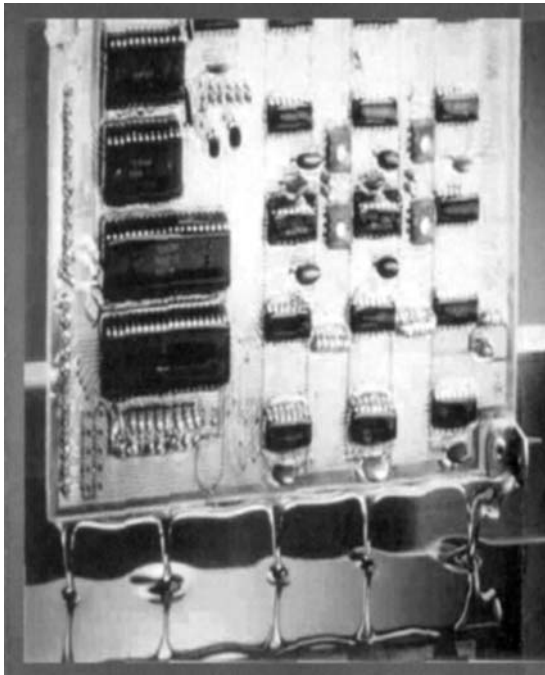


Figure 3.11. Printed circuit board assembly dip coated with silicone. (*Courtesy Dow Corning.*)

The rate of withdrawal of the part from the tank is yet another factor critical for good results. A slow withdrawal rate is best because it produces uniform thickness. Rapid withdrawal produces coatings that are thin at the top and thick at the bottom. In such cases, a bead of coating may remain at

the bottom edge of the part that blisters on curing. Edge beads, also called tears, are best removed prior to curing by blotting or wicking the excess coating with an absorbent material. Adequate air drying to remove solvents is recommended since entrapped volatiles cause the coating to blister during subsequent oven cure. Optimum dry conditions (degree of dryness and amount of residual solvent left in the coating) may be established by analytical tests such as weight loss versus time and infrared spectrometric analysis.

With some systems, hot dipping may be used to improve wettability and minimize pinholes. Hot dipping consists of preheating the part to approximately 75°C and dipping it into the coating bath maintained at room temperature. This technique presupposes that the part can tolerate the preheat temperature. Because of the repeated exposure of the bath to the preheated parts, care must be taken to maintain the bath at a relatively constant viscosity. Preheated parts may be dipped in vinyl plastisol which becomes gelled by the heat leaving a solid layer on the surface. An alternate method entails dipping the part at ambient temperature into a molten resin. The coating solidifies on removal from the heated bath. Resins used for hot dip coating are normally thermoplastic types. In all cases, contaminants from the parts that are dipped can build up in the coating bath through long or heavy use and thus the bath should be monitored and replenished periodically. With high-viscosity coatings, such as the 100% solids types, air bubbles may become entrapped when the two components are mixed. In such cases, vacuum degassing is commonly used to eliminate this problem. Most coating suppliers provide guidelines for dip coating that are specific to their coating materials.

The final thickness of a dip-coated part may range from a fraction of a mil to several hundred mils depending on the viscosity of the bath, the rates of immersion and withdrawal, the temperature of the bath, and the number of dips. With solvent-based coatings, thicknesses of a fraction of a mil to several mils are obtained after one dip cycle. Thicknesses can be increased by multiple dipping, but when this is impractical, a non-solvent-containing (100% solids) coating should be used. The use of 100% solids coatings usually results in buildups of 8 to 20 mils in a single dip.

In summary, dip coating involves many variables, among which are the viscosity of the bath, the temperature of the bath, the rate of withdrawal, temperature of the part, and temperature and humidity of the ambient. In spite of these many variables and the many controls that are required, dip coating offers an economical solution for large-scale production and automatic coating of parts.

3.5.8 Fluidized-bed Coating

Fluidized-bed coating, also referred to as aerated-bed coating, is a unique variation of dip coating that has found extensive commercial use. The basic process and modifications are the subject of numerous patents.^[24] The fluidized-bed process was invented in Germany by E. Gemmer, and a patent was issued in 1955 to Knapsack Griesheim.^[25] In the same year, it was introduced in the U. S. by the Polymer Corporation. Gemmer was awarded several other patents in the United States extending its coverage to thermosetting polymers.^[26] According to the fluidized-bed method, dry powdered resins or partially polymerized powdered coatings are placed in a container and set into motion by controlled-velocity air or inert gas that is introduced from the bottom of the container through a screen and porous membrane (Fig. 3.12). The resultant low-density powder is in constant motion and behaves as a low-viscosity, low surface tension fluid. The part to be coated is preconditioned by one of several methods to promote adhesion of the particles and then dipped into the fluidized bed. The principal pretreatment methods are:

- Preheating the part (usually a metal) to a temperature slightly higher than the melt or fusion temperature of the plastic powder.
- Applying a thin adhesive primer, a proprietary process that has an advantage over preheating in that areas may be selectively coated.
- Applying an electrostatic charge to the part to attract oppositely charged coating particles.

In all three cases, after the part is removed from the fluidized bed, it is normally heated in an oven. For epoxy and other thermosetting coatings, this postbaking step further fuses and cures the coating, improving its physical and electrical properties. For thermoplastic coatings, postbaking smooths the surface resulting in a less porous coating, an operation analogous to reflowing of solder.

Process Parameters. The number of process parameters affecting fluidized-bed coatings is very large: at least 20 have been reported.^[27] However, once these parameters have been fixed and controlled, the process can yield highly reproducible results. Comprehensive studies of the many variables have been made by Pettigrew^[28] and by Gaynor.^[29]

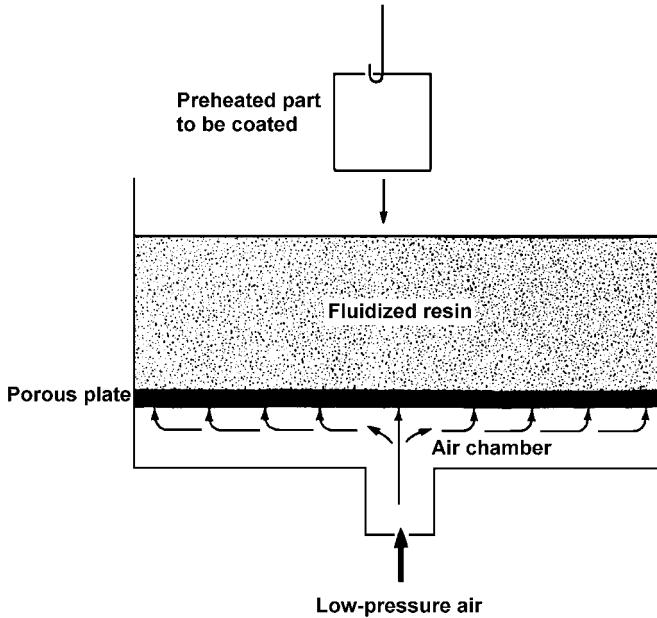


Figure 3.12. Fluidized-bed coating.

3.5.9 Electrostatic Fluidized-bed Coating

As the name implies, this process combines elements of both fluidized-bed and the electrostatic-spray processes. Standard fluidized-bed equipment is used, but in addition, the plastic particles are given a negative charge by applying a high-voltage (approximately 90,000 volts) direct current. The part to be coated is electrically grounded and suspended above the fluidized bed, so that the charged particles can be attracted to the part. The process has several advantages over the straight fluidized-bed process, among which are:

- The part to be coated does not need to be immersed.
- Preheating the part is not necessary for particle adhesion.
- Large fluidized beds are not needed to coat large parts.

- The process can be used to coat thin, low-mass parts such as wires that cannot be coated by the straight fluidized-bed process due to their poor heat retention.

The process has been found most useful in coating large complex parts and thin-gauge wire.

3.5.10 Electrocoating

Electrocoating, also known as E-coating, is also a form of dip coating. As in electrostatic spray coating, the coating particles are given a negative charge, but the coating is provided as an aqueous solution. An electrocoat system applies a dc charge to a metal part that is immersed in a bath of the oppositely charged coating particles. The coating is thus attracted to the charged metal part and deposited as a even, continuous film. The electrical nature of the application and the complete immersion of the part ensure uniform coverage. Electrocoating is used primarily for coating commercial and consumer metal items, especially in large scale production such as the painting of automobiles. Negatively-charged epoxy formulations (cathodic epoxy) are best for corrosion protection of metal parts from salt spray and humidity.

3.5.11 Vacuum Impregnation

Vacuum impregnation, still another dip coating variation, employs vacuum or vacuum-pressure cycling during the dipping operation. The technique is widely used for the thorough coating (impregnation) of intricate parts containing numerous small cavities such as transformer and inductor coils, magnetic windings, and porous metal, metal oxide, and ceramic surfaces. Thorough impregnation is essential in many electrical-insulation applications because any remaining voids act as moisture traps or regions for corona discharge, resulting in insulation breakdown. This is especially true for high-voltage transformer insulation.

Porous parts may be impregnated simply by soaking them in the liquid resin or coating; however, vacuum evacuation aids in reducing the amount of entrapped air and moisture. The air is removed, then displaced by the coating. To do this more effectively, the part is evacuated before being immersed in the coating. After immersion, vacuum is again applied and

interrupted periodically to force the liquid into the pores. A sequence of vacuum followed by pressure is even more efficient for impregnating closely wound coils. The amount of vacuum and time of immersion required are determined by the temperature, viscosity, volatility, and pot life of the resin coating.

3.5.12 Needle-based Dispensing

Coatings may be deposited in selected areas of an electronic assembly using computer-programmed needle-based dispensing equipment. Advantages include greater transfer efficiency, precise deposition in defined areas, and consistent edge definition. Furthermore, closed-loop control over the coating eliminates contamination risks, minimizes viscosity variations, and avoids the cost of frequent purges and the discarding of unused coating. However, needle-base dispensing is not suitable for very high throughput coating operations—even with high-speed robotics due to the restriction of flow from the small diameters of the needles.

3.5.13 Automatic Selective Dispensing

Unatomized automatic dispensing equipment can be used for very high throughput coating of printed wiring boards and other electronic assemblies. According to this process, a non-atomized dispensing module moves at a fixed height above the assembly, thus overcoming the speed limitations of contact-based, needle-dispensing systems and eliminating the overspray associated with atomized systems.^[30] Advanced equipment is now available that permits conformal coating of a high mix of circuit boards using a wide range of non-solvent-based and solvent-based coatings having viscosities ranging from 30 to 3,500 centipoise. By varying the volume and dispensing pressure and by the use of shaping air jets, coatings can be dispensed in a thin bead, a monofilament, or a swirl pattern (Fig. 3.13). As with needle-based dispensing, selective deposition is possible, thus avoiding masking. A closed fluid system is used, avoiding viscosity variations. For applications requiring two different coatings or different thicknesses of the same coating on the same board, equipment with dual heads that deposits the two variations in a single operation can be used.

A non-atomized film coater's fan pattern can be varied electromechanically providing a wide range of dispensing patterns. When coating a

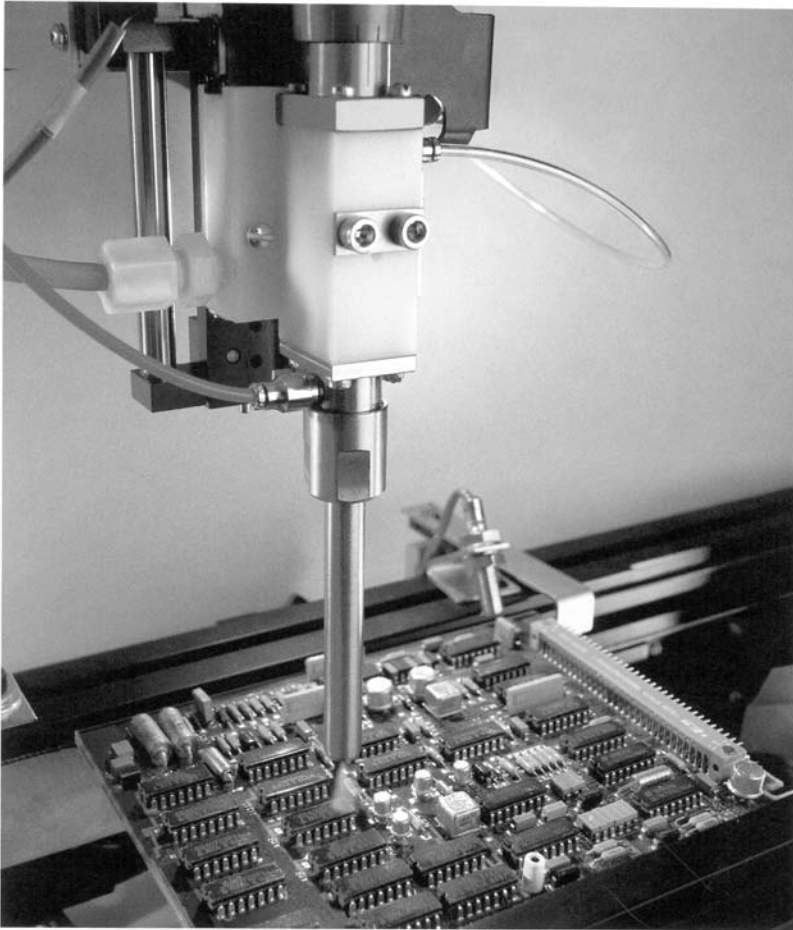


Figure 3.13. In-line automated selective coating system, Century® C-740 Series. (Courtesy Asymtek, A Nordson Co.)

printed circuit board, a small width may be needed in a tight area, whereas a wider width may be needed to coat a large area. Because the fan width is related to the fluid pressure, a software-controlled pressure regulator adjusts the pressure to set the desired width. Multiple fan widths can be set and calibrated with the fan width control system and stored in the computer program. By automatically controlling these multiple widths, accurate, repeatable edges are produced while increasing throughput.^[31]

3.5.14 Vapor Deposition

Vapor or vacuum deposition of coatings, although a highly desirable method, can be employed only for a few polymer types. Unlike metals, organic polymeric materials cannot be heated to their vaporization temperatures, even under high vacuum, without gross decomposition and destruction of their physical and electrical properties. This is particularly true for the two-part highly cross-linked thermosetting polymers such as epoxies, polyurethanes, and phenolics. With these systems, charring and carbonization occur before vaporization takes place.^[32]

Thermoplastics such as polyethylene have been reported to deposit from the vapor phase. Polyethylene was deposited as a film 900 to 2,500 angstroms thick by vaporizing solid polyethylene at 290°C and 10^{-4} torr.^[33] High deposition rates resulted in poor films that had small inclusions of solid polyethylene embedded in them. This problem was alleviated by inserting a baffle between the vapor source and the part to be coated.

Some success has also been achieved in vapor depositing Teflon and other fluorocarbon polymers. Teflon was depolymerized at 538°C in a vacuum of 10^{-5} to 10^{-6} torr and reported to repolymerize as an adherent film on a cold substrate.^[34] A Teflon-like coating was also sputtered from a Teflon target, but, even here, scission of the high-molecular-weight polymer into smaller fragments and some discoloration due to the formation of free radicals occurred.^[35]

Except for p-polyxylylene (parylene), the vapor deposition of polymers has not been practical. The deposition of p-polyxylylene is both unique and practical. Its key benefits for electronic applications were discussed in Ch. 2. The starting material is a white non-toxic solid that is easy to handle. The solid dimers of p-xylene are sublimed and pyrolyzed under moderate vacuum and the gaseous diradicals flow into a deposition chamber where they combine into long chain polymers on the electronic assembly that is maintained at room temperature. There is no subsequent curing step as with other polymer coatings; deposition and polymerization occur simultaneously. Figure 3.14 shows a production parylene deposition system, Model 2060V, available from Specialty Coatings Systems.

3.5.15 Screen Printing

Coatings formulated with thixotropic and wetting agents can be applied by screen printing, that is, by squeegee through a stainless steel mesh

screen. The addition of thixotropic agents, such as colloidal silica, thickens the coatings allowing them to be screen printed or brushed with little flow-out. For screen printing, surfaces must be fairly flat. Coating thicknesses may be varied from a fraction of a mil to several mils, depending on the screen mesh size and the number of coats applied. After the deposition parameters have been established, reproducible thicknesses and dimensions are obtained. To eliminate pinholes and other imperfections, it is advisable, as with other coating methods, to apply and superimpose two or three layers, with each layer partially or fully cured prior to applying the next layer. By using screens with a patterned photoresist, insulative coatings can be applied to selected areas of ceramic or epoxy laminate substrates, often used to isolate thin or thick film conductors or resistors from active devices that are assembled over them. Photoemulsion compositions containing gelatin chromate or photoresists are used in preparing the screens. Line widths and spacings of 5 mils are easily produced while advancements are being made to improve definitions to 2-mil lines and spacings. Screenable epoxies, polyurethanes, and other formulations are commercially available. Typical screen-printed epoxies may be cured at 80° to 150°C and provide 1-mil-thick coatings.



Figure 3.14. Parylene vapor deposition system: Model 2060V. (Courtesy, Specialty Coatings Systems, Div. of Speedline Technologies.)

The screen-printing process for applying conductor, resistor, and dielectric pastes in selected areas of a ceramic substrate is a highly developed art, widely used in fabricating thick-film microcircuits. Other applications include applying solder paste to printed circuit boards for surface mounting of components, applying polymer maskants to prevent solder from bridging conductors, and applying adhesives on multichip module substrates for die attachment. Automated screen printers are available from several manufacturers, one of which is shown in Fig. 3.15.



Figure 3.15. Automated screen printing system including MSP-885. (Courtesy AMI, Affiliated Manufacturers, Inc.)

Automated equipment for screen printing large panels up to 24×36 inches is available. With this equipment, photoimageable dielectric coatings, solder maskants, and legends can be applied uniformly over large areas, for example, in the production of BGA panels. Circuit Automation's DP-1500 coater has a capability to coat large dual-sided panels or circuit boards in a vertical direction. The screen-printing process provides precise metering of the coating over the circuitry and uniform coverage on even the highest conductor traces by forcing the coating between spaces without skips.^[36]

3.5.16 Roller Coating

Roller coating is a highly mechanized and closely controlled process for coating flat stock. It provides a means for applying a fixed amount of liquid coating to one or both sides of any sheet or strip requiring an even coating. Thus, roller coating is used for applying photoresists to copper-laminate stock on which etched circuitry is subsequently formed, in applying solder maskants to printed wiring boards, and in applying thin dielectric films on metal foil in fabricating capacitors.

In roller coating, the liquid coating is transferred from a reservoir pan to the flat surface by means of a series of metering and printing rolls. The printing roll may be embossed to lay down a pattern or the metering roll may be lithographed to print a functional or decorative design. After coating, the part is passed through the drying and curing zones of an oven, and the sheets are stacked or the strip is rerolled. Roller coating is widely used commercially for applying decorative coatings to metal stock for cans, bottle caps, toys, television parts, automobile instrument panels, and lighting fixtures.

3.5.17 Spin Coating

Spin coating is the standard process for applying reproducible, uniformly thin (micrometer thickness) dielectric coatings to wafers and substrates. Spin coating is used extensively to apply photoresist as part of the fabrication process for semiconductor devices and thin-film circuits. However, it is also gaining prominence as the preferred application method for interlayer dielectrics such as polyimides in fabricating integrated circuits, thin-film multilayer substrates, and chip-scale packaging.

The first step in spin coating consists of placing the substrate on a motor-driven rotary vacuum chuck mounted in a bowl. The coating is dispensed onto the center of the substrate and the spinner is turned on causing the coating to flow outward and be evenly distributed by centrifugal force. In general, an excess of coating solution is used to assure good substrate coverage. Typical film thicknesses range from a few tenths of a micrometer to one mil. The resulting thickness is a function of the solution viscosity and the spinner speed and acceleration. Thicker coatings can be obtained by increasing the viscosity of the solution or reducing the spin speed

or both. Typically, thickness is a hyperbolic function of the spin speed; thinner coatings are obtained at higher speeds.

Substrates most often used for spun-on coatings are circular wafers such as silicon or alumina, although square and rectangular sizes can also be accommodated. In the latter cases, coatings will be thicker at the edges and corners and uniformity will be harder to achieve. In all cases, it is important that the substrates be very smooth and flat; often polishing the substrates is necessary to get reproducible thicknesses.

Thicknesses may also be varied by changing the solids content and thus the viscosity of a solvent-based coating. In non-solvent coatings, reactive diluents can be used to lower viscosities. In spin coating, both the viscosity and the spin speed affect the thickness, thinner coatings being formed from lower viscosity formulations at higher spin speeds. Figures 3.16 and 3.17 show the effect of spin speed on coating thickness for two polyimides having different viscosities.

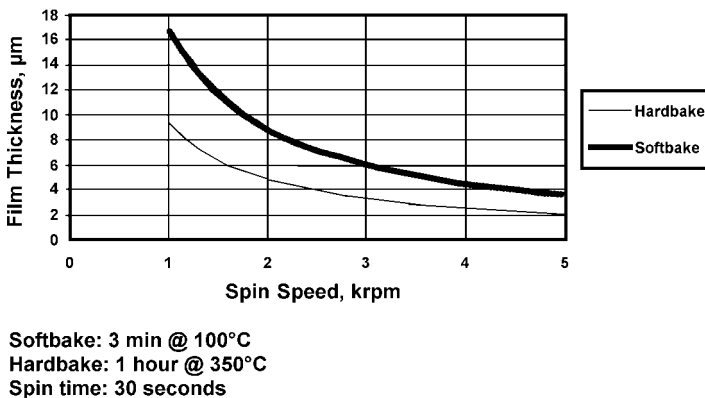


Figure 3.16. Spin speed vs thickness for photosensitive polyimide, Durimide[®] 7505 (low viscosity). (Courtesy Arch Chemicals, Inc.)

*Durimide[®] is a registered trademark of Arch Chemicals, Inc.

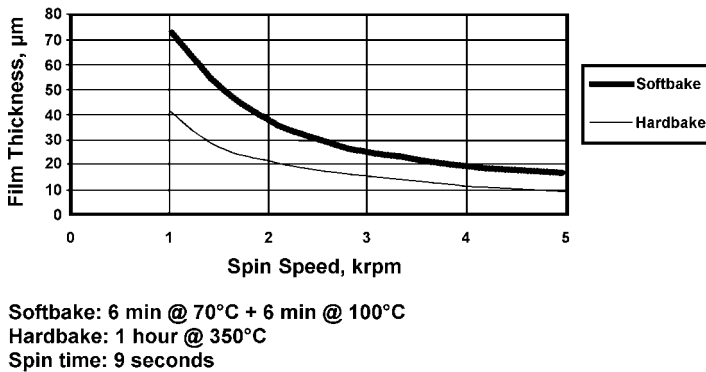


Figure 3.17. Spin speed vs thickness for photosensitive polyimide, Durimide 7520 (high viscosity). (Courtesy Arch Chemicals, Inc.)

3.5.18 Extrusion Coating

Extrusion coating is a process for directly applying coatings (typically photoresist, polyimide, and other polymers) to a substrate without spinning and without significant material waste. The process is an alternative to the more traditional spin coating that has been the predominant method in semiconductor, flat panel, and related industries. In essence, the method uses a precision extrusion die, that is moved at a close fixed distance, linearly with respect to the substrate. Simultaneously, the process fluid is metered through the die, forming a coating bead that ultimately deposits a thin uniform film onto the substrate. Precise control of a number of parameters is necessary to achieve the desired coating results. The primary advantages of extrusion coating over spin coating are:^[37]

- Reduced material waste. Polymer coating waste is less than 5% compared with more than 90% for spin coating.
- Ability to coat large rectangular or square substrate sizes.
- Deposition of very thin coatings from 1–2 μm to thick coatings (up to 4 mils) in a single pass, depending on the coating viscosity and the equipment parameters.
- Little or no edge bead.
- Uniformity equal to or better than spin coating (less than $\pm 3\%$).

Extrusion coating was initially developed for the flat panel display industry where it has been used for applying photoresist, color filter photoresist, and polyimide, primarily to large glass substrates. Further development resulted in extrusion-only processes that met or exceeded the coating results obtained from the spin process.

Extrusion coating is competing with spin coating because of its advantage in conserving coating material and its capability of coating large panels where it has found its greatest application and where spin coating is impractical.^[37] It has also been used in fabricating MCM multilayer substrates from large panels by depositing controlled films of polyimide or BCB (benzocyclobutene) dielectric.^[38] In semiconductor manufacturing, extrusion coating is used to deposit photoresist onto silicon or gallium arsenide wafers.

FAS Technologies has been the pioneer in developing and commercializing extrusion coating and coating equipment. The FAS extrusion coaters have tightly calibrated digital electro-hydraulic pumps to push a thin layer of the liquid film through the coating die directly onto the substrate. The substrate is held stationary and the extrusion head is held at a predetermined height. The extrusion head is then moved over the substrate resulting in a uniform coating. Accurate computer-controlled speed and head height assure a uniform film of the correct amount of coating.^{[39][40]} Production extruders capable of coating very large substrate sizes (up to 1200 × 1600 mm) are available from FAS (Fig. 3.18).

3.5.19 Meniscus Coating

Meniscus coating is yet another method for applying uniform coatings to large flat surfaces. The process involves generating a meniscus or thin layer of the coating on top of an applicator and transferring the meniscus to a substrate. The applicator consists of a tube that is either porous or has a slot at its top (Fig. 3.19). The pores or slot are located along the length of the tube perpendicular to the direction of coating. For a coating that contains no fillers, a porous applicator is used, while coatings that have filler particles must use a slotted applicator. The coating is continuously pumped into one end of the applicator tube and recirculated as it drips from the bottom of the tube into a reservoir.^[41] The substrate is secured to a vacuum chuck then inverted so that the substrate is suspended 8–10 mils above the applicator. The substrate is then moved past the applicator, or optionally, the applicator may be moved past the substrate. As the substrate passes beyond

the applicator, the meniscus splits and recoils towards both the applicator and substrate.

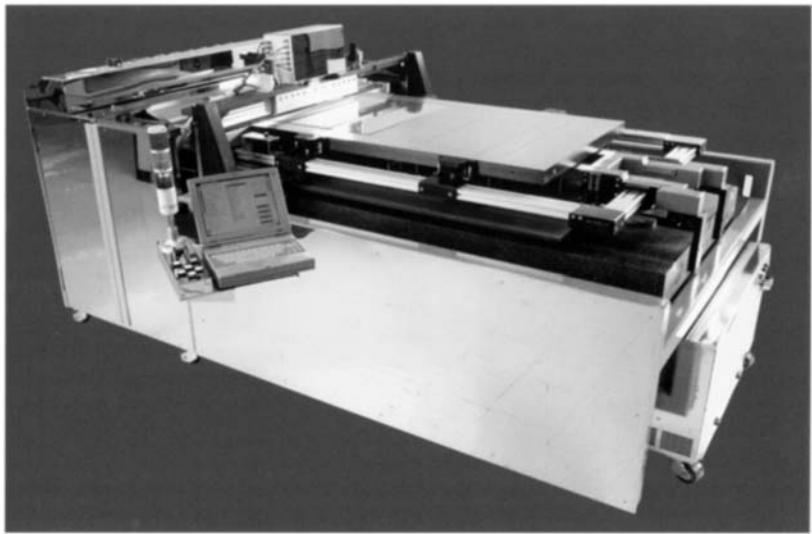


Figure 3.18. Moving-head extrusion coating system. (Courtesy FAS Technologies.)

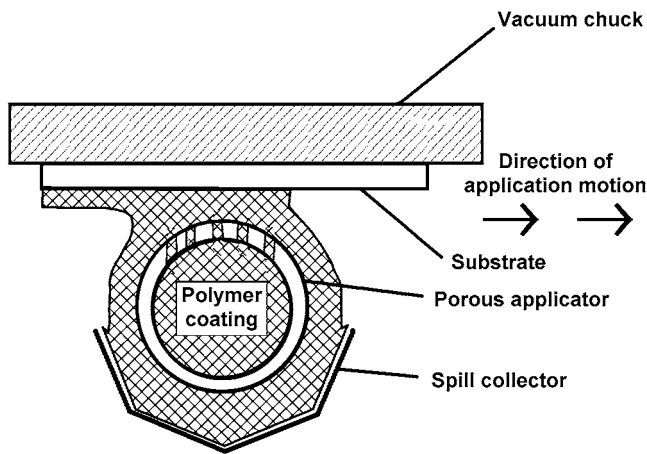


Figure 3.19. Schematic for meniscus coating process.

Meniscus coating of photoresists, photocurable coatings, and dielectrics is applicable to the fabrication of large flat panel displays and the large area processing of thin-film multilayer substrates for multichip modules.^[42]

3.5.20 Curtain Coating

Like roller coating and meniscus coating, curtain coating is yet another process for applying a coating to large flat surfaces. In curtain coating, a bath with a slot in the base allows a continuous flow (curtain) of coating to fall into a gap between two conveyor belts. The parts to be coated are moved along the conveyor at a controlled speed and receive the coating on their upper surfaces (Fig. 3.20). Curtain coating is useful in depositing photoresists, solder maskants, and dielectric insulation in the processing of printed circuit boards, multichip module substrates, and flat panel displays.

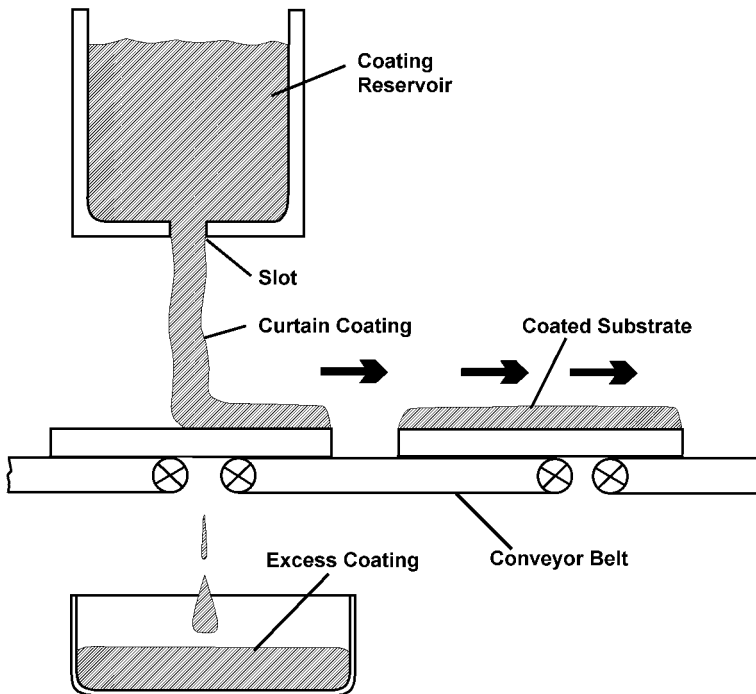


Figure 3.20. Schematic for curtain coating process.

3.5.21 Brush Coating

Brushing does not lend itself to production and results in non-uniform and non-reproducible thicknesses even for small engineering quantities. Brushing is used mainly to touch up or repair a coating in a damaged area, to cover spots where components have been removed and replaced, and to cover pinholes left from electrical test probing. Applying the coating with a small camel's hair brush is ideal for these small touch-up jobs.

3.6 CURING AND POLYMERIZATION PROCESSES

Various methods are used to cure or polymerize organic coatings. Heat curing is the most widely used method and is applicable to most epoxies, polyurethanes, silicones, and polyimides. With new government regulations on volatile emissions and energy conservation and the need to shorten curing times to increase production, curing methods such as ultraviolet light polymerization, moisture curing, microwave curing, and e-beam curing are becoming more prevalent.

3.6.1 Heat Curing

All solvent-based coatings require drying which consists of evaporating the solvent at room temperature or at an elevated temperature. If the solvent-based formulation contains the prepolymerized coating, no further polymerization or curing may be necessary. If the solvent contains mixtures of monomers and oligomers further curing will be necessary to polymerize or cross link the smaller molecules. This is usually accomplished by exposure to elevated temperature for a period of time.

Two-part systems (resin and hardener or resin and catalyst) generally require elevated temperatures for complete cure and polymerization. Some epoxies and polyurethanes begin to polymerize quickly after mixing in the hardener or catalyst (short pot lives) while others require a definite elevated temperature to begin the polymerization process. In all cases, exposure to an elevated temperature for a period of time is required to achieve complete cure.

Step Curing. Curing at a single temperature does not always result in optimum properties for a coating. Initial curing at lower temperatures

allows time for moisture and other volatiles to escape. Step curing at progressively higher temperatures is often required to complete the cure, reduce stresses, and reduce subsequent outgassing from the coating. One device manufacturer reported that by doing a five-step cure, each at a progressively higher temperature, the amount of moisture in an encapsulant was reduced by a factor of four.^[43] Step curing of some polymer coatings, such as benzocyclobutene at the high temperatures, may have to be performed in a nitrogen ambient or in a vacuum to avoid oxidation and decomposition of the polymer.

Equipment. The choice of equipment to heat-cure coatings depends largely on the desired properties of the cured product and the availability and degree of facility automation. For batch processes and single-temperature curing, a *convection oven* is all that is necessary. Convection ovens maintain an even temperature by circulating heated air or nitrogen through the chamber.

For assembly-line processes, where parts are produced in series, a *conveyorized belt furnace* is used. An oven loses its temperature stability each time the door is opened, for example to insert more parts—a problem not encountered with the conveyorized belt furnace. Conveyorized belt furnaces have heated zones that can be maintained at several temperatures so that step curing is easily performed. By changing the belt speed, the dwell time in each heated zone can be adjusted and controlled. A conveyorized belt furnace may also be placed in-line with an automatic spray or dip-coating system.

A variation of the conveyorized belt furnace is one in which the infrared energy is used to cure the coating instead of radiant heat. Infrared energy is absorbed by the carbon-carbon bonds of the polymer coating as well as by the carbon-hydrogen and other bonds. The bonds begin to vibrate at a rapid rate causing localized heating of the coating. If the wavelength of the IR energy is narrow, only the organic coating will be heated, rendering the process cooler overall than radiant heating.

3.6.2 Moisture Curing

Some prepolymer resins or monomers contain functional groups that are blocked and unreactive until exposed to atmospheric moisture. Moisture reacts with the blocked groups freeing the functional groups allowing them to polymerize. Most RTV silicones and some polyurethanes cure in this manner. Optimum electrical and physical properties usually

require 24 to 48 hours of exposure to air at a minimum of 30% RH and sometimes require a short thermal post-cure. For this reason, manufacturing facilities located in hot, dry climates should avoid selecting conformal coatings that rely on moisture curing. The mechanisms and chemistries of moisture curable coatings were treated in Ch. 2.

3.6.3 Ultraviolet Photocuring

Shortening the time and temperature of curing is a current issue that is being explored in order to conserve energy, increase production throughput, and reduce costs. One approach is through the use of photocurable coatings. Although photocurable coatings have been used for over a century as photoresists, primarily in photoengraving and printing processes,^[44] they have only recently gained favor in the electronics industry. Rapid uv-curing coatings are now available from several suppliers and all the major polymer types have been modified or formulated so that they can be polymerized on exposure to uv light. Ultraviolet-curing coatings are largely based on acrylic or acrylic-modified polymers. They are generally one-part, 100% solids, thus avoiding solvent emissions. When stored properly, their shelf lives range from six months to several years.

Beneficial properties such as rapid cure, reduced solvent emissions, room temperature cures, and the ability to coat heat-sensitive devices and circuits make photocurable compositions attractive for many electronic applications. In addition, some photocured coatings have been reported to possess enhanced physical and mechanical properties,^[45] and, because of their short cure times (seconds), lend themselves well to completely automated production lines.^[46] Optimum curing occurs in the wavelength range of 250 to 400 nanometers with a radiant output of at least 150 milliwatts per square centimeter.^[47] Generally, medium pressure mercury vapor lamps are used. Many companies that sell uv-curable coatings also sell compatible curing equipment ranging from portable, hand-held wands for spot curing coatings, adhesives, sealants, and encapsulants^[48] to conveyORIZED-belt systems (Fig. 3.21) for curing conformal coatings and marking inks.

Ultraviolet and uv/visible radiation-curing equipment can emit light at specific frequencies matching the absorption bands of photosensitive groups in polymeric coatings and adhesives. The shape and intensity of the emitted light can be varied to flood a large area, to focus the beam for high-intensity high-speed curing, or to focus the beam on a small area (spot curing) which is beneficial in rework and repair.

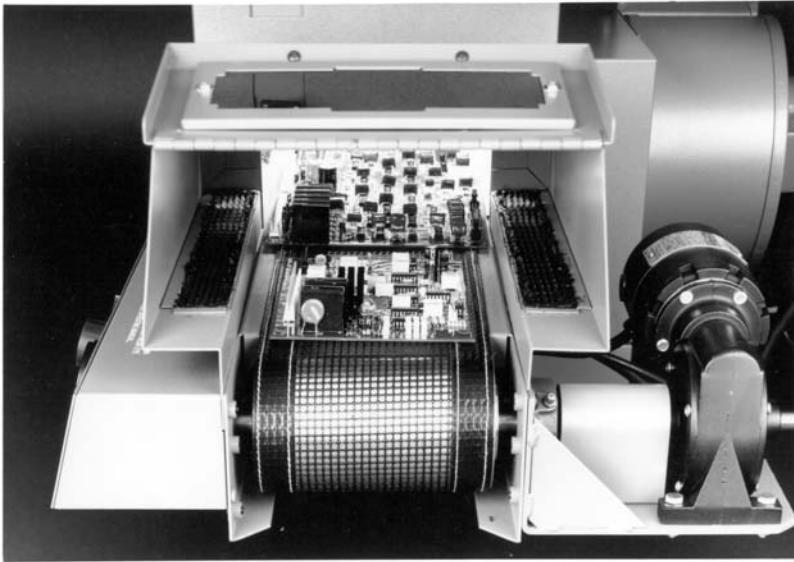


Figure 3.21. Conveyor uv-curing system. (Courtesy Dymax Corp.)

A major limitation in using photocured coatings on printed wiring assemblies is the inaccessibility of light to cure portions of the coating that are shadowed by large components. To obviate this, a double cure mechanism is used, for example, uv curing followed by heat curing or moisture curing. Some new polymer resins have been synthesized that combine in one molecule both the photosensitive group and the moisture cure group, for example, a polyurethane that is uv cured, but can subsequently be moisture cured to assure that the shadowed areas are also cured.^[49]

Photoinitiation. Most photocurable coatings require a photoinitiator to start the polymerization process. Photons from the ultraviolet source react with the photoinitiator to generate active catalysts that join and cross-link monomers and oligomers into high-molecular-weight polymer structures that are insoluble and resistant to chemicals. Thus most photosensitive coatings are negative-acting types.

Photo-induced polymerization may be of two types: *free-radical* or *cationic*. Free-radical polymerization requires high intensity uv radiation, results in rapid curing, and permits the application of a wide range of coating

thicknesses. Although photocured coatings based on free-radical mechanisms are the most widely used, coatings that cure by a cationic mechanism have some unique benefits and are gaining greater attention. Among these benefits are:

1. Only low-intensity uv radiation is required
2. Curing continues after the radiation source has been removed and all the photoinitiator has been depleted.^[48]

The cationic process allows areas not directly exposed to the light source to be cured, called “dark” or “shadow” cure, whereas the free-radical process requires complete exposure to uv light for effective curing.^[50] The choice of free-radical or cationic-cure coatings depends largely on the application. For example, cationic curing is best for curing a die-attach adhesive while free-radical curing is best for defining precise patterns of tight tolerances.

In most cases, uv exposure should still be followed by a secondary heat cure because some coating is shadowed by an irregular topography or flow beneath devices. Such secondary heat cures are not as long a duration nor do they require as high a temperature as normal heat-curing systems. Ultraviolet exposure time to obtain a tack-free film can range from less than a second to several minutes depending on the specific formulation, the intensity and wavelength of the uv radiation, and the thickness of the coating. Some examples of uv-curing conformal coatings are given in Table 3.5.

Free-radical Photopolymerization. Free radicals used in photoinitiation are generated by one of two methods: intermolecular hydrogen abstraction or intramolecular photocleavage. Both methods require absorption of light energy, followed by excitation to produce the active free radicals. Examples of compounds that undergo intermolecular hydrogen abstraction are benzophenone, benzil, and 9,10-anthraquinone. Examples of compounds that undergo intramolecular photocleavage include benzoin ether and phenyl-1,2-propanedione-2-o-benzoyloxime. The free radicals react with monomers and oligomers to initiate polymerization. Competing with polymerization is the decay and recombination of the free radicals and reactions of the free radicals with the growing polymer chain and with air oxygen. A general reaction scheme is shown in Fig. 3.22. Oxygen inhibition can be avoided or controlled by adding oxygen scavengers to the coating formulation or by curing in an inert ambient.

Table 3.5. Properties of Ultraviolet-cured Conformal Coatings

Item No.	Description	Appearance	Viscosity (cp)	UVC-6/F300 Conveyor speed (ft/min)	UVC-6/5002 Conveyor speed (ft/min)	Secondary Heat Cure (if necessary)
984-LVUF	Hard coating, environmentally resistant, highly fluorescent for easy inspection	Clear, fluorescent	150	3–9 (1–2 sec exposure)	1–3 (25 sec exposure)	30 min @ 120°C
9-984-LVF	Very fast curing, hard and fluorescent for high-speed production	Clear, fluorescent	150	10–25 (<1 sec exposure)	3–5 (12 sec exposure)	60 min @ 110°C or 30 min @ 120°C
9-20557	Flexible coating with superior adhesion to PCB materials and excellent thermal shock resistance	Clear, fluorescent	2,500	3–9 (1–2 sec exposure)	1–3 (25 sec exposure)	60 min @ 110°C or 30 min @ 120°C
984 Sure Cure®	Two-part system like 984-LVUF which cures in areas shadowed from light at RT	Clear, fluorescent	125	2–5 (2–3 sec exposure)	1 (50 sec exposure)	Unnecessary, heat will accelerate the 2-part cure
9-984-B	Like 9-984-LVF; cures to an opaque black finish to hide components or circuitry	Deep blue or black	6,000	10–25 (<1 sec exposure)	3–5 (12 sec exposure)	60 min @ 110°C or 30 min @ 120°C

(Courtesy Dymax Corp.)

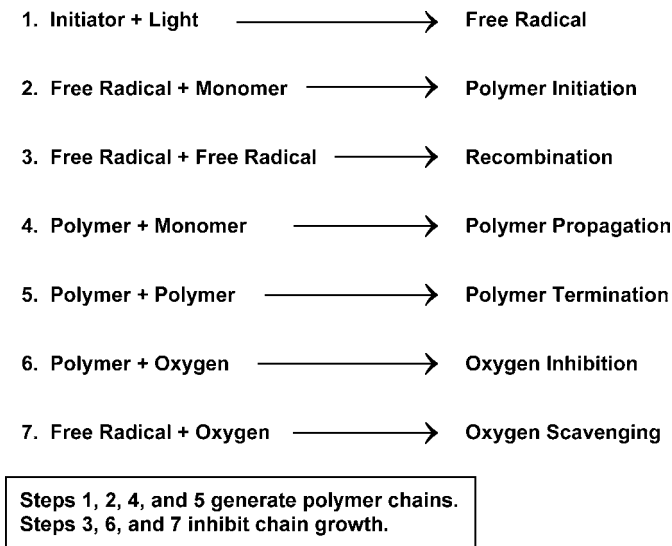


Figure 3.22. General reactions for free-radical photopolymerization.

Cationic Photopolymerization. In cationic photopolymerization, compounds that convert to Lewis acids* on exposure to uv light are used as photoinitiators. Among these compounds are aryldiazonium salts, diaryliodonium salts, and triarylsulfonium salts. The Lewis acids generated are long-lived and continue to catalyze polymerization after the uv source has been removed. This ensures curing in shadowed areas and under components.^[51] A further benefit of cationic curing is that an inert atmosphere is not necessary during curing since the reactions are not inhibited by oxygen.

3.6.4 Ultraviolet Polymerization of Gaseous Monomers

Gaseous monomers adsorbed onto a surface may be polymerized by exposure to uv light either in the presence or absence of air. The most

*A Lewis acid is defined as a compound whose electron orbitals can accept electrons, e.g., boron trifluoride. Conversely, a Lewis base is an electron donor, e.g., triethylamine or other tertiary amines.

effective uv wavelength range has been found to be between 2,000 Å and 3,500 Å and may be generated from a 700-watt medium pressure Hanovia mercury-arc lamp. The deposition chamber is evacuated to about 10^{-6} torr to remove moisture and the gaseous monomer is then introduced and maintained at approximately 4 torr during irradiation.

Monomers that have been found most suitable for ultraviolet polymerization are those containing double bonds (unsaturation). Such bonds open up by a free-radical mechanism, allowing a head-to-tail coupling, with the formation of thin solid films. Styrene, butadiene, methylmethacrylate, acrolein, and divinylbenzene are a few examples of monomers that have been polymerized in this manner. The uv polymerization of methylmethacrylate was reported as early as 1937. Melville described the deposition of a solid film on the walls of a vessel containing the gaseous monomer on exposure to uv light.^[52] Subsequently, during the 1960s, the uv polymerization of other monomers was reported including acrolein, divinylbenzene,^[53] butadiene,^[54] tetrafluoroethylene, and hexachlorobutadiene.^[55]

3.6.5 Microwave Curing

Variable frequency microwave (VFM) curing is a recently developed process for rapid curing of polymer coatings, adhesives, and encapsulants.^[56] It differs from conventional microwave processing in using swept frequencies rather than a fixed frequency. Variable frequency microwave utilizes three parameters: central frequency, frequency bandwidth, and sweep rate. Through the sweeping process, problems of non-uniformities in temperature and arcing associated with conventional microwave ovens are avoided. Variable frequency microwave curing is reported to be 2 to 10 times faster than conventional heat curing. A further advantage is that it permits uniform distribution and precise control of microwave energy and heats large sections uniformly. Compared with conventional heat curing, VFM curing was found to offer similar die stress levels and reliability and reduced warpage of FR-4 laminate substrates onto which it was applied.^[57] Since 1994, Lambda Technologies has pioneered the VFM process and has commercialized it through the development of microwave equipment.

3.6.6 Electron-beam Polymerization

The polymerization of gases by electron-beam (e-beam) exposure was discovered accidentally. During experiments with electron tubes and electron-beam equipment, it was noted that thin films formed and clouded the inside of the tube. These films were identified as resulting from trace amounts of contaminant gases entering the chamber from silicone oil used in the vacuum pump. For years, these films were considered a nuisance,^[58] but in 1954 it was suggested that e-beam polymerization could be useful as a new method for depositing ultrathin polymers,^[59] and, in 1958, the significance of this technique in fabricating microelectronic circuits and devices was reported.^[60]

In effecting polymerization, the electron beam generates free radicals, ion radicals, and other activated species from liquids or gases adsorbed on a surface. These activated species are short-lived and quickly combine to form long-chain solid polymers. In this respect, e-beam polymerization is similar to uv polymerization. Also, as with uv polymerization, gases or liquids used are those that contain double bonds (ethylenic groups). Thus tetrafluoroethylene has been polymerized with high-energy electrons. Under the same energy conditions, copolymers of tetrafluoroethylene with hexafluoropropene, polyvinylidene fluoride, and other ethylenic polymers have been prepared.^[61] The continuous and rapid curing of styrene, polyesters, diallylphthalate, and vinyl carbazole monomers to form 1-mil-thick coatings using an e-beam source of 50 to 250 keV was reported by Davison.^[62] Styrenated polyesters, polyvinylchloride plastisols, epoxy acrylics, and acrylic monomers have also been polymerized in films 0.5 to 125 mils thick using an e-beam source of 300 kV, 25 mA, and total output of 7.5 kW.^[63]

The advantages of applying and curing coatings by e-beam exposure are the speed of curing and the fact that heat is not required, which obviates the possible degradation of heat-sensitive devices.^[64] Thin films may also be deposited in selected areas without masking by programming and directing the beam. Very fine lines and areas may thus be defined.^[65] However, in spite of these advantages, the e-beam process has found limited application because of the high initial equipment cost, subsequent high operating cost, shielding problems, and the sensitivity of many semiconductor devices to electron radiation. Depending on the electron energy, overheating and damage to the substrate can occur. Still another problem encountered not only with e-beam curing, but also with curing most ethylenic

monomers by the free-radical mechanism, is the inhibition of cure that occurs in the presence of atmospheric oxygen.^[63] Films often remain tacky and partially cured. Techniques to prevent this by excluding oxygen during the cure include evacuation, use of an inert gas ambient, or use of oxygen scavengers.

3.6.7 Glow-discharge/Plasma Polymerization

The glow-discharge method for depositing and polymerizing thin films, also known as the electric- or silent-discharge method, entails striking an electrical discharge between two electrodes in the presence of a monomer gas. A potential of several hundred to several thousand volts is employed. Under dc conditions, the substrate to be coated is made the anode or is attached in some manner to the anode. In ac discharge, the substrate is placed between the anode and the cathode. A third variation of glow-discharge uses radio-frequency-excited molecules and does not require the use of electrodes. This method is referred to as *electrodeless discharge* or *plasma polymerization*. The need for low-dielectric-constant thin films as interlayer insulation for high-speed circuits has made plasma polymerization an area of intense study.

In plasma polymerization, a monomer is excited by radio frequency or microwave energy forming active species, primarily free radicals and ions. These activated species combine to form thin polymer films on a surface. The physical and electrical properties of the resulting polymers depend on the energy frequency,^[66] the monomer gas pressure,^[67] and the reactor design,^[68] as well as the monomer itself and the surface onto which the coating is deposited. Some surfaces lend themselves well to the formation of strong chemical bonds, while others are rather passive resulting in weak adhesion. The energy used can vary from low radio frequencies (13 MHz) to high microwave frequencies (2.5 GHz).^[69] A typical pressure is 100 millitorr, although higher pressures have been studied.^[67]

To polymerize, the monomers must possess active groups such as double bonds, oxygen, fluorine, amines, or combinations of these. Mixtures of two or more monomers may also be used to create new classes of polymers having unique properties.^[70] A large number of monomers have been polymerized by glow discharge, producing films from several hundred to 10,000 angstroms thick. Bradley and Hammes,^[71] for example, reported the formation of films from over 40 different monomers and provided

considerable data on their electrical properties at various temperatures. However, no data were given on the exact characterization of the polymer films. Thirty different monomers were polymerized by radio-frequency plasma by Smolinsky and Heiss^[72] as potential thin-film capacitor dielectrics. Of these, the best films were derived from dimethylpolysiloxane, triethylsilane, diethylvinylsilane, vinyltrimethylsilane, heptene-2, cyclohexene, styrene, valeronitrile, and 2,5-dimethyl-2,4-hexadiene. Films were defined in terms of their electrical and physical properties; but again, as with other investigations, no structural or compositional characterizations were given.

The glow-discharge technique has also been used to produce thin polymeric films from halogenated olefins, including fluorinated derivatives.^{[73]–[74]} These films, found suitable as dielectric coatings, were formed by the application of a potential of several hundred volts between electrodes.^[75]

Finally, a series of hydrocarbon and fluorocarbon films was prepared by the electrodeless discharge method, with isobutylene, ethylene, acetylene, diacetylene, toluene, trifluoroethylene, and tetrafluoroethylene used as starting materials.^[76] Films formed from ethylene, acetylene, and diacetylene possessed structures analogous to highly cross-linked polyethylene. Films derived from toluene showed structures (using infrared spectroscopy) similar to polystyrene, while films derived from the fluorinated monomers were assumed to be Teflon-like in structure.

Key advantages of the glow-discharge or RF plasma methods are the simultaneous deposition and polymerization and the complete coating coverage that they afford. The large spread in the angle of incidence with which the activated gas molecules strike the surface allows the polymers to form within and behind all crevices and to cover all surface imperfections, resulting in an integral coating.^[77] Other advantages include: choice of a wide variety of monomer starting materials, low substrate temperature (the part may be kept even at room temperature), and no necessity for a high vacuum. On the negative side, the properties of plasma-polymerized thin films have been difficult to reproduce because of the large number of variables influencing their formation. Often free radicals remain in the thin films causing instability and degradation.^[78]

An effective use of plasma has been to induce surface changes in already cured polymers. Exposure of a polymer to plasma can alter surface properties such as wettability, adhesion, surface resistivity, and the friction coefficient.^[79] Polar or non-polar groups can also be grafted onto a polymer surface in the presence of a plasma rendering the surface either hydrophilic or hydrophobic. Fluorocarbon plasmas generated from carbon tetrafluoride

or hexafluoroethane, for example, have been used to produce a Teflon-like surface on an organic polymer, rendering it hydrophobic.^[80] Other functional groups such as hydroxyl or amino groups can also be grafted to a polymer surface by using allyl alcohol or allylamine plasmas, respectively, rendering the surface hydrophilic.^[81]

3.6.8 Gamma-Radiation Curing

As with other forms of radiation energy, gamma radiation can be used to polymerize or co-polymerize certain gaseous, liquid, or solid monomers. Gamma-radiation-induced reactions are similar in nature and mechanism to those induced by uv radiation. Consequently, the same classes of polymers used for uv curing are amenable to gamma curing. These include the general class of ethylenic compounds such as vinyls, acrylics, allylics, and polyesters. Epoxy resins, however, are difficult to polymerize by gamma irradiation. High dosages of 4×10^8 rads and greater are required and, even so, only a small percentage increase in molecular weight occurs.^[82] However, indirect techniques may be used to radiation cure epoxies. The epoxy resin may be modified to incorporate vinyl or ethylenic groups that are radiation sensitive. Gamma irradiation can then induce polymerization through these functional groups.

As with plasma, another use of gamma radiation consists of grafting gaseous or liquid monomers onto the surfaces of solid plastics or coatings, thus altering the surfaces to improve their wetting, antistatic, adhesion, or surface resistivity properties, depending on the group that is grafted. As an example, acrylic groups have been grafted onto Teflon film to give it antistatic properties.^[83] Other specific applications in which the moisture resistance, chemical resistance, and radiation stability of polymers have been improved by gamma irradiation grafting have been described by DasGupta.^[84]

Commercial gamma-radiation equipment utilizes one of three gamma sources: cobalt 60, cesium 137, or iridium 192. Dose rates may range from 5×10^4 rads/hour to 6.4×10^4 rads/hour.

Although extensive experimental work has been performed on using gamma radiation to polymerize monomers, very little is reported on the practical applications of this technique for electronics. However, gamma-radiation curing, as well as other radiation-curing methods, hold much promise for future electronic applications. Among some potential uses are the curing of insulating coatings or capacitor dielectrics, the fabrication of

detailed microinsulation patterns, and the development of materials having precise bulk or surface electrical properties.

3.7 MANUFACTURING ISSUES

Manufacturing must be aware of and address some special issues relating to coatings. Among these are cross contamination of storage containers, dispensing equipment, and curing ovens where the same equipment is used for several different coatings. Thorough cleaning before processing the second coating type is important to avoid poor adhesion or inhibition of cure. Manufacturing is also responsible for the safety of operating personnel and must take measures to prevent exposure to volatile emissions, flammable solvents, and toxic materials during processing of the coatings. Inspection to assure that each part has been thoroughly and uniformly coated is important, but not easy. Finally, manufacturing must have a reliable rework process in cases where a high-value part must be repaired. Procedures are necessary to remove the coating, replace a malfunctioning part, and recoat without affecting the reliability of the rest of the assembly.

3.7.1 Cross Contamination

The constituents of some coatings, adhesives, and encapsulants have a tendency to migrate to other portions of an assembly and degrade the adhesion and integrity of subsequently applied coatings or adhesives. These constituents, generally low-molecular-weight species, may also volatilize during cure and contaminate the curing ovens. The early silicone formulations presented many manufacturing problems since they had a tendency to migrate. Once an oven was used to cure silicones, it became contaminated and could only be used for curing other silicones. To avoid any problem, manufacturing should dedicate a separate curing oven for silicones. The use of a single spray system for dispensing both silicones and other polymer coatings should also be avoided. Although recent silicone formulations are touted as non-migrating, there is still a risk because the low surface tension of silicones affects the wettability of other polymer types such as epoxies, polyurethanes, and acrylics. Residual silicone that deposits on a printed wiring board during processing results in “fish eyes,” cratering, and loss of

adhesion of a subsequently coated board.^[85] Even if ovens and other processing apparatus are not used for silicones, they should be cleaned periodically to avoid other types of cross contamination since some curing mechanisms, especially those involving free-radical addition cures, can also be inhibited by such contaminants.

3.7.2 Volatile Organic Emissions

Of increasing concern, are solvents and other volatile organic compounds (VOC) that are released into the atmosphere during the curing or drying of coatings. Volatile organics that enter into photochemical reactions, for example, decompose or form free radicals with uv light and cause ozone depletion in the upper atmosphere. Regulations for minimizing or prohibiting their use have been enacted by the Environmental Protection Agency (EPA). Many formulations in which xylene or toluene is the solvent are being reformulated to replace these volatile solvents by others having zero or low VOC emissions. The use of 100% solids and uv-curing coatings is also accelerating.

Solvent-based, resin/catalyst or resin/hardener formulations that are heat cured have been used for many years, but with ever increasing concerns about organic volatiles and by-product emissions contaminating the environment, new formulations having low VOC content are entering the market. These are either water-based or contain no organic solvents (100% solids). Volatile organic-compound-exempt materials are defined as those that do not participate in atmospheric photochemical reactions. The VOC content of an organic coating is the weight of the volatile emissions from a sample under specified bake conditions after subtracting the exempt solvents and water present. Bakeout is generally one hour at $110^{\circ} \pm 5^{\circ}\text{C}$.

3.7.3 Flammability and Toxicity

When xylene, isopropanol, or other flammable solvents are used in spray or dip coating formulations or in cleaning operations, supplier safety instructions should be followed. Adequate ventilation should be provided to avoid high concentrations of solvents and other organic materials. All containers of solvents should be grounded to avoid the possibility of static discharge and a fire or explosion from occurring. Whenever possible non-flammable solvents or aqueous solutions should be used.

Material Safety Data Sheets (MSDS) must be available for each organic material or chemical used in a manufacturing area. The MSDS contains information on the storage and handling, toxicity, personnel protection, first aid, spill and leak procedures, and procedures for waste disposal. Material Safety Data Sheets must be provided by the supplier or manufacturer of the chemical and must be maintained and readily available at the user's site.

3.7.4 Inspection

Generally, coatings used for electronic applications are applied 1 to 5 mils thick and are either transparent or translucent. As such, it is difficult to determine if a part has been completely coated. For inspection purposes, small amounts (0.1 to 1%) of uv indicators such as Calcofluor or aminocoumarin may be incorporated into the formulation. Inspection of the coated parts under a uv lamp (black lamp) can then assist in determining areas that were not coated. In some cases, non-destructive thickness measurements at several locations of the part can be made to determine the uniformity of the coating. Dip coating, for example, tends to bead and be thicker at the edge that is withdrawn from the bath while spray coating thicknesses can vary throughout the part. If it is not possible to measure thickness of the coating on the part, a sample part with a masked-off area can be coated concurrently with the production parts and thickness measurements made at several locations. The sample card can also be used to conduct other quality assurance tests such as adhesion, hardness, and solvent resistance.

Inspection Criteria. Visual defects in conformal coatings may consist of voids, blisters, fisheyes, orange peel, lifting, flaking, ripples, discoloration, and embedded contaminants. Some of these defects are unacceptable because they directly affect the function and reliability of the coating (for example, moisture penetration) or the electrical performance of the module while other anomalies may be acceptable to varying degrees depending on their frequency and location. Acceptance criteria are specified in many military and industry specifications of which IPC-A-610, "Acceptability of Electronic Assemblies," Sec. 9.1, is quite thorough, providing visual criteria through photographic examples.

Thickness Control. Thicknesses of coatings may range from 0.1 mil (2.5 μm), in the case of vapor-deposited parylenes, to over 10 mils for some elastomeric silicones. The thickness at which a coating is considered

an *encapsulant* and no longer a coating is not well defined. One definition is that an encapsulant completely embeds all the components and gross features of an assembly whereas coatings simply conform to the topology of the components. However, with advances in microelectronics, a gray area exists. For example, with fine-line features, as in thin-film interconnect substrates and integrated circuits, coatings such as BCB and polyimide, that planarize the surfaces actually encapsulate the circuit features, yet they are still considered coatings.

Controlling the thickness is part science and part art. An operator trained in spray coating can consistently and repeatedly deposit the same thickness. The spray pressure, distance of the spray nozzle from the part, and angle of spray are all part of the art. Robotic spray equipment, once programmed, can also consistently deposit the same thickness. From a science standpoint, the viscosity of the coating and maintaining a constant viscosity are critical. The viscosities of solvent-based coatings, in particular, need to be controlled because of evaporation of solvent. Periodic viscosity measurements must be made and solvent added to adjust for the optimum viscosity. Viscosity may also increase due to premature polymerization especially for coatings whose cures are initiated by oxygen or moisture in the air. For example, in processing a moisture-cured polyurethane, a blanket of dry nitrogen over the coating prevents polymerization and prolongs its use.

Several methods and apparatus may be used to measure thicknesses and viscosities. These are discussed in Ch. 6 "Test Methods."

3.7.5 Rework and Repair

Most commercial electronic modules are designed as throw away items. They are either not coated or are coated with an inexpensive varnish or molded in plastic. Most are low-cost, plastic-encapsulated microcircuits (PEMs) where rework is not cost-effective nor practical.

The ability to rework, however, is very important for complex high-density modules, some of which may be valued at many thousands of dollars or where schedules or availability do not permit them to be refabricated. An example is the two-sided Master Events Controller (MEC) board for the Space Shuttle (Fig. 3.23). This is one of 13 similar boards which, together with two power supplies, comprise the MEC which receives, verifies, and executes commands from four computers during crucial lift-off and staging sequences. Each PWA contains hundreds of expensive components and is coated with an RTV silicone.

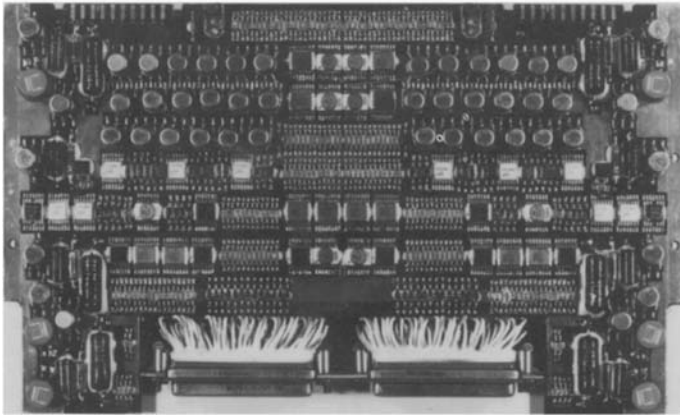


Figure 3.23. Space shuttle printed wiring board coated with RTV silicone.

Removal and replacement of a faulty device after coating presents a challenge in benignly and selectively removing the coating, detaching the component, selectively cleaning the affected area, reassembling the new component, and recoating. Thermoplastic coatings that melt and flow under a hot solder iron are convenient since the solder iron can be used to melt through the coating and remove a solder-attached component in one step. Polyurethane and acrylic coatings, especially, lend themselves to this type of rework. The coating removal method selected will depend on the type of coating used and the compatibility of the method with the rest of the assembly. For example, a method may be effective in removing the coating, but may also remove markings or damage other portions of the assembly. The most widely used rework methods are given in Table 3.6.

Removal and replacement of faulty wire-bonded or solder-attached components that have been overcoated is easiest if the overcoating is a polyurethane or an acrylic. A hot solder iron softens and melts most polyurethanes allowing removal of the component (Fig. 3.24). After cleaning the attachment site, a new component can be solder attached, and the rework area recoated. Acrylic coatings are also easily removed by dissolving in solvents such as Freons, toluene, xylene, or ketones. Selected areas of the coating can be removed by swabbing with the solvent or the entire coating can be removed in a vapor degreaser, provided the chosen solvent doesn't attack other portions of the module such as markings or other plastics.

Table 3.6. Rework and Repair Methods

Method	Comments
Melting or softening with a hot solder iron	Best for thermoplastics such as polyurethanes and acrylics
Dissolving with appropriate solvents	Best for some silicones, acrylics, and soft baked polyimides
Chemical strippers	Useful for silicones and polyurethanes
Softening with hot air or nitrogen gun and applying a force such as scraping	Best for thermosetting coatings such as epoxies and phenolics
Cutting and peeling or lifting	Best for soft silicones
Abrasion	All hard coatings
Plasma etching using an oxidizing gas	Parylene and polyimides
Laser ablation	Parylene and polyimides
Swelling with solvents and lifting	RTV silicones

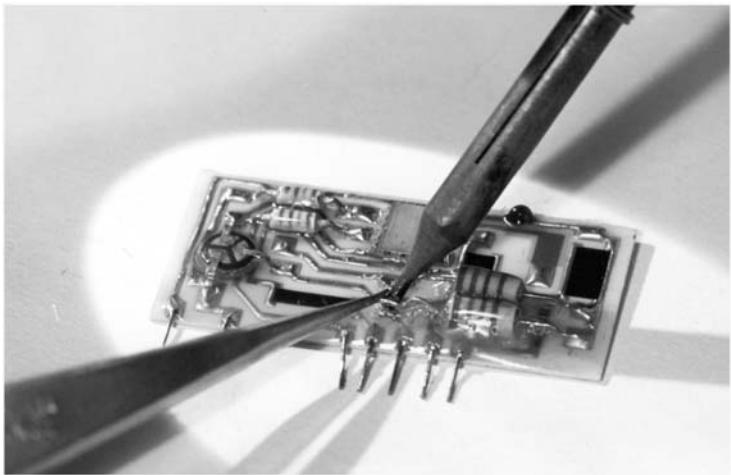


Figure 3.24. Rework using a hot solder iron to melt through polyurethane coating.

Epoxy polyamides can be softened and removed with a hot solder iron also, but if heat is applied too long, decomposition and charring of the epoxy coating results (Table 3.7). Such dark-colored residues not only give a poor appearance, but may affect subsequent solderability. Epoxies cured with amines or other catalysts and hardeners behave similarly; many of them immediately char without going through a softening stage.

Soft elastomeric silicones can be removed by cutting through, then peeling or lifting. When immersed in chlorinated or fluorinated organic solvents, silicones will also swell and can be more easily removed mechanically. For example, RTV silicones can swell 50–300% in volume in a matter of 5 to 10 minutes when immersed in various Freons. Alcohols also swell RTV silicones, but to a lesser extent: from 1% in methanol to 20% in isopropanol. Other harder silicones may be dissolved on prolonged immersion in tetramethylguanidine.

One drawback to the use of solvents is that the coating removal is difficult to localize; usually the entire assembly must be immersed which then presents the risk of damaging other areas. Also, swelling of the coating can generate stresses that may induce other failure modes, and the process is slow requiring immersion for several days. Some attempts have been made to localize the solvent by preparing a thixotropic paste of the solvent with Cab-O-Sil or colloidal silica. Thixotropic compositions containing over 90% solvent will not flow under normal conditions, and thus allow the solvent to remain over a selected area. The process is, however, slow with the added problem of having to periodically replenish solvent that evaporates.

Parylene and fully cured epoxies and polyimides are among the most difficult coatings to remove. Epoxies are generally highly cross-linked molecules that are resistant to most acids, bases, and organic solvents. Epoxies also do not melt, but decompose and char as the temperature is increased. Some epoxies can be softened at temperatures above their T_g and, while in the softened state, can be gradually removed by applying lateral pressure.

Parylene coatings are insoluble in all known organic solvents and chemicals and will not soften or melt except at extremely high temperatures. The best methods for removal are by plasma etching, YAG (uv) laser ablation, or mechanical abrasion. Ultraviolet laser ablation is used to precisely remove small areas of parylene coating that are difficult to remove by other methods. Polyimides are also best removed by plasma etching, laser ablation, or scraping.

Table 3.7. Removability Characteristics of Circuit-board Coatings

Coating Type	Part A	Part B	pbw, A:B	Cure, hrs/°C	Removability with Hot Solder Iron*
Epoxy Polyamide	Epon 828	Versamid 115, Shell curing agent Z	50:50	3/65	Softens and becomes cheesy
Epoxy Amine	Epon 1001	Diethylene triamine	60:15	3/65	Softens and becomes cheesy
Epoxy Polyamide	Epon 1001	Versamid 115, Shell curing agent Z	100:30	3/65	Softens and becomes cheesy
Epoxy Polyamide	Epon 828	Versamid 115, Shell curing agent Z	50:50	2/80 + 2/150	Softens and becomes cheesy
Polyurethane	Mobay Modur CB-60	Castor oil	-	3/65	Liquifies

*315°C tip, 20-sec dwell.

All coatings were formulated with suitable solvents for spray or dip application.

Polyimides after soft baking, but prior to hard baking, may be removed using a strong solvent such as N-methyl pyrrolidone (NMP) or proprietary strippers at elevated temperature. Once fully cured, polyimide coatings cannot be removed by solvents or chemicals. Plasma etching using a 5:1 ratio of oxygen to carbon tetrafluoride appears to be the most effective method for removing cured polyimide.

Once the coating has been removed and a component replaced, recoating with the original coating may present a problem, especially in field repair. The original coating may have been deposited by special equipment or processes under controlled conditions which may not be available in the field. Hence, a coating, other than the original, that is easily processed needs to be used. The coating must be compatible with the original coating and provide the same environmental protection and electrical characteristics. A notable example is the repair of parylene-coated circuit boards where recoating with parylene would require vapor deposition equipment. Low-cost, field-friendly materials and processes were evaluated and found to be reliable. Flexible polyurethanes such as DeSoto-Product Research's PR-1592, Vantico's Uralane 5750, or Conathane CE-1155 were found to be good repair coatings for polyurethanes, epoxies, and acrylics, and, with primers, also for parylene. The materials were applied by brushing or spraying and required only moderate temperatures for curing.^[86]

REFERENCES

1. Particle Atlas Electronics Edition, CD-ROM, McCrone Research Institute, Chicago, IL (1998)
2. Kenyon, W. G., Printed Wiring Board Cleaning (C. Harper, ed.), *Electronic Assembly Fabrication*, Ch. 8, McGraw-Hill (2002)
3. Post Solder Semiaqueous Cleaning Handbook, IPC-SA-61 (Apr. 1987)
4. Aqueous Post Solder Cleaning Handbook, IPC-AC-62A (Jan. 1996)
5. Guidelines for Cleaning Printed Boards and Assemblies, IPC-CH-65A (Aug. 1999)
6. Cala, F., and Reynolds, R., Post Assembly Cleaning of BGAs, *SMT* (Apr. 1997); Cala, F., and Winston, W., *Handbook of Aqueous Cleaning Technology for Electronic Assemblies*, Electrochemical Publications, Asahi House, Isle of Man, British Isles (1996)

7. Koon, J., and Burrell, R., Low Residue Soldering of Military Electronics, *Circuits Assembly* (Apr. 1995)
8. Licari, J. J., and Enlow, L., *Hybrid Microcircuit Technology Handbook*, 2nd Ed., Noyes Publ., Park Ridge, NJ (1998)
9. EPA Regulation 40, CFR Parts 9 and 63 (Dec. 2, 1994)
10. Fuchs, F. J., Ultrasonic Cleaning: Fundamental Theory and Application, CAE Ultrasonics Website, caeultrasonics.com
11. Jeffrey, L. R., Ultrasonic Cleaning, Metal Finishing Guidebook, *Metals and Plastics Publ.*, Westwood, NJ (1967)
12. Uner, J., et al., The Application of Atmosphere Pressure to Various Steps in Integrated Circuit Packaging, *Proc. 3rd Annual Semiconductor Packaging Symp.*, SemiconWest (2000)
13. White, M. L., Removal of Die Bond Epoxy Bleed Material by Oxygen Plasma, *Proc. 32nd Electronic Components Conf.*, IEEE (1982)
14. Bunshah, R. F., (ed.), *Handbook of Deposition Technologies for Films and Coatings, Science, Applications and Technology*, Noyes Publ., Park Ridge, NJ (1994)
15. Ahn, S., Yoon, H., and Oh, S., Reliability Improvement of Plastic Ball Grid Array Package by UV/Ozone Cleaning, *Proc. 1st Int. Symp. on Ball Grid Array Technol.*, ISHM, Los Angeles (Oct. 1995)
16. Dalton, M., and Cline, C. M., CO₂ Snow/Pellet Cleaning/Super Critical Fluid, *Precision Cleaning*, III, No. 11 (Dec. 1995)
17. Whitlock, W., Dry Surface Cleaning with CO₂ Snow, *Proc. 20th Annual Meeting of the Fine Particle Society* (Aug. 1989)
18. Peterson, R. V., and Bower, C. W., Contamination Removal by CO₂ Jet Spray, *SPIE*, Vol. 1329 (1990)
19. Zito, R. R., Removal of Adsorbed Gases with CO₂ Snow, *SPIE*, Vol. 1494 (1991)
20. Lin, R., et al., Moisture Induced Package Cracking in Plastic Encapsulated Surface Mount Components During Solder Reflow Process, *Proc. Int. Reliability Physics Symp.*, IEEE (1988)
21. Lau, J. H., (ed.), *Ball Grid Array Technology*, McGraw-Hill (1995)
22. Ramig, A., Powder Coatings Technology, Status and Future Opportunities, *Proc. ACS Div. of Polymeric Mater.*, Sci. and Engin., Vol. 55 (1986)
23. Von Fischer, W., and Bobalek, E. G., *Organic Protective Coatings*, Reinhold, NY (1953)
24. Davis, W. J., Methods and Apparatus for Applying Protective Coatings, U. S. Patent 3004861 (Oct. 1961); Dettling, C. J., Fluidized Bed Coating Method, U. S. Patent 2974060 (Mar. 1961)

25. Gemmer, E., Process and Apparatus for the Preparation of Protective Coatings from Pulverulent Synthetic Thermoplastic Materials, German Patent 933019 (Sep. 1955)
26. Gemmer, E., Fluidized Bed Coating Process, U. S. Patent 2974059 (Mar. 1961); Gemmer, E., Fluidized Bed Coating Process for Coating with Thermosetting Materials, U. S. Patent 3090696 (May 1963)
27. Landrock, A. H., The Coating of Aluminum with Plastics by the Fluidized Bed and Electrostatic Powder Techniques, Plastec Note 18, Plastics Technical Evaluation Center, Picatinny Arsenal, NJ (Feb. 1968)
28. Pettigrew, C. K., Fluidized Bed Coatings, *Modern Plastics*, Part 1, 43(12) (Aug. 1966); and Part 2, 44(1) (Sep. 1966)
29. Gaynor, J., Robinson, A. H., Allen, M., and Stone, E. E., Variables in Fluidized Bed Coatings, *Modern Plastics*, 43(5) (Jan. 1966)
30. Donges, W., Conformal Coating Optimization, *Surface Mount Technol.* (Aug. 2001)
31. Reighard, M. A., and Barendt, N. A., Advancements in Conformal Coating Process Controls, *Proc. NEPCON West*, Anaheim, CA (Feb. 2000)
32. White, P., Thin Film Dielectrics, *Insulation* (Sep. 1963)
33. White, M., Vacuum Evaporation of Polythene, *Vacuum*, 15:449 (1965)
34. *Proc. of the 7th Conf. Soc. Vacuum Coaters*, pp. 78–81 (1964)
35. Licari, J. J., unpublished work (ca. 1980)
36. Circuit Automation, DP-1500-2X, DP-1500-2XL Data Sheets (Oct. 1997)
37. Extrusion Coating Considered Applicable to 300 mm Wafers, *Solid State Technol.* (Jun. 2000)
38. Wells, G. T., Gibson, G., and Newquist, C., Large Area Processing (LAP) Performance Studies on Extrusion Coating, *Int. Symp. Microelectronics*, Philadelphia (1997)
39. Kalman, J., Embedded Systems Improve Flat Panel Production, *Electronic Design News*, Cahners Publ. Co. (Oct. 16, 1996)
40. Kamen, E. W., and Popescu, C., Modeling of Extrusion Coating for Applications in Electronic Manufacturing, *Manufacturing Technol. Conf.*, San Jose, CA (Feb. 1999)
41. Krauss, A. F., Kamen, E. W., Chng, C. M., and The, A. C., Process Control of Material Deposition by Meniscus Coating for Low-Cost MCM Prototyping, *Int. Symp. Microelectronics*, Philadelphia (1997)
42. Garrou, P., et al., Large Area Processing: Meniscus Coating of Thin Film Polymer Dielectric and Photoresist, *Int. Symp. Microelectronics*, Philadelphia (1997)

43. Lowry, R. K., Moisture Process Control and Mass Spectrometry Correlations, *Proc. RADC/NBS Int. Workshop on Moisture Measurement and Control for Microelectronics (IV)* (1986)
44. DeForest, W. F., *Photoresist Materials and Processes*, McGraw-Hill, New York (1975)
45. Hoyle, C. E., Photocurable Coatings, *Proc. ACS Div. of Polymeric Mater., Sci. and Engin.*, Vol. 55 (1986)
46. Puder, A. T., The Role of Ultraviolet Curing in PC Board Assembly Automation, *Electronics* (Jun. 1986)
47. Schick, S., Ultraviolet Curing, A New Path to Productivity, *Proc. Int. Soc. Hybrid Microelectronics* (1986)
48. Schick, S., Portable Ultraviolet System Provides High Intensity Cures, *Adhesives Age* (Apr. 1986)
49. Wieler, M., and Suppa, M., Thick Film Coating Materials and Fast Conformal Coating Process, *Proc. APEX*, San Diego (Jan. 2002)
50. Conrod, J., and Nargi-Toth, K., Photodefinable Dielectric Materials for High Density Printed Wiring Board Applications, *IPC Printed Circuits Expo* (Mar. 6, 1996)
51. Koleske, J. V., and Austin, T. M., A New UV-curable Conformal Coating and an Accelerated Moisture Resistance Test Method, *IPC 29th Annual Meeting* (1986)
52. Melville, H. W., *Proc. Royal Society*, A163:511, London (1937); Melville, H. W., *Proc. Royal Society*, A167:99, London (1938)
53. Gregor, L. V., and McGee, H. L., Electrical Insulation Conf., *Natl Academy of Science/Natl Research Council Publ. No. 1680* (1963)
54. White, P., *Electrochem Technol.*, 4:468 (1966)
55. Thin Film Polymers, General Electric Public Information Unit, Schenectady, NY (Jul. 1967)
56. Fathi, Z., et al., Innovative Curing of High Reliability Advanced Polymeric Encapsulants, *Proc. NEPCON West* (1998)
57. Zou, Y., Harris, J., Ahmad, I., Tucker, D., and Fathi, Z., Comparison of Die Level Stresses in Chip-on-Board Packages Processed with Conventional and VFM Encapsulant Curing, *Proc. High Density Packaging and MCM Conf.*, Denver, CO (Apr. 1999)
58. Poole, K. M., *Proc. Phys. Soc.*, Vol. B66542, London (1953)
59. Ennos, A. E., *Brit. J. Applied Physics*, 5:27 (1954)

60. Buck, D. A., and Shoulders, K. R., *Proc. Eastern Joint Computer Conf.*, Philadelphia (1958)
61. Muehlberg, P. E., et al., Process for Making Tetrafluoroethylene Polymers, U. S. Patent 3170858 (Feb. 1965)
62. Davison, W. H. T., Irradiation of Materials, Australian Patent 248844 (Jan. 1964)
63. Radiation Dynamics: Radiation Curing of Substrates, *Prod. Finishing*, 20(5) (May 1967)
64. Schimtz, J. V., and Lawton, E. J., Process for Applying Protective Coatings by Means of High Energy Electrons, U. S. Patent 2900277 (Aug. 1959)
65. White, P., Preparation and Properties of Dielectric Layers Formed by Surface Irradiation Techniques, *Insulation* (May 1967)
66. Claude, R., and Moisan, M., Comparison of Microwave and Lower Frequency Discharges for Plasma Polymerization, *Proc. ACS Div. Polymeric Mater.*, Sci. and Engin., Vol. 56 (1987)
67. Amouroux, J., et al., Comparison Between Atmospheric Pressure and Low-Pressure Plasma Polymerization, *Proc. ACS Div. Polymeric Mater.*, Sci. and Engin., Vol. 56 (1987)
68. Yeh, Y. S., et al., Influence of Reactor Design Factor on the Deposition of Plasma Polymerization, *Proc. ACS Div. Polymeric Mater.*, Sci. and Engin., Vol. 56 (1987)
69. Wertheimer, M. H., and Moisan, J., *J. Vac. Sci. Technol.*, A3(6):2643 (1985)
70. Sadhir, R. K., et al., Deposition and Characterization of Plasma Polymerized Films of Hexafluorobenzene and Ammonia, *Proc. of ACS Div. Polymeric Mater.*, Sci. and Engin., Vol. 56 (1987)
71. Bradley, A., and Hammes, J., Electrical Properties of Thin Organic Films, *J. Electrochemical Soc.* (Jan. 1963)
72. Smolinsky, G., and Heiss, J. H., Thin Organic Films Formed by a Glow Discharge Technique, *Proc. ACS*, 28(1) (Apr. 1968)
73. Goodman, J., *J. Polymer Science*, 44:551 (1960)
74. Bamford, C. H., et al., Uses of Electric Discharge in Polymer Science, *Soc. Chem. Ind. Monograph*, Vol. 17 (1963)
75. Coleman, J. H., Polymerizing Method and Apparatus, U. S. Patent 3068510 (Dec. 1959) and U. S. Patent 3069283 (Feb. 1959)
76. Redmond, J. P., and Pitas, A. F., *Investigation of Polymeric Coatings by Electrodeless Discharge, Final Report*, NASA Contract NASW-1625 (May 1968)
77. Caswell, H. L., Fabrication of Thin-Film Insulation, *Electrical Insulation Conf.*, Natl. Acad. Sci./Natl. Research Council Publ. 1238 (1965)

78. Numata, K., et al., Characteristics of Ionized Cluster Deposition of Polyethylene Films, *Proc. ACS Div. Polymeric Mater., Sci. and Engin.*, Vol. 56(1987)
79. Hudis, M., *Techniques and Applications of Plasma Chemistry*, Wiley, New York (1974)
80. Klauser, M., et al., Surface Modification of Polymers with Fluorine Containing Plasma: Deposition vs. Replacement Reactions, *Proc. ACS Div. Polymeric Mater., Sci. and Engin.*, Vol. 56 (1987)
81. Gombotz, W. R., and Hoffman, A. S., Functionalization of Polymeric Films by Plasma Polymerization of Allyl Alcohol and Allylamine, *Proc. ACS Div. Polymeric Mater., Sci. and Engin.*, Vol. 56 (1987)
82. Khimchenko, Y. I., et al., Effect of Gamma Irradiation on the Structure of Epoxy Resin and Organometallic Polymers Based on Epoxy Resin, Academy of Sciences U.S.S.R., Institute of General and Inorganic Chemistry, (translated by J. Kourilo, Aerospace Technology Division, Library of Congress) (Jun. 1964)
83. Nakagawa, K., and Manaka, K., Antistatic Treatment of Teflon Films by Radiation Induced Graft Polymerization, *Genshiryoku Kogyo*, 11(11):47–50, Japan (1965); *Chemical Abstracts*, 95733r (1967)
84. DasGupta, S., The Use of Cobalt-60 for the Production of Industrially Important Materials, *Canadian Nuclear Assoc. Conf., Montreal (May 27–29, 1963)*
85. Wall, K. J., New Silicone Conformal Coating and Potential for Cross-Contamination, *Etronix Conf.*, Anaheim, CA (Feb. 2001)
86. Dunaetz, R. A., et al., *Repair of Conformally Coated Printed Wiring Board Assemblies*, Final Technical Report, AFWAL-TR-80-4086 (Sep. 1980)

Applications

Applications for organic polymer coatings have grown over the years, paralleling advances made in microelectronics. From the traditional conformal coatings used to protect printed wiring boards and insulate wire, coatings are now used as high-performance dielectrics as an integral step in the processing of semiconductor chips, multichip module interconnect substrates, flip-chip devices, and ball-grid-array packages. Polymer coatings, especially the polyimides and benzocyclobutenes (BCB), now play a major role in the electronic functioning of assemblies such as RF, microwave, and high-speed circuits. In addition, with the increased use of sensors in automobiles and in implanted medical devices, coatings have had to play a new role in meeting diverse requirements. Examples are protecting electronic circuits in the hot and dirty near-engine environment of automobiles and from the biofluids of the human body. It is also anticipated that dielectric coatings will be specifically engineered for emerging optoelectric and MEMS (Micro-electromechanical systems) applications.

Besides the permanent protective coatings and dielectrics, this chapter addresses coatings that are temporary, yet essential, in the processing of microelectronic circuits. Among these temporary or sacrificial coatings are the photoresists and maskants used during etching, plating, and soldering operations.

4.1 CONFORMAL COATINGS FOR PRINTED WIRING ASSEMBLIES (PWA)

Organic polymer coatings have been used for over forty years as moisture protective conformal coatings for printed circuit boards (PCB) and for printed wiring assemblies (PWA) used in high-reliability military and space applications and, to a lesser extent, in commercial electronic hardware.^{[1][2]} The main functions of organic conformal coatings for PWAs include:

- Preventing leakage currents and catastrophic electrical failures due to moisture and contaminants.
- Preventing corrosion of solder, copper, and other metal surfaces.
- Preventing or reducing tin whisker growth, metal migration, and conductive anodic filament (CAF) formation.^[3]
- Reducing or preventing arcing and corona discharge.
- Providing mechanical support and improving the fatigue life of solder joints and components during mechanical shock or vibration.

Coatings belonging to the generic families of acrylics, silicones, polyxylylenes, epoxies, and polyurethanes are specified in, and some have been qualified to, MIL-I-46058C or IPC-CC-830A. In most PWAs, the devices are already packaged in hermetically sealed or epoxy-molded packages, then solder attached to the board. In such cases, the purposes of the conformal coating are to prevent moisture, salts, and other contaminants from corroding the exposed solder joints and conductor traces and to reduce the amount of moisture that may be absorbed by the board material itself which results in degradation of electrical insulating properties. The coating must be of high purity and of a molecular structure that its insulation resistance will be high and will not significantly degrade under humidity-temperature exposures. The ten-day humidity-temperature cycling test specified in MIL-I-46058C or MIL-STD-202 is widely used to compare and qualify coatings for printed wiring boards (Fig. 4.1).

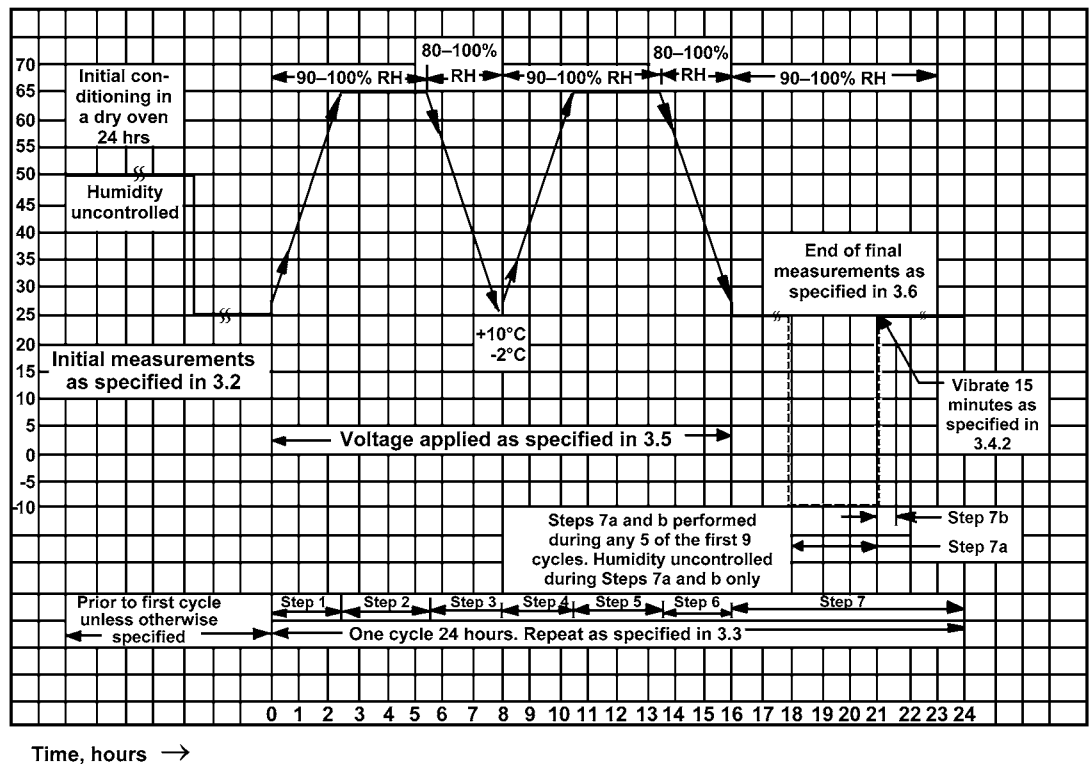


Figure 4.1. One-day graph of ten-day humidity-temperature cycling per MIL-STD-202, Method 106.

Generally, the insulation resistance of the coating drops on initial exposure to moisture during the first day, then levels off. High-purity coatings such as fluorocarbons, silicones, and parylenes have shown better insulation properties under humid conditions than some epoxy coatings (Fig. 4.2). Decreases in insulation resistance as much as nine decades have been reported for uncoated laminates, but with a suitable protective coating, the decrease may be only one to three decades under the same conditions^[4] (Table 4.1). Coatings afford similar protection to epoxy-glass laminates under even more severe stresses of combined temperature, humidity, and applied voltage^[5] (Table 4.2).

The sharp and rapid decrease in insulation resistance of most polymer coatings occurs during the first humidity cycle with some recovery occurring in subsequent cycles. It has been postulated that coatings absorb water quickly during the first cycle and, accelerated by the applied voltage, partial hydrolysis of the coating constituents occurs. This then results in a breakdown of the coating in the region of the hot conductors and causes the insulation resistance to drop. However, because of differences in their moisture absorption and permeability properties and in their inherent purity, not all coatings undergo a sharp initial drop. Figure 4.3 shows a significant difference between a coating qualified to a military specification and a commercial-grade coating.^[4]

Besides the beneficial effects on insulation resistance, conformal coatings reduce or prevent arcing and corona discharge in closely-spaced conductors that are exposed to high voltages. Conformal coatings allow the design engineer greater freedom in designing closer conductor line spacings at higher voltage capabilities. The increased electrical insulation afforded by an epoxy coating on a G-10 laminate board with 62-mil conductor spacing was reported by McGuiness.^[6] In this report, flashover voltage for the coated board was 5,000 volts compared with 1,600 volts for the uncoated board. The effectiveness of the coatings in allowing closer spacings for various voltages is shown in Table 4.3. In more recent high-density multilayer PCBs, where bare-chip devices are used, for example, Chip-on-Board (COB), improved barrier properties and compatibility with devices are required.^{[7][8]}

The conformal coating of high-voltage power supplies and dc-dc converters is essential in preventing dielectric breakdown and arc over. It is critical that any high-voltage circuit be thoroughly clean and dry prior to conformal coating. With the trend towards using water-based fluxes and water cleaning, there is an increased risk of water absorption and retention within the board, hence vacuum baking or other means of drying becomes

necessary. A dc-dc converter printed wiring assembly coated with a polyurethane is shown in Fig. 4.4.

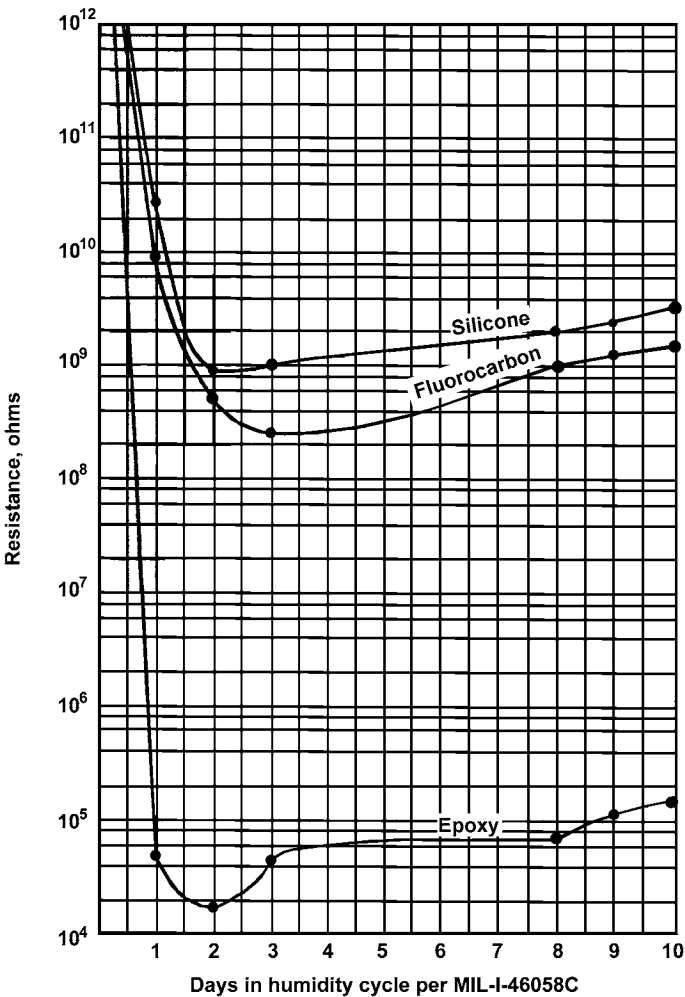


Figure 4.2. Effect of humidity and temperature cycling on the insulation resistance of some polymer coatings.

Table 4.1. Humidity Effects on Insulation Resistance of Circuit Boards^[4]

Sample	Insulation Resistance, ohms		
	Initial	After Cycle 5	After Cycle 10
<i>A</i>			
Uncoated	1.5×10^{12}	3×10^7	5×10^4
Coated	1×10^{12}	3×10^9	2×10^9
<i>B</i>			
Uncoated	3×10^{12}	5×10^7	5×10^3
Coated	3.1×10^{12}	5×10^{11}	4×10^{11}
<i>C</i>			
Uncoated	3×10^{12}	5.5×10^7	1.5×10^6
Coated	3×10^{12}	3×10^{11}	4.1×10^{10}

Conformal coatings can be formulated using many different chemistries and are normally applied by spraying, dipping, brushing, or flow coating. Cured thicknesses range from approximately 1 to 3 mils for the AR, ER, and UR types, 2 to 8 mils for the SR types, and 0.5 to 2 mils for the XY types. The cured coatings are chosen based on their dielectric properties such as dielectric constant, dissipation factor, insulation resistance, dielectric breakdown voltage, and the stability of these parameters under elevated temperature, humidity, and high-frequency conditions. Early formulations that were based on solvent carriers and long cure times are being replaced with non-solvent containing (100% solids) compositions and formulations that cure in minutes instead of hours. Using non-solvent formulations is important in avoiding the entrapment of solvents in the coating which can cause voids and loss of adhesion. Organic solvents also need to be avoided to meet recent state and federal regulations relating to the discharge of organic oxygen-depleting solvents (ODS) into the atmosphere. Traditional highly volatile organic solvents are being replaced by solvents having low VOC (Volatile Organic Compounds) emissions.

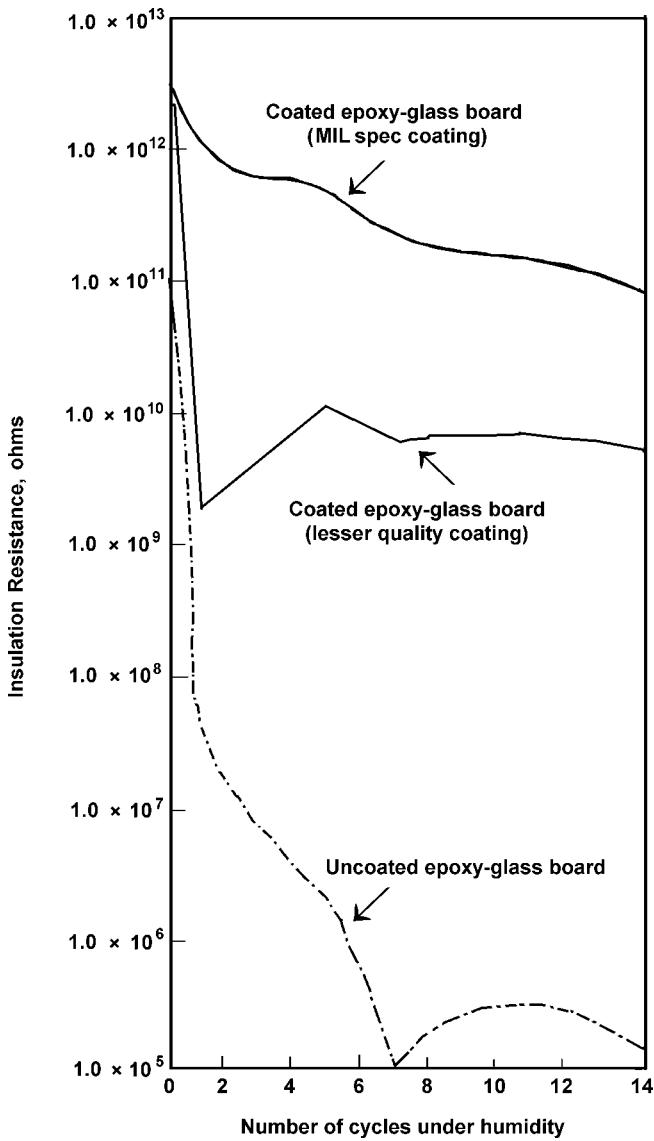


Figure 4.3. Insulation resistance of coated and uncoated circuit boards in humidity cycling according to MIL-I-46058.^[4]

Table 4.3. Minimum Spacings for Uncoated vs Coated Conductors and Parts

Voltage between Conductors (dc or ac peaks)	Spacing (mm)			
	Uncoated, Bare Board ¹	Polymer Coated, Bare Board ¹	Uncoated, Assembly ²	Polymer Coated Assembly ²
0–15	0.1	0.05	0.13	0.13
16–30	0.1	0.05	0.25	0.13
31–50	0.6	0.13	0.4	0.13
51–100	1.5	0.13	0.5	0.13
101–150	3.2	0.4	0.8	0.4
151–170	3.2	0.4	0.8	0.4
171–250	6.4	0.4	0.8	0.4
251–300	12.5	0.4	0.8	0.8
301–500	12.5	0.8	1.5	0.8
¹ External conductors (sea level to 3050 m). ² External component lead/termination (any elevation). <i>(Data abstracted from IPC-2221.)</i>				

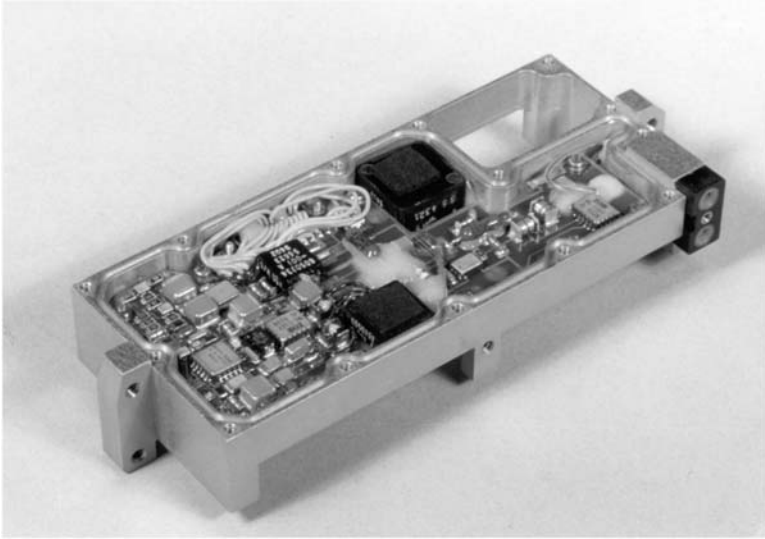


Figure 4.4. High-voltage dc-dc converter coated with polyurethane. (*Courtesy Babcock Electronics.*)

4.1.1 Conformal Coating Performance

The performance and long-term reliability of conformal coated PWAs depend not only on the type of coating selected and its curing conditions, but also on the nature of the surfaces to which it is applied and the cleanliness and dryness of those surfaces. Circuit boards consisting of epoxy-glass and polyimide-glass laminates can absorb large amounts of moisture especially during aqueous cleaning. Flux residues are generally hygroscopic and augment the absorption and retention of moisture. If not cleaned and dried well, a subsequently applied conformal coating such as polyurethane will blister and lose adhesion. Adhesion of coatings to gold-plated surfaces or to Teflon-insulated wire is poor and, unless these surfaces are primed, physically roughened, or chemically etched, the coating will peel off.

4.1.2 Specifications for Conformal Coatings

MIL-I-46058C, *Insulating Compound, Electrical (For Coating Printed Circuit Assemblies)* and IPC-CC-830A, *Qualification and Performance of Electrical Insulating Compound for Printed Board Assemblies* describe five polymer types that are widely used as printed wiring board conformal coatings. These types and their designations are:

Type AR	Acrylic resin
Type ER	Epoxy resin
Type SR	Silicone resin
Type UR	Polyurethane resin
Type XY	Paraxylylene

There are also coatings that combine two of these types such as ARUR, a combination of acrylic and polyurethane resins.

IPC-CC-830A is an industry specification closely paralleling the military specification. It has become the dominant specification since MIL-I-46058 has been canceled for new designs. Other applicable specifications are MIL-P-55110E, *Printed Wiring Assemblies* and UL746C, *Polymeric Materials-Use in Electrical Equipment Evaluations*, which specifies Underwriters Laboratories' tests for flammability. Coatings for military and high-reliability applications should meet the requirements of these specifications. In addition, for space applications, further requirements are superimposed, such as outgassing in a thermal-vacuum environment and vulnerability to radiation and atomic oxygen. A listing of organic coatings along with other polymeric materials that have been tested for outgassing and their results are given in NASA Reference Publication 1124, Revision 4, June 1997. Other requirements for space vehicles are given in MIL-HDBK-1547A, July 1998, *Electronic Parts, Materials, and Processes for Space and Launch Vehicles*.

Many excellent conformal coatings are on the market, some of which have been qualified to military and space specifications. Some commercially available coatings with a brief description of each are listed in Table 4.4.

Table 4.4. Typical Conformal Coatings for Printed Wiring Assemblies

Tradename	Manufacturer	Chemical Type	Characteristics
Uralane 5750 A/B Uralane LV	Vantico	Polyurethane	Two-part soft repairable coating. Qual to MIL-I-46058; meets NASA outgassing
Solithane 113 cured with C113-300	Uniroyal	Polyurethane	Low curing temps. from RT to 149°C. Meets NASA outgassing
Conathane CE-1155	Cytec Industries	Polyurethane	Two-part, solvent based coating, qual to MIL-I-46058; meets NASA outgassing
Conathane CC-1195	Cytec Industries	Polyurethane	Two-part, solvent based, cure at room or elevated temperature, continuous use to 130°C.
Conathane CE-1175	Cytec Industries	Polyurethane	One-part, water based; meets MIL-I-46058
Conathane CE-1164	Cytec Industries	Polyurethane	One-part solvent based, air dry, room RT moisture cure; meets MIL-I-46058
Solithane 113	Thiokol	Polyurethane	Meets NASA outgassing requirements
HumiSeal 1A33	Chase Corp., HumiSeal Div.	Polyurethane	One-part, air/oxygen cure; Qual to MIL-I-46058 and IPC-CC-830
HumiSeal 1A20	Chase Corp., HumiSeal Div.	Polyurethane	One-part, moisture cure, resistant to solvents and chemicals, contains fluorescent tracer, qual to MIL-I-46058
HumiSeal 2A64	Chase Corp., HumiSeal Div.	Polyurethane	Two-part, solvent based, high solids, low viscosity for easy application, contains fluorescent tracer, meets MIL-I-46058
HumiSeal 1B12	Chase Corp., HumiSeal Div.	Acrylic	One-part, RT cure

(cont'd.)

Table 4.4. (cont'd.)

Tradename	Manufacturer	Chemical Type	Characteristics
HumiSeal 1B73	Chase Corp., HumiSeal Div.	Acrylic	One-part, fast air drying, contains fluorescent tracer, meets MIL-I -46058
HumiSeal 1B73LSE	Chase Corp., HumiSeal Div.	Acrylic	Same as 1B73 but with legal solvent emissions
HumiSeal 1B31	Chase Corp., HumiSeal Div.	Acrylic	One-part, repairable, flexible, fluoresces under uv light, qual to MIL-I-46058
Conap CE-1170	Cytec Industries	Acrylic	One-part, solvent based, RT cure, meets MIL-I-46058, repairable
Conap CC-1191	Cytec Industries	Acrylic	One-part solvent-based, fast drying, repairable
Novec EGC-1700	3M Specialty Materials	Fluoro-acrylate	One-part, 2% in hydrofluoroether solvent, no VOCs, low surface energy repels water, thermal stability to 175°C
ECC4865	General Electric	Silicone	One part, clear solventless, low viscosity, thermal cure
HumiSeal 1C49	Chase Corp., HumiSeal Div.	Silicone	100% solids, room temp. cure, continuous use temp. to 200° C, meets MIL-I-46058
HumiSeal 1C51	Chase Corp., HumiSeal Div.	Silicone	100% solids, heat cure, continuous use temp. to 200° C, meets MIL-I-46058
DC-1900 Series (3-1953, 3-1965)	Dow Corning	Silicone	100% solids, low VOC emissions, one-part, moisture/condensation cure at RT or elevated temp.
Sylgard 1-4128	Dow Corning	Silicone	Two-part, 100% solids, addition cure with heat
Sylgard 1-4105	Dow Corning	Silicone	One-part, 100% solids, thermal cure

(cont'd.)

Table 4.4. (cont'd.)

Tradename	Manufacturer	Chemical Type	Characteristics
DC-3140	Dow Corning	Silicone	One-part RTV, 100% solids
DC-1-2577	Dow Corning	Silicone	One-part, solvent-based, RT cure or rapid heat cure with catalyst, meets MIL-I-46058
NuSil R-1075	NuSil	Silicone	One-part moisture cure RTV silicone dispersion conformal coating for printed circuit boards, 60% solids in trichloroethane
SWS RSV S-10	Wacker Silicones	Silicone	100% solids conformal coating for rigid and flexible printed circuit boards
Semicosil® 992 JC	Wacker Silicones	One-part, peroxide cure silicone	Semiconductor white junction coating, heat curing, high viscosity, low ion content
Elastosil® RT 745	Wacker Silicones	Addition cure silicone	Low viscosity, low inhibition, self adhesive
Semicosil® 935	Wacker Silicones	Addition cure silicone	Transparent, long pot life (1 week), low hardness
Semicosil® 964	Wacker Silicones	One-part moisture cure silicone	Sprayable solvent-free, fast curing, bluish color
Dispersion Coating T84	Wacker Silicones	One-part moisture cure silicone	Solvent-based, yellowish, medium hardness, fast curing
MP 15L	Wacker Silicones	One-part, resin solution, condensation cure silicone	Heat curing, transparent, high abrasion resistance, good mechanical properties
Silicoat	Transcene	One-part moisture cure silicone	Clear, RT cure 12 hrs; xylene thinner, $k = 2.65 @ 100 \text{ Hz}$; $DF = 0.0037 @ 100 \text{ Hz}$; $BV = 500 \text{ V/mil}$

4.1.3 Qualification of Conformal Coatings

Although many coatings have been qualified to MIL-I-46058C, the current standard for qualification is IPC-CC-830A which follows MIL-I-46058C very closely, but uses many of the test methods of IPC-TM-650. Basically, qualification is performed using a test coupon: the IPC-B-25A Multipurpose Test Board that consists of several comb patterns whereby insulation resistance measurements can be made before and after subjecting the coated board to humidity/temperature cycling and other physical and electrical tests. These tests include: fungus resistance, shelf life, fluorescence, appearance, thickness, flammability, dielectric withstanding voltage, moisture and insulation resistance, thermal shock, temperature/humidity cycling, and hydrolytic stability. The conditions for the humidity/temperature cycling test are slightly different from those specified in MIL-I-46058C or MIL-STD-202. Two test conditions are described: Class T in which the coated test board is aged at $65^{\circ}\text{C} \pm 2^{\circ}\text{C}$ and $90\% \pm 3\%$ RH for 24 hours without bias and Class H in which the coated board is cycled from 25° to $65^{\circ}\text{C} \pm 2^{\circ}\text{C}$ and $90\% -5/+3\%$ RH with 50 Vdc applied for a total of 160 hours. Insulation resistance measurements are made at 100 Vdc. Insulation resistance must be 1×10^8 ohms minimum for most electronic applications and 5×10^8 ohms for the high-end applications.

The IPC-B-25A test board is also used for the fungus test and other qualification tests. A simpler Y pattern test board is more practical for use in production for in-process control.

Qualification of PWB conformal coatings for space, automotive, and other specific applications will require meeting additional application-specific tests such as outgassing and radiation resistance for space and high-temperature resistance for automotive.

4.2 COATINGS FOR SEMICONDUCTOR SINGLE CHIP AND MULTICHIP MODULES

The use of high-performance polymer coatings in the semiconductor industry has grown considerably during the past decade. High-purity, temperature-stable polyimides and benzocyclobutenes are now widely used to complement and even replace the standard glassivation and passivation

layers of semiconductor device surfaces. Further, high-purity silicones and polyimides are effective in relieving stresses on semiconductor junctions and multichip assembled devices particularly when followed by plastic encapsulation. Finally, photoimageable polyimides and BCB coatings have been developed and are being widely used to redistribute bonding pads on semiconductor devices in preparation for solder bumping.

4.2.1 Environmental Protection and Passivation

In many cases, the use of thin-film coatings to protect single chip and multichip modules from moisture and other harsh environments presents an opportunity to reduce the weight, volume, and cost of electronic modules by over fifty percent. In fact, most of the weight and volume reduction achieved by converting PWBs to MCMs can easily be lost by hermetically sealing them in large bulky ceramic or metal packages.

Extending the application of polymer coatings to protect bare chip devices, as in hybrid microcircuits or multichip modules presents a challenge because the chips are not prepackaged. Organic coatings and encapsulants must be compatible with exposed thin-film conductor traces, marginal passivations, and fine wire bonds or flip-chip interconnections.

Early passivation materials consisted of glasses or silicon oxides that contained imperfections such as pinholes and microcracks. This, together with polymer overcoatings that contained large amounts of ions and that absorbed and permeated large amounts of moisture, resulted in many failures in the first generation of packaged devices and gave plastics a bad reputation. With advances that have been made in the purity and physical properties of polymer coatings and encapsulants during the past twenty years together with improvements in device passivation materials and processes, almost all devices today are plastic encapsulated microcircuits (PEMs) and provide sufficient reliability for commercial and industrial applications.

Nevertheless, concerns still exist in using plastic encapsulated or polymer coated devices in high reliability military and space applications. Even though the semiconductor die surface may be well passivated, exposed aluminum metallization at the wire bond pads, the wire itself, and solder, if used to attach flip-chip devices, are still susceptible to corrosion and stresses. Processes to render the devices hermetic and long-term storage studies are being addressed by the Army through several contracts.^{[9][10]}

Many semiconductor devices that are subsequently plastic molded are coated with a polyimide as a buffer to dissipate stresses, but the adhesion of the polyimide to the device and to the molding compound is critical to reliability in subsequent humidity exposure or solder reflow temperatures. Marginal adhesion has been demonstrated by delamination at those interfaces and by popcorning due to the absorption and sudden release of moisture.^[11]

The interface between the polyimide and the device appears to be more vulnerable than that between the polyimide and the molding compound. The durability of this interface can be measured by subjecting test specimens to the pressure cooker test (PCT) in which they are exposed to 120°C at 100% RH under 2 atm of pressure. The elongation at break, *T_g*, and tape pull adhesion can then be measured as a function of time. Silicon wafers having a silicon nitride passivation were coated with approximately 15 µm of a Durimide® polyimide and cured at 350°C for one hour. All samples passed the tape pull adhesion test after 250, 500, and 1,000 hours of PCT with no loss of adhesion. However, when measuring percent elongation, a polyimide cured for one hour at 350°C failed after 200 hours of PCT, while samples cured at 350°C for 2 hours or 400°C for 30 minutes, although experiencing considerable embrittlement, were still viable after 1,000 hours PCT (Fig. 4.5).

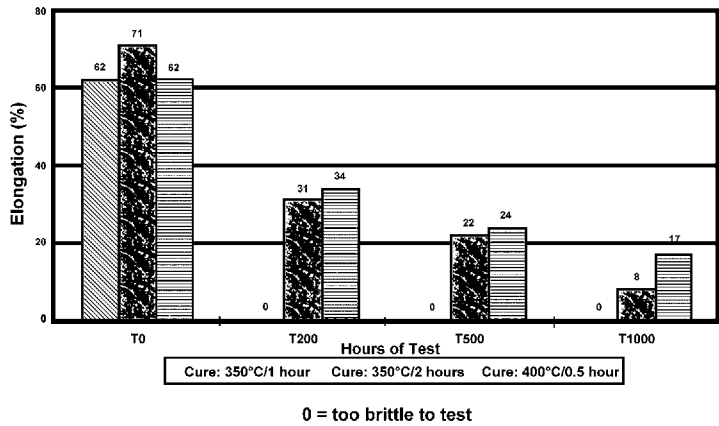


Figure 4.5. Effect of PCT conditions on the mechanical properties of Durimide® 7000 polyimide film. (Courtesy Arch Chemicals, Inc.)

*Durimide® is a registered tradename of Arch Chemicals, Inc.

4.2.2 Reconfiguration and Redistribution of Die Bonding Pads

Dielectric coatings may be used to form an additional layer of electrical interconnections beyond those already formed during wafer fabrication. Processes have been developed to alter the bonding pad topography both at the die (wafer) level and at the substrate level using polymer dielectrics. For example, a bonding pad can be reconfigured, changing its size and shape, by spin coating a photocurable BCB layer over the entire surface, exposing to uv through a mask having the image of the desired geometry, and developing it (Fig. 4.6). Dielectrics such as BCB or polyimides may also be used to redistribute peripheral bonding pads on a die to form an area array of pads to permit solder bumping for flip-chip bonding or ball grid array packages (Fig. 4.7). Likewise, internal pads on a die can be redistributed to one side to permit wire bonding of vertically stacked dice. In these processes, a dielectric coating is spun or otherwise deposited onto the single chips, or preferably onto the dice at the wafer stage, vias are formed over the original pads, the entire surface is then metallized, and finally, through a photoresist and etching process, conductor lines are formed that route and rearrange the pads to new positions on the die (Fig. 4.8). Photoimageable dielectric coatings are desirable because fewer steps are involved compared to using photoresists, but image resolution, uv exposure, and focus must all be taken into account for best results.^[12] Dielectric coatings must have a high degree of planarization, have good electrical properties, be able to withstand temperatures as high as 250°C that may be used in solder attach and solder reflow processes, and have low moisture absorption. Polyimides have a long history of use, but the BCB Cyclotenes* have several properties such as lower dielectric constants, lower moisture absorptions, and a high degree of planarization that gives them an advantage over polyimides for the new generation of high-speed, high-frequency devices.

Photoimageable polyimides and BCB resins produce excellent via and line definitions when used as plating resists in the fabrication of solder bumps or gold bumps on semiconductor wafers for flip chip devices. Both dielectrics are being used as stress buffer coatings and as interlayer dielectrics. Figure 4.9 shows the definition achieved from an 8.8- μm -thick film of Durimide 7510 after hard bake. During the curing process, going from

*Cyclotene® is a registered tradename of Dow Chemical Co.

a soft bake to a hard bake, a weight loss occurs that is reflected in a film thickness reduction of 40–50%, yet pattern definition is not significantly affected by this. A final bake temperature of 350°C for 30 minutes is considered a minimum for most polyimides whether they are photocured or not. However, temperatures as high as 400°C for 1 hour may be required for some applications to assure complete imidization and removal of the water formed during imidization.

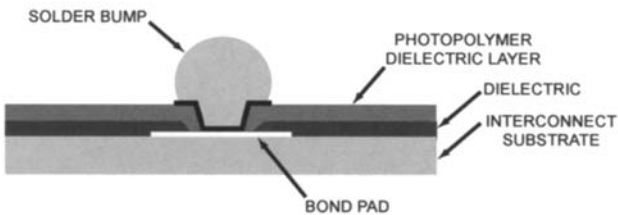


Figure 4.6. Reconfiguring of bonding pad for solder bumping.

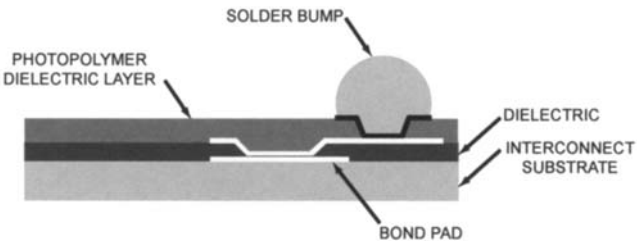


Figure. 4.7. Redistribution of bond pads for solder bumping.

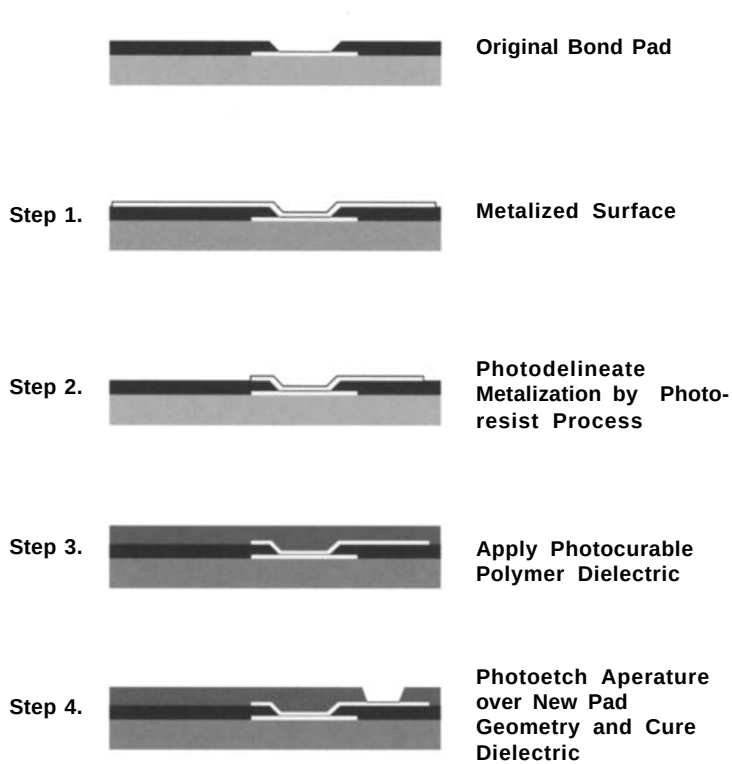


Figure 4.8. Process steps in redistributing the bond pads.

4.2.3 Semiconductor Junction Coatings and Stress Buffers

Organic coatings are used directly on semiconductor surfaces prior to plastic molding or glob-top encapsulation to stabilize semiconductor junctions and dissipate stresses. High-purity silicones, polyimides, and BCBs are used because of their wide operating temperatures (-65° to 275°C for silicones), high breakdown voltages (500 to 1,000 V/mil), electrical stabilities minimizing leakage currents and surface effects, and compatibility with epoxy molding or encapsulation.

Hardbake 350°C/120 min
HBFT 8.8μm

After cure

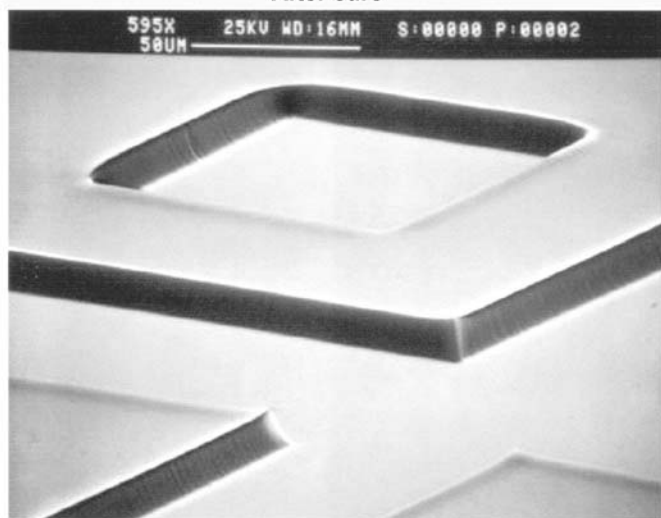


Figure 4.9. Broadband exposure of photoimageable polyimide, Durimide 7510.
(Courtesy Arch Chemicals, Inc.)

Epoxy molding compounds or encapsulants may impart stresses of several thousand pounds per square inch, especially if they are rigid. Stresses may be reduced by fifty percent or more by using flexible molding resins, appropriate fillers, or by applying a stress-relief coating prior to encapsulation. Silicone and polyimide coatings are especially suited for this function because of their high thermal stabilities and compatibility with both the active devices and the encapsulant. Polyimides can be applied at the wafer stage not only as buffer coatings, but also to facilitate processing of the chips. Buffer coats provide protection to the finished die during backgrinding, singulation, and assembly resulting in improved yields. Buffer coatings can be applied by spin coating, then photodelineated, and cured in a manner similar to other semiconductor fabrication batch processes. They may also be applied by automated selective dispensing. Polyimide stress buffers have been successfully applied at the wafer stage in fabricating memory chips, logic chips, and ASIC devices.^{[13][14]}

High-purity soft silicones and silicone gels have also been used to relieve stresses induced by subsequent transfer molding or encapsulating with epoxies. Silicones are also effective in protecting electronic components from vibration and shock. Stress-relief coatings must be flexible and possess a low modulus of elasticity. Silicones meet these requirements and have found many applications in component packaging. For example, transistors and ICs may be coated with 10 to 20 mils of a silicone, then encapsulated, glob topped, or transfer molded with an epoxy or another silicone. The stress-relief coatings applied to semiconductor devices should be localized so that they cover only the active surface, metallization, and a portion of the internal leads. The coating should not be allowed to spread to the edges of the device or onto the leads where it might affect the adhesion and moisture permeability of the subsequently applied molding compound or the solderability of the leads. Because of these restrictions, a practical method is to dispense the coating in small drops from a microsyringe that can be either manual or automated. The location of the barrier coating relative to the encapsulant is shown in Fig. 4.10 for a widely used dual-in-line IC package.

The effectiveness of flexible dip coatings to relieve stresses is shown in Fig. 4.11 where strain gages coated with silicone, then potted in a polyamide-cured epoxy, were measured and compared with those potted in the epoxy only.^{[15][16]}

In other studies, stresses of 5,000 psi at -40°C initially measured for components embedded in a silica-filled epoxy were greatly reduced when the components were precoated with an RTV silicone coating. At -40°C , a

1-mil-thick silicone coating reduced the stress to 3,500 psi while an 8-mil-thick silicone further reduced the stress to less than 400 psi.^{[17][18]}

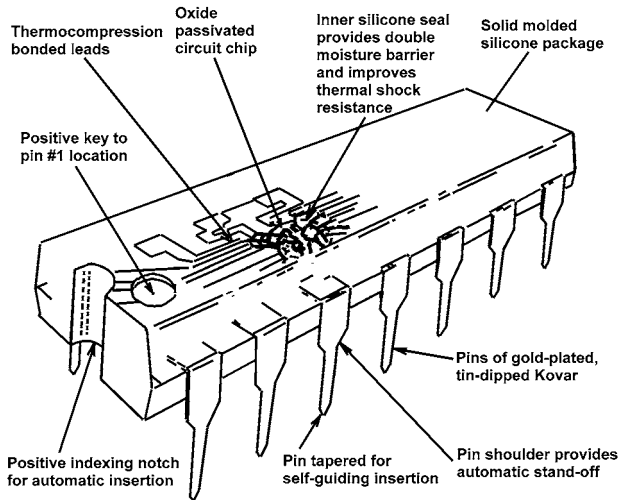


Figure 4.10. Plastic-molded integrated circuit showing position of the silicone barrier coating.

4.3 COATINGS FOR DISCRETE PASSIVE DEVICES

Coatings are applied as the final step in the fabrication of resistor and capacitor chips to protect them from handling, humidity, temperature, and long-term storage. Overcoatings also protect the devices from chemicals used at the assembly level such as flux, solder, and cleaning solutions. Additionally, coatings provide a medium for marking and identifying the component. Widely used coatings include epoxies, phenolics, polyurethanes, silicones, and acrylics.

Specially formulated silicones are used to protect power resistors and other discrete devices from high temperature operation or exposures. Silicone formulations that incorporate aluminum silicates are reported to provide thermal resistance up to 350°C. They may also be formulated with a thixotropic additive to allow a single coating application by dipping. In addition to their thermal performance, these coatings preserve all the desirable dielectric properties of silicones.^[19]

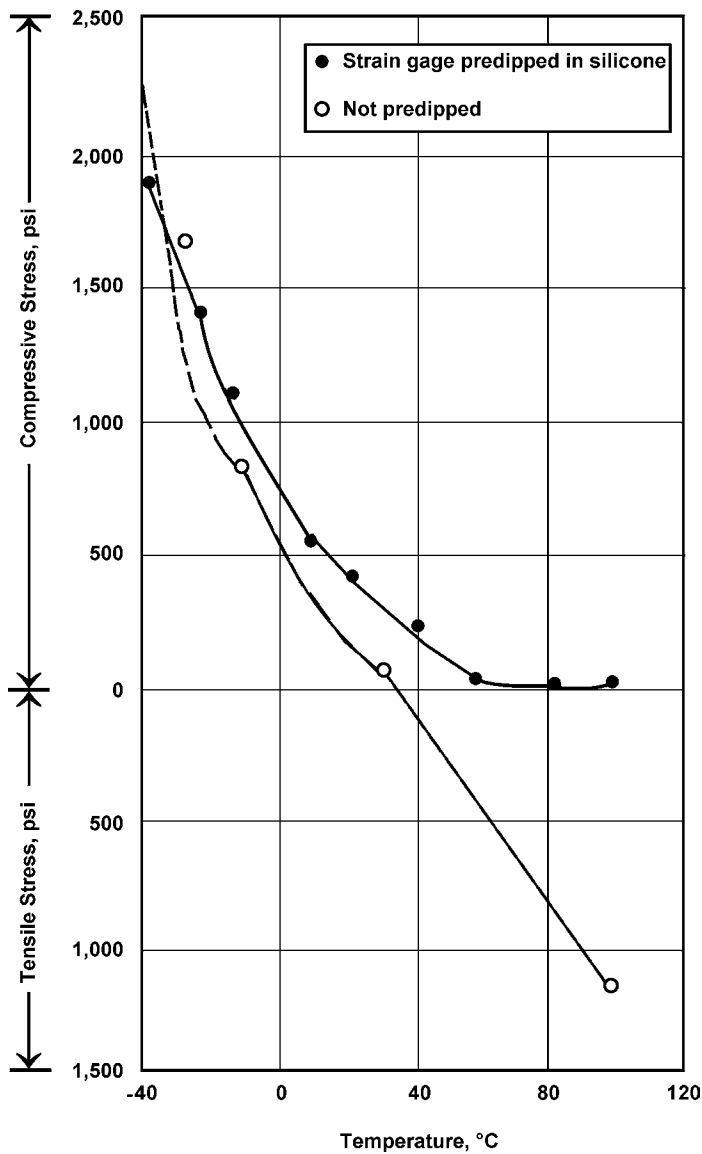


Figure 4.11. Effect of flexible silicone precoat on stress from polyamide-cured epoxy.

Coatings are applied by dip, spray, vacuum impregnation, and fluidized-bed methods. The fluidized-bed process has been used successfully in coating and sealing wire-wound resistors, thin-film resistors, thick-film resistors, and capacitors. However, the fluidized-bed process has not been found reliable in coating bare chip transistors and IC devices because of the high-temperatures required to fuse and adhere the particles and because of limitations on the types of coatings that can be applied by fluidized bed. Many thermoplastic powders that are ideal from a processing standpoint lack the electrical and thermal properties required for microelectronic devices.

Coils, transformers, and irregular-shaped components can effectively be coated by vacuum impregnation using a low-to-moderate viscosity, 100% solids coating. Epoxies and silicones are widely used. The parts and the coating should be evacuated separately to remove air and moisture from all surfaces and interstices, then, while still under vacuum, the parts are immersed in the coating, withdrawn, and cured.

4.4 MULTILAYER CIRCUIT BOARD FABRICATION

Epoxy coatings may be used in lieu of prepreg in the fabrication of multilayer PCBs. Coatings formulated with suitable thixotropic and wetting agents may be squeegeed through a screen so that interconnect vias are left open. Several layers can be superimposed, each being partially or completely cured before the next layer is applied, thus reducing the probability of pinholes and increasing the coating to a desired thickness. Thicknesses of a fraction of a mil to greater than 6 mils may be attained, depending on the screen mesh size, the viscosity of the coating, and the number of applications. Once the desired thickness is obtained and the epoxy has been cured, the epoxy surface is then sensitized, plated, and photoetched to form the conductor traces and to interconnect the vias. Pattern plating may also be used as an alternate process to form the conductor lines.^[1] The process is repeated for each layer. A four-conductor-layer multilayer board prepared by this process is shown in Fig. 4.12.

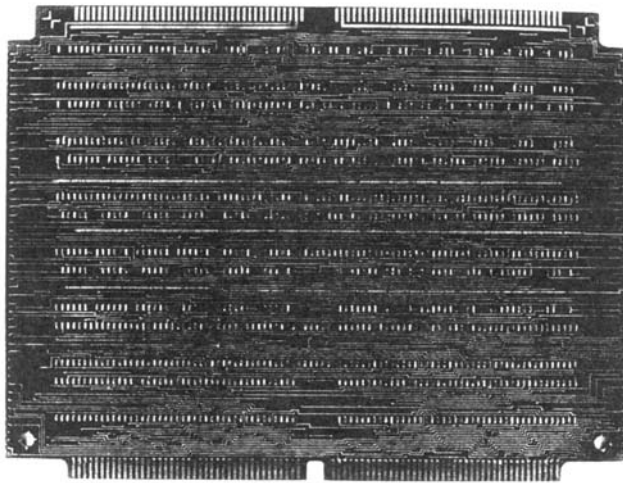


Figure 4.12. Four-layer multilayer circuit board prepared by screen-printing an epoxy coating.

Finer lines, spacings, and vias have been made using a photoimageable epoxy or epoxy-acrylate coating that can be screen printed or curtain coated over the entire surface of a plastic PCB, exposed to uv light, developed, and cured. The epoxy surface is then sensitized, plated with electroless copper, and the copper conductor lines photodelineated. Additional layers are produced in the same manner, resulting in an MCM-L type multichip module substrate that is lower in cost than its polyimide MCM-D counterpart. Work performed at Hughes Microelectronics Division in the early 1990s demonstrated 21- μm -diameter vias and 25- μm -wide conductor lines using Imagecure[®], a photosensitive epoxy dielectric produced by Coates Circuit Products. The PWB-type processes employed are more commercially available and less expensive than the semiconductor processes of sputtering thin-film metals and spin coating dielectrics required for MCM-D modules.^[20]

4.5 INTERLAYER DIELECTRIC COATINGS FOR MULTICHIP MODULE SUBSTRATES

A relatively new application for polymer coatings is as an interlayer dielectric in the fabrication of high-density, multilayer substrates to interconnect chips in multichip modules. The MCM-D types (Deposited Dielectric) provide the highest density and finest dimensions. They are fabricated using sequential thin-film deposition and photolithographic etching processes similar to those used in semiconductor fabrication. Polymer films used as interlayers must have low dielectric constants (4 or less) to be used for high-speed digital and analog circuits. These circuits are generally referred to as HDMI (high-density multichip interconnect) or HDI (high-density interconnect). A widely used process involves sequentially forming the multilayer structure on silicon, alumina, or aluminum nitride wafers. A polyimide precursor resin coating is first spun onto the wafer, then cured in steps up to 425°C. Vias are then plasma etched using a photoresist as a sacrificial mask or using a photopatterned metal or spun-on-glass (SOG) mask. After removal of the mask, thin-film metal, typically aluminum, gold, or copper, is sputtered or vapor deposited over the entire surface, simultaneously coating the surface and the walls of the vias. The metal is then patterned to form the conductor traces by another photolithography step. These processes are repeated by spin coating another layer of polyimide, curing, etching vias, and metallizing until the desired number of signal, ground, power, and die bonding planes are produced (Fig. 4.13).^[21] Figure 4.14 shows an MCM-D microprocessor in which the 1.8 × 3.8 inch interconnect substrate was fabricated using polyimide as the interlayer dielectric. Other variations of this process exist including using polymer films other than polyimide and forming vias by a variety of methods (see Sec. 4.5.1). This process is the common one for fabricating interconnect substrates for the MCM-D version of multichip modules. The interconnect substrate is fabricated first and the chips are assembled last, thus referred to as the *chips-last* process.

A second rather unique process was developed by General Electric in which the chips are laid down first in a closely packed array and the interconnect layers are formed over the chips, eliminating the need for wire bonds or flip-chip bonds.^{[22]–[24]} This process is also referred to as the *chips-first, overlay*, or *HDI process*. A Kapton[®] (polyimide) film is laminated over the chips. Vias, coinciding with the I/O pads of the dice, are formed by programmed laser ablation of the polyimide. The polyimide surface is then metallized by sputtering titanium or chromium as a barrier and adhesion

layer, and followed by copper. Finally, conductor traces are formed using photoresist and a laser scanning process to harden the photoresist. To produce subsequent conductor layers, a liquid polyimide is spin-coated or sprayed and cured, and the processes for via formation, metallization, and etching are repeated (Fig. 4.15). Typical reported dimensions are 25- μ m-diameter vias, 25- μ m linewidths and 50- μ m spacings.

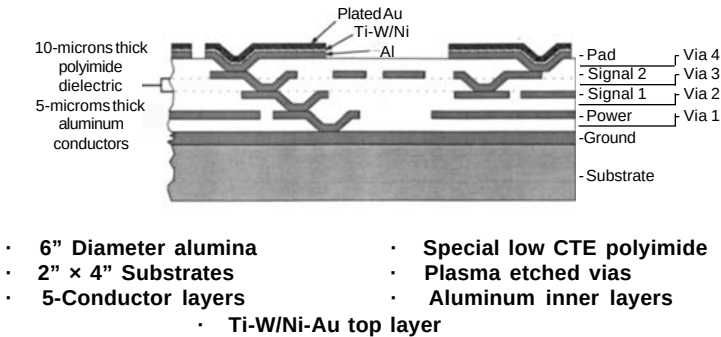


Figure 4.13. Cross-section of MCM-D interconnect substrate (chips last) showing polyimide interlayer dielectric.

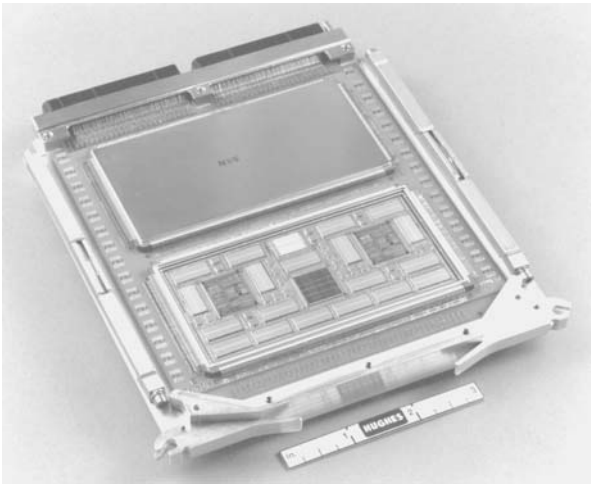


Figure 4.14. MCM-D microprocessor fabricated using polyimide interlayers. (Courtesy of Hughes Microelectronics.)

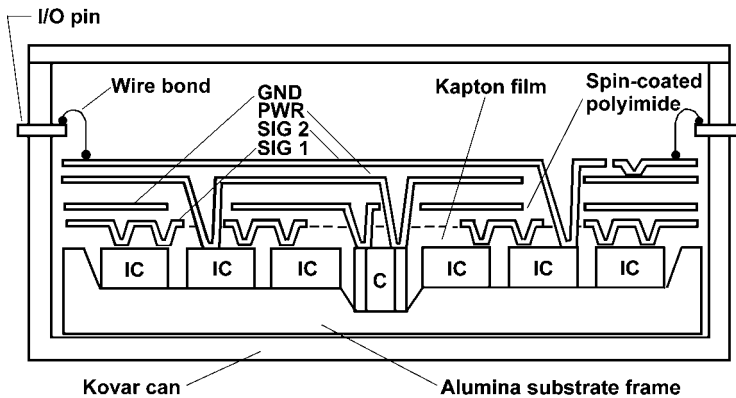


Figure 4.15. Cross-section of a chips first HDI assembly using polyimide dielectric.

A variation of the chip-first process involves attaching silicon chips that have been thinned down to 2 mils onto a substrate, coating and completely encapsulating the chip and substrate with a photoimageable epoxy, exposing it to uv light through a mask, and developing to form vias directly over the chip bonding pads. After curing, the epoxy is sensitized and electroless plated with copper. In lieu of the liquid epoxy, a metallized dielectric film may be laminated onto the chip surface, vias laser drilled, and electrical connections made by electroplating copper^[25] (Fig. 4.16). The chip-in-package concept is also proposed for stacking chips vertically and interconnecting through ball grid arrays or built-up vias around the sides of the chips; the constructions are referred to as a *system-in-a-package (SiP)*.

Coatings used as interlayer dielectrics must be thermally stable, compatible with subsequent chemical, plasma, or laser processing steps, must not outgas, must be planarizing, and must be easily etched to form fine vias. Both the polyimides and Cyclotene are solvent-based formulations that when adequately cured meet these requirements. Thicknesses of spin coated and cured films may range from 2 μm to 15 μm and can be controlled by adjusting the viscosities (percent solids) of the solution coating and the spin speed.

The suitability of DuPont PI 2611 polyimide (now available from HD MicroSystems) as an interlayer dielectric was extensively studied by Hughes Microelectronics under a Navy contract.^[26] Multilayer substrates fabricated with PI 2611 polyimide passed physical and electrical tests after

500 temperature cycles (-65° to 150°C), 1,000 hours of aging at 150°C , and 500 cycles thermal shock. Separately, the thermal stability of PI 2611, measured by thermal gravimetric analysis (TGA), was excellent up to approximately 500°C . (Fig. 4.17). Isothermal weight loss at 400°C was only 0.05 mg during the first few minutes while bringing the sample up to temperature (probably due to adsorbed moisture or low-molecular-weight species) and only 0.02 mg after a 7-hour exposure (Fig. 4.18). Chemical stability after thermal aging was verified by infrared (IR) spectroscopy. There was no change in the IR spectrum after 1,000 hours at 150°C (Fig. 4.19).

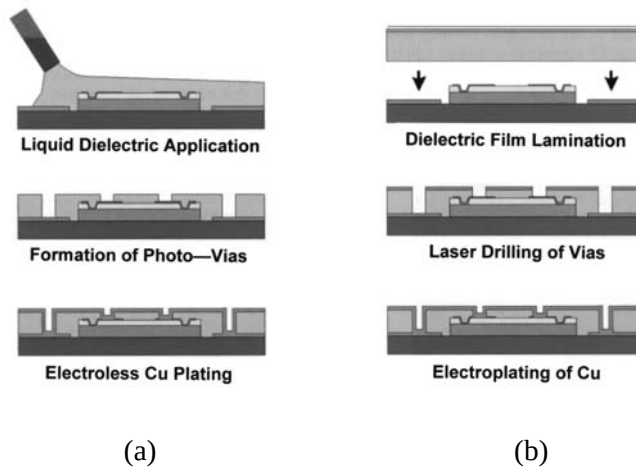


Figure 4.16. Concepts for Chip-in-Polymer; (a) chip embedded with a liquid photosensitive coating, (b) chip embedded by a laminate. (Courtesy of Fraunhofer IZM.)

Although some polyimides have high water absorptions, PI 2611 absorbed only 0.34% after 24-hours in boiling water. PI 2611 also passed NASA outgassing tests for toxicity, volatile condensable materials (VCM), and total mass loss (TML) (Table 4.5).

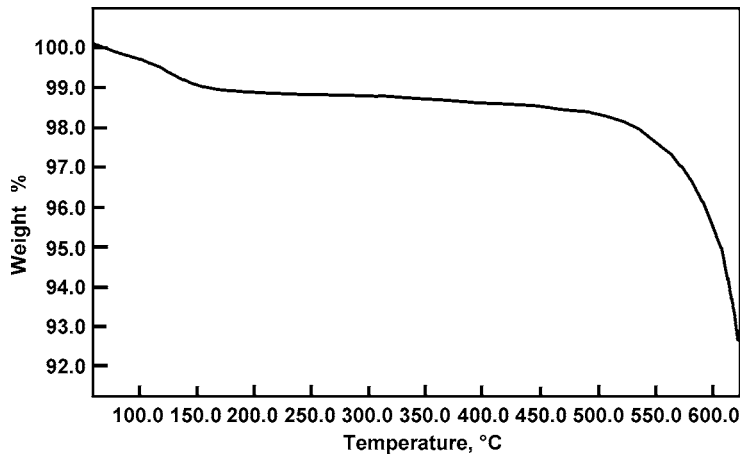


Figure 4.17. Thermal gravimetric analysis (TGA) curve for DuPont PI 2611 polyimide.

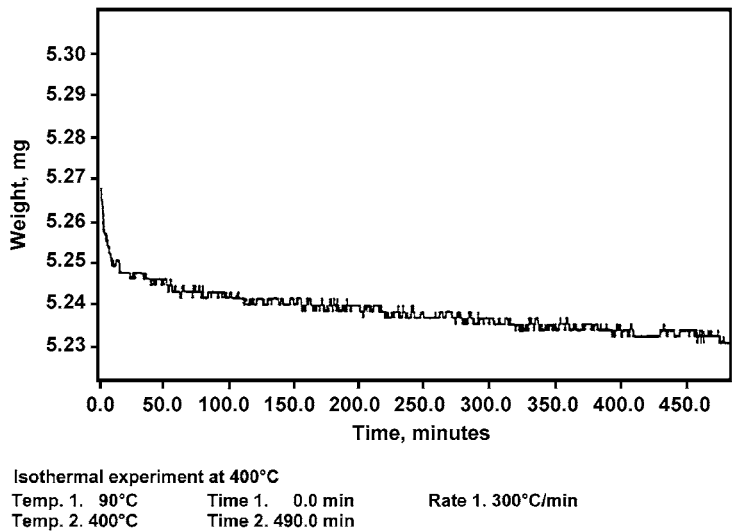


Figure 4.18. Isothermal stability of PI 2611 polyimide at 400°C.

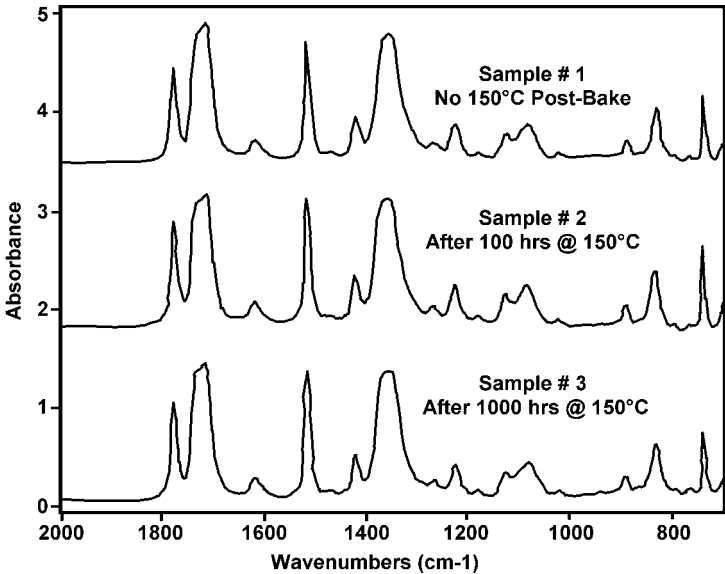


Figure 4.19. Infrared absorption spectra for PI 2611 polyimide, before and after 150°C aging.

Table 4.5. Outgassing Evaluation of DuPont PI 2611 Polyimide*

Test	Test Method	Conditions	Results
Toxic off gassed products	NHB8060.1C, Test 7	120°F	Passed
Volatile condensible material (VCM)	MSFC-Spec-1443	125°C, <10 ⁻⁶ torr, 24 hr; collector plate at 10°C	<0.01% (passed)
Total mass loss (TML)	MSFC-Spec-1443	125°C, <10 ⁻⁶ torr, 24 hr	0.68% (passed)
Optical degradation	MSFC-Spec-1443	% change in reflectance	Passed, no change
*Tests performed by NASA/MSFC, Material Code 00082, April 19, 1993.			

4.5.1 Formation of Microvias in Dielectric Coatings

The ability to form thousands of vias as small as 15- μm in diameter in a dielectric that may be 5 to 15- μm thick is essential in fabricating very high density multilayer interconnect substrates and chip-scale packages (CSP). After metallizing the vias and photodelineating the conductors, hundreds to thousands of z-direction interconnections can be produced, allowing the close-packing and interconnection of VLSIC (Very Large Scale Integrated Circuit) chips. Polyimide, the most widely used dielectric, will be used as the example in the following discussion of via-forming processes.

Vias may be formed in polyimide films by one of four methods: dry plasma etching, wet etching using a photoresist, wet etching using photodefinable dielectrics, or laser ablation. In all processes, vias of 35- μm diameters or smaller can be etched in a dielectric thickness of 25 μm or less.^[27]

Dry Plasma Etching. According to this process, the polyimide precursor (polyamic-acid) is deposited onto a wafer, usually by spin coating, and fully cured (imidized). A temporary resist mask (photoresist or thin metallization) is then applied in which the desired via pattern is generated. The mask must be capable of withstanding the etching solutions or must etch at a slower rate than the polyimide. Next, vias are etched in the exposed polyimide by a reactive plasma, a process also called *reactive ion etching* (RIE). The plasma may be formed from oxidizing gases such as mixtures of sulfur hexafluoride (SF_6) and oxygen, or carbon tetrafluoride (CF_4) and oxygen. After the vias are etched, the temporary mask is removed (Fig. 4.20).

Wet Etching. Vias may also be wet etched at the polyimide precursor stage prior to imidization. After spin-coating the polyamic-acid solution onto the wafer, it is baked to evaporate the solvents, soft baked, then overcoated with a temporary mask in which the vias are patterned using a positive photoresist. After exposure to ultraviolet light, the photoresist is developed using an aqueous alkaline solution that serves a dual role. It simultaneously hardens the photoresist in the unexposed areas and dissolves the exposed photoresist and the underlying precursor. After the hardened photoresist is removed, the polyimide precursor is imidized by heating to 350°C and, in some cases, up to 425°C to assure a more complete cure (Fig. 4.21). This wet etch process is specific to polyimides and is based on the solubility of the carboxylic acid portion of the precursor in alkaline solutions such as ammonium hydroxide, tetramethylammonium hydroxide, or sodium hydroxide.

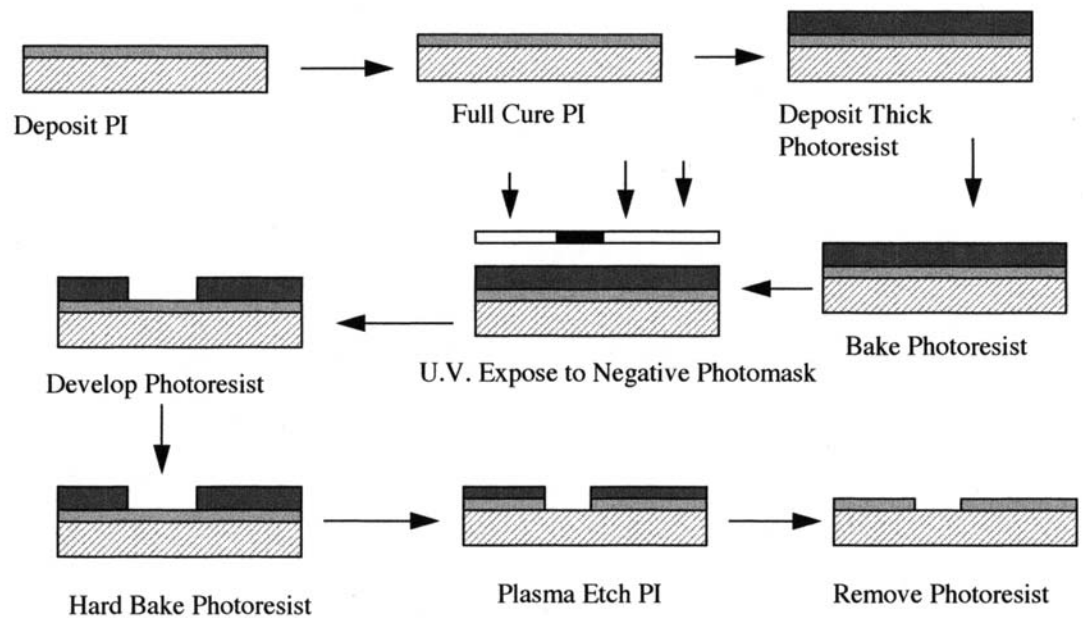


Figure 4.20. Microvias formed by dry plasma etching.

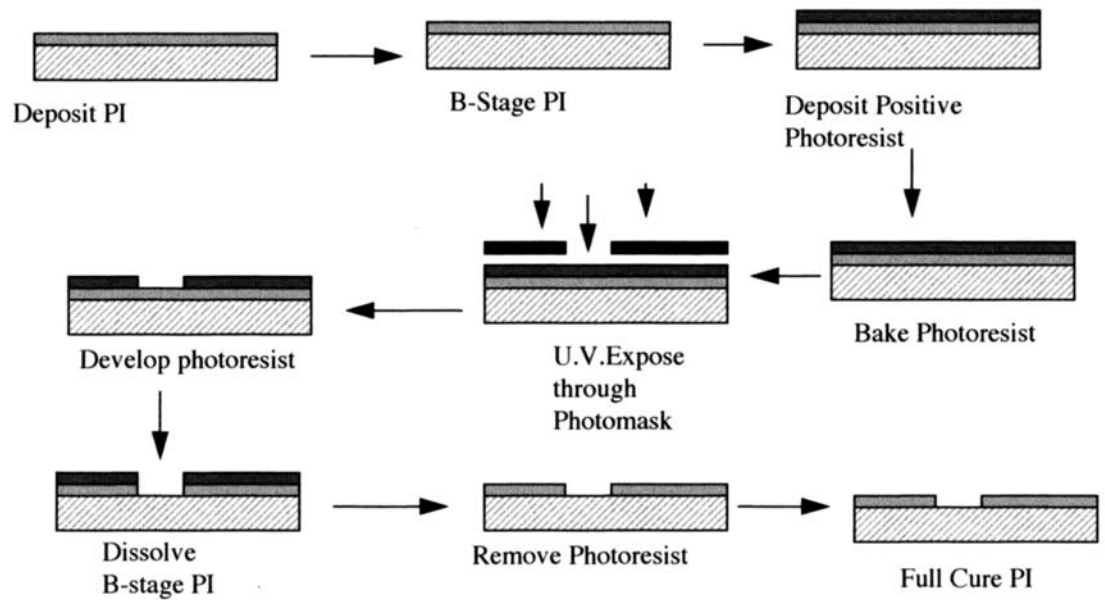


Figure 4.21. Microvias formed by wet chemical etching.

Although somewhat more economical than dry etching, wet etching does not produce the fine microvias achieved with dry etching, and thus is more suited to forming coarser features such as bond pads or large vias. Wet etching is isotropic, etching laterally and vertically at the same rate, thus producing sloped vias.

Photoimageable Polymer Processes. With the introduction of photoimageable polymer coatings, the number of process steps necessary to form vias has been significantly reduced (up to 60%) resulting in cost savings (Fig. 4.22). In the case of a photoimageable polyimide, the process involves spin coating the polyimide, soft baking, and exposing to uv light which causes the polymer to crosslink and harden. The masked areas remain solvent soluble and are removed during the development step. Finally, the coating is heat cured at 200° to 350°C which simultaneously imidizes the polymer and decomposes and volatilizes the cross-linking groups that initially rendered the polymer photosensitive. Photodefinable polyimides with thicknesses up to 40 μm have been developed for fabricating chip-scale packages (CSP).^[28] Well-defined vias as small as 10 μm in diameter in a 9- μm -thick photoimageable polyimide coating have been produced (Fig. 4.23). Table 4.6 compares the properties of a photodefinable polyimide with a conventional one.^[29]

Besides polyimides, other coatings such as benzocyclobutene, some fluorocarbon polymers, and epoxies can be used as interlayer dielectrics. Dow Chemical's Cyclotene, a BCB, has been extensively studied and is being used as an interlayer dielectric in fabricating thin-film multichip module (MCM-D) substrates.^[30] Photodefinable versions of BCB have also been developed for interlayer dielectrics and other semiconductor applications. Cyclotene is particularly useful in fabricating high-speed, high-frequency devices and interconnect substrates because of its low dielectric constant and dissipation factor which remain fairly constant over a wide frequency range (see Ch. 2).

Photodefinable epoxy formulations, having a high T_g of 168°C, have also been developed and are useful in fabricating high-density printed wiring boards.^{[31][32]} Microvias, either of the blind or buried types, can be formed in the epoxy after exposure to uv radiation through a photomask and development using an aqueous solution. High-density multilayer PWBs formed from photodefinable epoxies can be a low-cost alternative to analogous polyimide boards, however, optimum dielectric and thermal properties, in both cases, require subsequent elevated temperature cures. A subsequent cure of two hours at 160°C for the epoxy is necessary to achieve a T_g of 168°C.

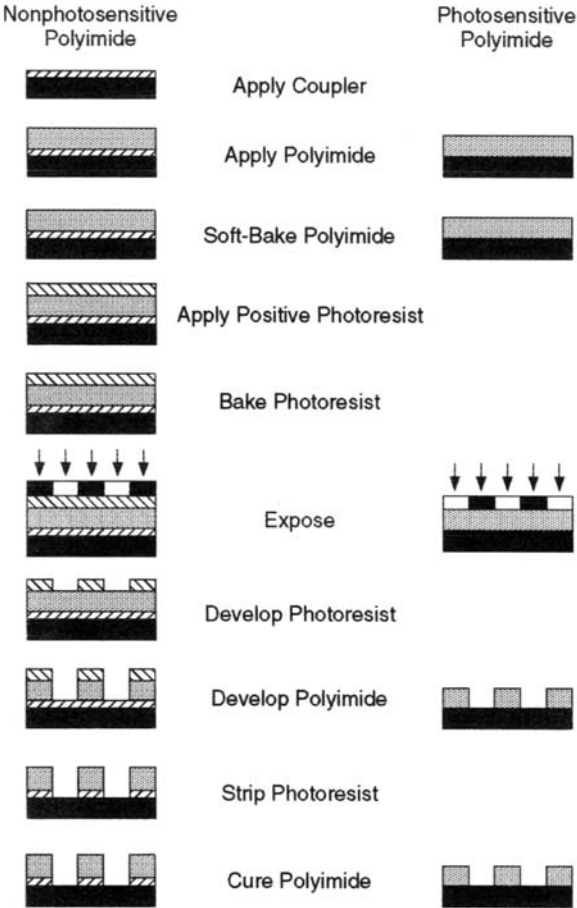


Figure 4.22. Microvia formation steps: Non-photosensitive polyimide (wet etch) vs photosensitive polyimide.

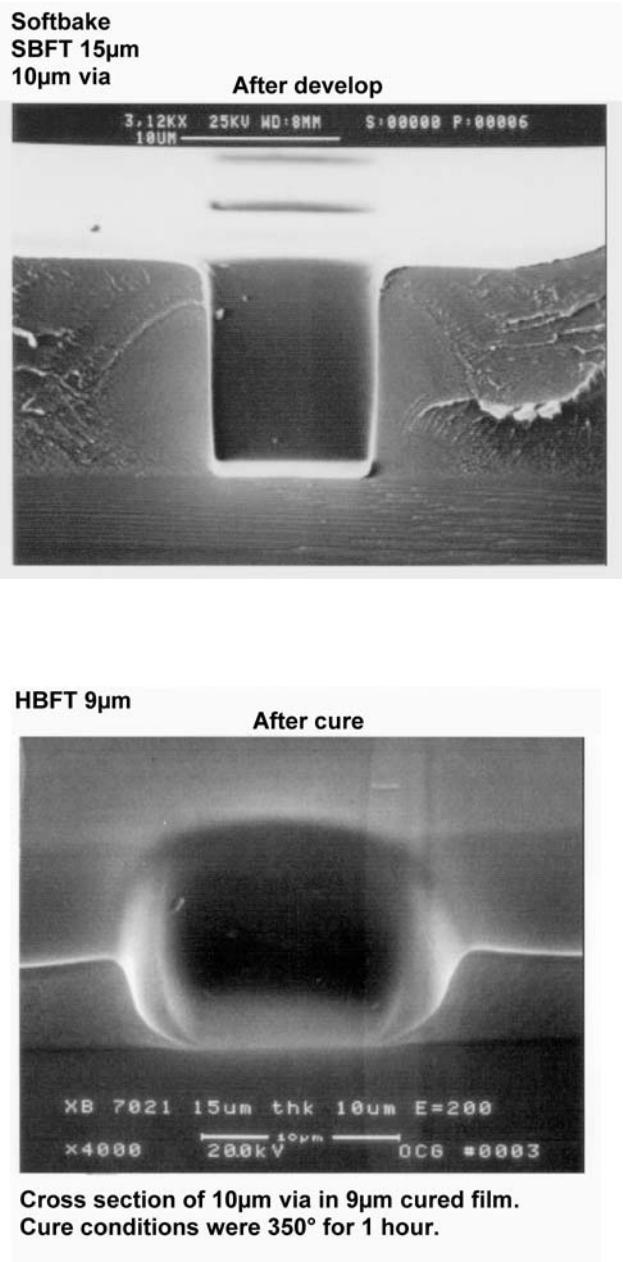


Figure 4.23. Microvias formed from photoimageable polyimide. (Courtesy Arch Chemicals, Inc.)

Table 4.6. Cured Film Properties* of DuPont's Photodefinable and Non-photodefinable Polyimides^[29]

	Non-photodefined (PI 2611)	Photodefined (PI 2741)
Thermal Properties		
Glass Transition Temp., °C	350	365
Decomposition Temp., °C	620	620
% Weight Loss (500°C in air, 2 hr)	1.0	1.5
CTE, ppm/°C	5	10
Residual Stress, MPa	10	20
Mechanical Properties		
Young's Modulus, GPa	6.6	6.1
Tensile Strength, MPa	600	330
Elongation to Break, %	60	50
Electrical Properties		
Dielectric Constant @ 1 kHz, 0% RH	2.9	3.0
Water Absorption, wt % @ 50% RH	0.8	1.2
*Cured at 400°C in nitrogen.		

Laser Ablation. Vias may also be formed by dry etching the cured polyimide using laser ablation in which case the dielectric is volatilized in selected areas by a focused laser beam. Using the excimer laser to etch polyimide and other polymer coatings has been extensively studied. It is reported that thin polyimide films can be efficiently etched in air with a pulsed excimer laser at wavelengths of 248, 308, and 351 nm.^[33] There are three variations of laser etching: direct-write, scanning laser ablation (SLA), and projection. An excimer laser can be used in either a scanning mode or a direct-writing mode (programmed focused beam). The SLA is a batch process. A metal or inorganic mask having the via pattern is first generated on the dielectric layer by the normal photolithographic process. A laser beam is then allowed to flood the entire surface through the mask, followed by removal of the mask.^[34] Although SLA is a batch process, the types and number of steps required are almost identical to those of the RIE process. In the direct-write method, however, the laser beam is focused and programmed to form each via separately, without the need for a hard mask or a conformal mask.

Projection laser ablation utilizes a separate hard mask to project the via pattern onto the substrate, analogous to conventional semiconductor photolithographic steppers. Projection laser ablation is especially suitable for high production.

A fourth, more recent, process for forming microvias involves Litel Instruments' patented direct-laser ablation through a holographic phase mask. According to this process, a proprietary holographic phase mask is first constructed based on the layout of the vias and a 1:1 correspondence between the application-specific vias and the holographic lenses of the mask. A low-fluence laser beam is then scanned across the mask whereupon the lenses concentrate and focus the laser energy to the desired via locations, ablating and removing all material from the via holes (Fig. 4.24). The process is especially suited for polyimide and BCB dielectric coatings, although other polymer coatings and films can be used. The key advantages over other via forming processes are that it:

- avoids the use of photoresists
- reduces the number of processing steps
- produces rapid via drilling ($4 \text{ in}^2/\text{sec}$)
- avoids laser damage to the mask due to low fluence beam at mask plane

Litel reports that 125,000 vias of $15\text{-}\mu\text{m}$ diameter in 1-mil-thick polyimide can be formed in less than one minute. Vias as small as $10\text{-}\mu\text{m}$ diameter in 10-mil-thick dielectric are also reported.^[35]

4.5.2 Supported Microbridge Crossovers

Another application for polyimide coatings is in the fabrication of supported microbridge crossovers as an alternate to air-gap microbridges. The general process for forming air-gap microbridges involves forming a copper support upon which the bridge is formed, then etching the copper to generate the air gap (see Fig. 4.25). Air-gap microbridge connections are valuable in microwave and Monolithic Microwave Integrated Circuit (MMIC) devices due to the very low dielectric constant and capacitance of air. However, there is a limit to the length of the bridge span that can be formed without it collapsing. Also, meandering bridges cannot be made. The use of polyimide as a permanent support (microramps) allows longer spans and more complex interconnections, but the higher dielectric constant of the polyimide must be considered in the design.^[36]

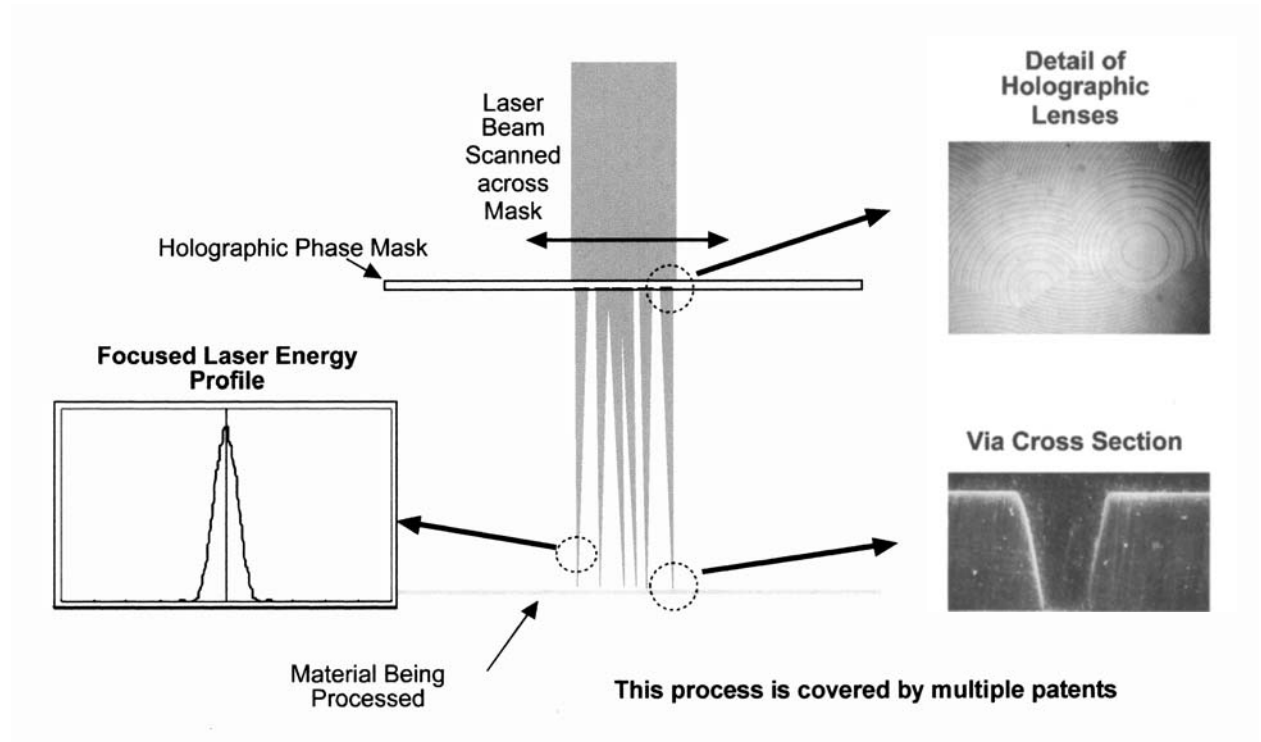
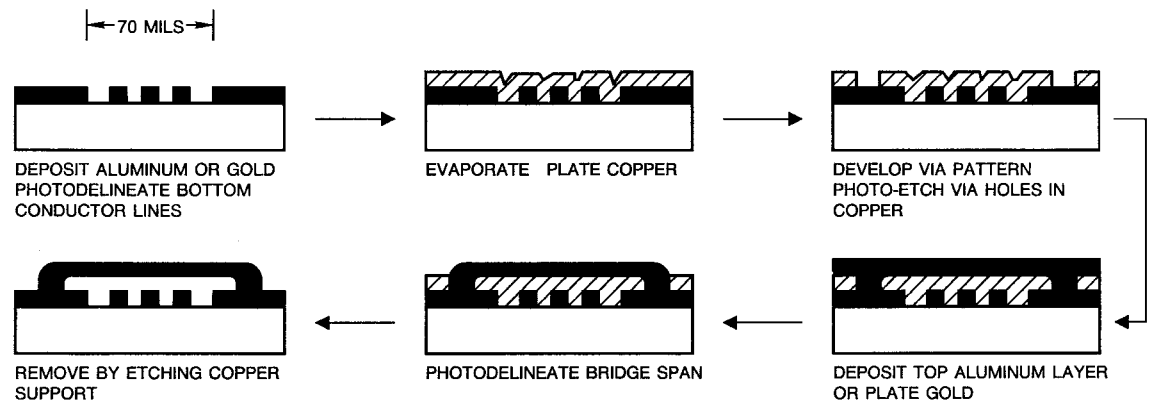


Figure 4.24. Microvia formation: Holographic laser process. (Courtesy Litel Instruments.)



SUPPORTED BRIDGES

SAME AS ABOVE EXCEPT POLYIMIDE IS USED IN LIEU OF COPPER AND IS NOT REMOVED IN THE FINAL STEP

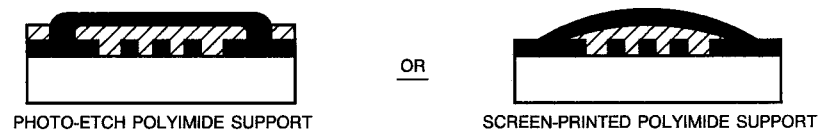


Figure 4.25. Fabrication steps for air-gap microbridge and supported bridge interconnect substrates.

4.6 POLYMER WAVEGUIDES

Polymer coatings are finding new applications in optoelectronics where many of their attributes important for semiconductor and MCM fine-line delineations are also applicable to the fabrication of waveguides. Photolithographic processes and photocurable materials such as polyimides, BCB, and epoxies are used to form precise grooves in the coating for the transmission of light. Most of these processes have already been described in connection with via formation except that, in the case of waveguides, long narrow grooves are formed in the dielectric coating. Polymer technology for waveguides is still in a state of flux because of the wide variety of materials and processes that can be used and the need to achieve low losses within the structure and at the connections. However, the rewards can be great because of the potential for cost reduction over current methods.

Polymer coatings such as BCB are being investigated for the fabrication of planar waveguides as potentially lower cost alternatives to optical fibers. Waveguides based on polymeric materials are less expensive due to fewer steps in the fabrication sequence than commonly used silicon-on-silicon waveguides. In one study, Multimode Interference (MMI) waveguides were fabricated using photodefinable BCB for the core material and a thermosetting BCB for the under- and over-cladding material on silicon wafers. Core widths and thicknesses were 7 μm .^[37]

In fabricating the waveguides, photoimageable polymer coatings such as polyimides, BCB, and epoxies are first spin-coated onto a rigid substrate. Silicon wafers, fused quartz, epoxy-glass laminate circuit boards, and ceramic circuit board materials have been used as substrates. The coating is then exposed to uv light and developed to form the grooves. Other etching methods common to semiconductor manufacturing have also been used, such as RIE, plasma etching, and laser ablation of a cured coating. Some rather unique techniques have been developed to create high transmission paths or guides in a coating by manipulating the refractive indices of the coating through diffusion of low-molecular-weight compounds or monomers into the coating in selected areas. Conversely, they can be created by selectively leaching out low-molecular-weight constituents from a partially cured coating followed by full curing. A good overview of these processes has been given by Booth.^[38]

Among desirable properties that polymers must have to be useful in waveguide applications are:

- Ability to delineate fine and uniform grooves in the coating.
- Ability to tailor the refractive index through partial or thorough polymerization, adding formulation ingredients, or diffusing into, or leaching out certain low-molecular-weight constituents.
- Uniform and stable refractive index.
- Smooth and uniform sidewalls after etching to assure minimal loss due to light scattering.
- CTE closely matching that of the substrate to avoid stresses and delamination that could affect light scattering.
- Resistance to subsequent high-temperature processing such as solder reflow.

4.7 SOLDER MASKANTS

Solder resist coatings (maskants) are heat-resistant polymer coatings applied to selected areas of a PWB prior to solder coating and component assembly. Solder maskants protect portions of the board during subsequent soldering and reflowing of solder. They are useful in preventing solder from splattering onto conductor traces or bridging conductors. Other benefits of solder masking include: reducing solder-pot contamination from copper or gold, protecting the circuit from handling and environmental damage, and providing isolation between components and conductor lines or vias when components are mounted directly over the conductor lines. Solder maskants are generally based on epoxy, acrylic, or epoxy-acrylic resins formulated with fillers and additives to render them screen printable in selected areas. They are heat cured and must withstand solder-exposure temperatures as high as 230°C (as high as 260°C for the no-lead solders)^[39] without chemical or physical degradation or loss of adhesion. Solder maskants are generally left on the board augmenting the moisture protection and electrical properties of the board material itself. Colorants are incorporated to aid in inspection and to distinguish one supplier's product from another.

Photoimageable liquid and dry-film solder maskants are also available. These may be cured in selected areas by exposing the fully coated

board to uv light through a photomask. Tests for the qualification and testing of solder maskants for PWBs are specified in IPC-SM-840.

Permanent solder maskants have found new applications with the advent of ball grid array (BGA), flip-chip, and chip-scale packages (CSP). The solder maskant is applied to the bottom of the substrate leaving apertures for the insertion of solder balls or for the plating up of flip-chip bumps (Fig. 4.26).

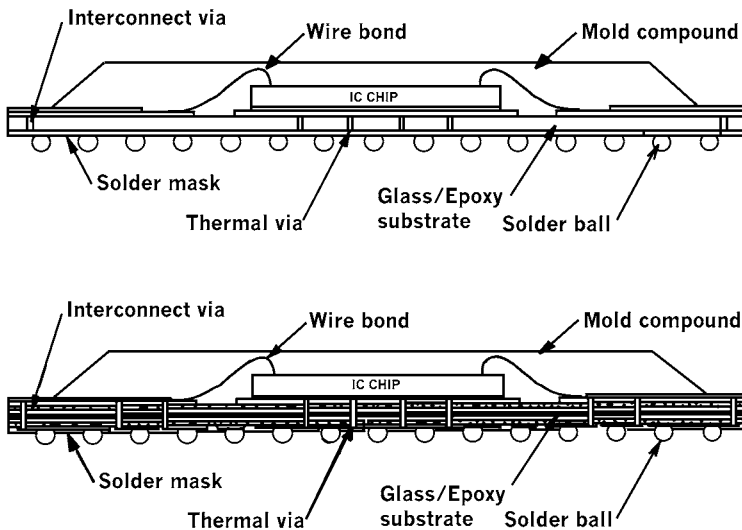


Figure 4.26. Ball grid array (BGA) multilayer package constructions; (top) double-sided construction, and (bottom) multilayer construction.

4.8 CHIP-SCALE AND BALL GRID ARRAY PACKAGES

Both solder maskants and dielectric coatings play key roles in the fabrication of chip-scale and ball-grid-array packaging of single chip and multichip modules.

4.8.1 Solder Maskants for CSP and BGA

Chip-scale packages (CSP) are available in a wide variety of configurations and materials of construction. However, most CSPs are of

the BGA configuration with solder bumps or solder balls on the bottom of a small interconnect substrate to which the die is interconnected. For commercial applications, the assembled die is plastic encapsulated.^[40] Solder maskants play a key role in the fabrication of these packages and are critical to reliability, especially at the interface of the solder maskant and the encapsulating compound. If the adhesion between the solder maskant and the encapsulant is marginal, delamination occurs, especially under conditions of elevated temperature and high humidity. Most solder maskants are compatible with the encapsulant (generally a mineral-filled epoxy), but some may require extra attention, such as surface roughening by plasma etching to improve adhesion. Photoimageable solder maskants are widely used in fabricating BGA packages because much tighter positional tolerances are required than for standard plastic packages.

4.8.2 Wafer-Level, Chip-Scale Packaging

Considerable research and development work and progress are being made by semiconductor manufacturers to form CSPs at the wafer level. Wafer-level CSPs produced by the semiconductor manufacturer have many advantages over packaging single chips at a separate packaging house. Advantages include reduced handling, no shipping, reduced contamination, and lower costs. With chip sizes decreasing and the number of I/Os per chip increasing, current methods of packaging chips separately often result in the package cost far exceeding the cost of the chip. Other advantages of wafer-scale packaging include smaller size packages (essentially a package that is the size of the die), potentially higher yields, and the potential for wafer-level testing and burning-in of the CSPs before dicing.

Both photodefinable and non-photodefinable BCB dielectric coatings are finding applications as additional passivation and planarization layers in the fabrication of these wafer-level CSPs. BCB coatings are used in redistributing interconnect pads and as an underbump compliant layer. Many variations of miniature CSPs produced at the wafer level are being developed, most of which use BCB dielectric coatings.^{[41]–[43]}

4.8.3 Alpha-Particle Emissions

High purity, specially formulated silicones are used in many chip-scale packages as encapsulants, coatings, and spacers for memory devices.

For these applications, packaging materials must have extremely low alpha emissions, especially for DRAMs, where alpha emissions from uranium and thorium are known to cause soft errors in the memory devices. Soft errors are random, non-recurring changes of single bits of information stored in a memory chip that lead to data errors. Radioactive uranium and thorium, the main sources of alpha particles, are naturally present in almost all materials. The main source in formulated resins is from the mineral fillers that are used to control viscosity and stresses. However, specially purified fillers and formulated silicones have been shown to contain low amounts of uranium and thorium (Table 4.7) and to emit extremely low amounts of alpha particles.^{[44][45]}

Table 4.7. Uranium and Thorium Contents for Several Dow Corning Silicones^[44]

Silicone	Use	U (ppb)	Th (ppb)
DC-6810	Chip-scale package encapsulant	22	54
DC-6811	Microelectronic encapsulant	0.1	1.3
DC-7910	Die-attach adhesive	0.08	0.63
DC-6910	Chip-scale package spacer	0.06	0.7

4.9 CHIP-ON-BOARD (COB) AND GLOB-TOP COATINGS

Chip-on-board (COB) is a fairly new packaging technology that combines the low-cost benefits of PWAs with the high densities of hybrid microcircuits. According to COB, bare chips are wire bonded or flip-chip interconnected to a PCB designed and fabricated with finer dimensions than normally used. The active chips requiring protection are then selectively encapsulated by dispensing a filled epoxy over the device, a process called *glob-topping*. In the board design, several ICs can be partitioned closely together and encapsulated as a unit. Although there is always a concern in using plastic encapsulants as the prime method for moisture protection, epoxy glob-top materials on the market have performed very well in many applications and environments. Reliability is enhanced by assuring a

good primary passivation at the die level and a low-stress, low-moisture-absorption encapsulant. Even so, overcoating the entire COB with a high-performance coating such as parylene produced improved results. In one report, DRAM devices glob-topped with either Hysol-Dexter FP-4402, FP-4450, or Dow Corning silicone HIPEC Q14939 and then overcoated with parylene, all passed 1,000 hours of 85/85 THB while control parts without encapsulant began to fail at 250 hours. Tests also carried out on epoxy-encapsulated ATC-01 triple track resistors (Sandia National Laboratory test chip) survived 1,000 temperature cycles from -55° to 125°C.^[46]

In other work, unpassivated ATC-01 chips were used to accelerate failures. After 1,000 hours of 85/85 followed by 100 hours of PCT, the uncoated controls had 86% failures while those coated with Parylene C had only 6.8% failures. Devices coated with a trilayer coating consisting of Parylene C, Cycлотene, and e-beam-deposited silicon dioxide further reduced the failures to approximately 3%. Under the same test conditions, passivated ATC-01 chips without any overcoating had failures of 45%.^[47]

4.10 PARTICLE IMMOBILIZING COATINGS AND PARTICLE GETTERS

Particles that remain on a circuit even after cleaning or that subsequently slough off from the circuit after sealing have been known to cause failures in hermetically-sealed microcircuits. Metallic particles such as slivers of wire, solder, or silver-conductive adhesive can cause electrical shorts while non-metallic particles such as alumina or silica fillers can cause abrasion and physical damage during vibration. Most hybrid microcircuit manufacturers use the Particle Impact Noise Detection (PIND) test on a sampling basis or on a 100% basis (for Class K, space-grade devices) to detect loose particles. If the circuits are well cleaned and no further sloughing of particles occurs, PIND testing is preferred over using a coating or a getter.^[8]

For some circuits, particles may be difficult to remove even after cleaning and, in these cases, organic coatings may be used to immobilize particles or getter them. Some NASA and military programs have required the use of coatings for greater reliability assurance. The function of the coating is to freeze in place all loose particles and to shield the circuit from any particles that may subsequently detach during vibration, mechanical

shock, constant acceleration, or actual use. Parylene and silicone coatings have been the most widely used particle-immobilizing coatings due to their high purity, excellent electrical insulation properties, and low outgassing (*cf.* Ch. 2). Because of the difficulty in removing parylene in reworking a coated circuit, more easily removable soft silicones and solvent-soluble block copolymers of silicones and styrene have been investigated and used. The styrene-modified silicone coatings are readily and completely soluble in toluene, xylene, the Freons*, and chlorinated solvents. The coatings can be removed quickly from the entire circuit by vapor degreasing with Freon TF solvent. In the original studies by Weigand and Licari, Dow Corning's DCX9-6326, a block copolymer of dimethylsiloxane and alpha-methylstyrene, was characterized for electrical, physical, and chemical properties, then applied to hybrid microcircuits and to printed wiring boards.^{[48]–[50]} These studies were later corroborated and expanded by David.^[51] In these studies, extensive long-term reliability data were collected on the effects of the coating on sensitive chip devices and on gold and aluminum wire bonds to thick-film gold conductor pads. Wire bond pull strengths and electrical resistance of a series of wire bonds were measured after 1,000 hours at 150°C and after 1,000 temperature cycles from -55° to 125°C. In all cases, the performance of the coated wire bonds was almost identical to the uncoated bonds and no electrical failures were noted. Although the silicone-styrene copolymer coatings are more economical to process from the standpoint of ease of removal for rework, ease of masking, and the lower cost of spray application, they are limited in availability.

In lieu of a coating, a particle getter may be applied to the inside of the lid prior to sealing. Getter materials consist of soft, sticky silicones. The effectiveness of silicone getters was demonstrated by several companies through controlled experiments in which known quantities of metal particles of various sizes were purposely added to a circuit containing the getter, then vibrated and evaluated for loose particles by PIND, x-ray, and electrical tests.^{[52][53]} The types of particles used were representative of those that might be trapped in a hermetically-sealed package and included gold wire, aluminum wire, solder balls, and pieces of eutectic alloys. As with other organic materials within a sealed package, outgassing from the getter material must be minimized by the appropriate cure and vacuum bake schedules. Silicone gels used as getters are available from both General Electric and Dow Corning.

*Freon® is a registered tradename of DuPont.

4.11 REINFORCEMENT OF INTERCONNECTIONS

Besides the environmental protection and electrical insulation properties that coatings afford, they can also reinforce wire bonds and flip-chip solder connections. Parylene is ideal for this purpose because of its toughness and ability to completely envelop the connections. Marginal or low-strength wire bonds can thus be encapsulated and prevented from subsequent rupture or intermittent opens.^[54]

Parylene has also been investigated as an undercoat to reinforce flip-chip and BGA solder connections, although the general practice is to fill the entire space between the solder balls with an epoxy underfill adhesive.^[55] Parylene coating was reported to improve the thermal fatigue life of solder joints in ceramic packages.^[56]

4.12 WIRE AND COIL COATINGS

Wire must be electrically insulated and environmentally and physically protected. A variety of polymer coatings can and are being used for this purpose. They are classified according to their thermal and physical endurance and manner of application. Wires may be dip-coated in a liquid bath of the resin solution, then cured or dried, wrapped with fibrous coverings or resin-impregnated coverings, wrapped with tape, or covered with extruded polymers. Large-diameter wire, as used in cables, is generally insulated by the extrusion of solid thermoplastic resins.^[57] Thermoplastic resins soften on heating then resolidify on cooling. During this process they can be shaped around a conductor wire by forcing the plastic material under pressure and heat through an orifice concurrently with the conductor. Extruded insulation such as polyvinyl chloride, polyethylene, or polytetrafluoroethylene (Teflon) is relatively thick compared to the diameter of the wire and is, therefore, used mainly for interconnect lead wires and cables. Tape wrapping involves the wrapping of thin tape or plastic film around the wire with a minimum of overlap. Several layers of tape can be used to build up the desired insulation thickness.

Finally, the insulation may be applied by dip coating or vacuum impregnation. The wire is moved through the liquid coating solution, then

dried or baked. The greatest use of liquid polymer coatings is to insulate and isolate thin magnet wire used in coils and windings for transformers, inductors, hermetic motors, automotive alternator stators, and solenoids. This section primarily addresses the liquid resin coatings for magnet wire insulation, but some properties of extruded types are mentioned for comparison. Further information on wire and cable materials may be found in the literature.^[58]

4.12.1 Magnet Wire Classifications

Magnet wire may be classified as coated wire (film insulation), wire insulated with fibrous wrappings, or wire with an impregnated fibrous wrapping. Wire coated with only an organic coating is frequently referred to as enameled wire.

The requirements and standards for insulated magnet wire are thoroughly treated in a National Electrical Manufacturers Association specification, NEMA-MW-1000, *Magnet Wire*. This specification consists of three parts:

1. Covers the scope, definitions, and sub-tier standards.
2. Contains extensive tables of properties and requirements for various sizes and insulations of magnet wire.
3. Describes test methods, among which are adhesion, flexibility, elongation, heat shock, springback, dielectric strength, continuity, completion of cure, coverage, solderability, solubility, thermal endurance, scrape resistance, and hydrolytic stability.

Insulated magnet wire is generally classified according to its thermal endurance and thermal index rating according to ASTM D2307, *Standard Test Method for Thermal Endurance of Film-Insulated Round Magnet Wire*. *Thermal endurance* is a measure of the stability of an electrical insulation material or combination of materials when maintained at elevated temperature for extended periods of time. The *thermal index* or *class* is a measure of the thermal stability of an insulation based on the temperature, in degrees Celsius, obtained by extrapolating the Arrhenius plot of life versus temperature to a specified time, usually 20,000 hours. Some major insulation types and their thermal classifications are given in Table 4.8.

Table 4.8. Examples of Magnet Wire Insulation Types and Thermal Classes

Insulation Type	Thermal Index, °C
Polyurethane	105
Polyurethane with self-bonding overcoat	105
Polyamide	105
Polyvinyl acetal	105
Polyvinyl acetal overcoated with polyamide	105
Polyurethane overcoated with polyamide	130
Epoxy	130
Polyester (amide) (imide) overcoated with polyamide	155
Polyester (amide) (imide)	180
Silicone-treated glass fiber	200
Polyamide-imide	200
Polyimide	220
<i>From NEMA-MW-1000.</i>	

4.12.2 Magnet Wire Constructions

Organic coatings are applied directly to copper or aluminum wire which may be round, square, or rectangular. One insulation type may be the only dielectric material needed but, for greater toughness, higher dielectric breakdown voltage, and moisture protection, the wire is often overcoated with a second and even a third insulative coating type. Generally, several layers of the same coating are applied to assure freedom from pinholes and maximum dielectric breakdown strength.

Figure 4.27 shows the construction for a dual-insulated wire using PolyThermaleze® 2000. The first insulation consists of several coats of a modified polyester that provides high thermal endurance, high temperature dielectric, overload resistance, resistance to thermoplastic flow, good adhesion, and flexibility. The top insulator, consisting of several coats of a modified polyamide-imide, provides heat shock resistance, moisture protection, surface toughness, and chemical resistance. Wire, so coated, meets Thermal Class 200 for copper and 220 for aluminum.

*PolyThermaleze® is a registered tradename of PD Wire and Cable, a Unit of Phelps Dodge.

A triple insulation that provides an outer bondable surface is shown in Fig. 4.28. Here the third or top layer consists of a modified polyester cement that forms a strong turn-to-turn bond throughout the winding and often eliminates the need for an impregnating varnish.

The properties of Bondeze and Thermaleze compared with other insulation types are given in Table 4.9.

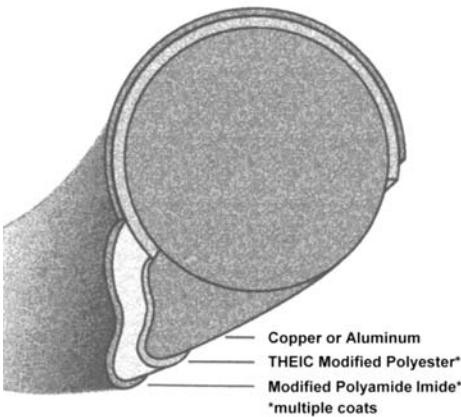


Figure 4.27. Construction of a dual-insulated wire: PolyThermaleze® 2000. (Courtesy PD Wire and Cable.)

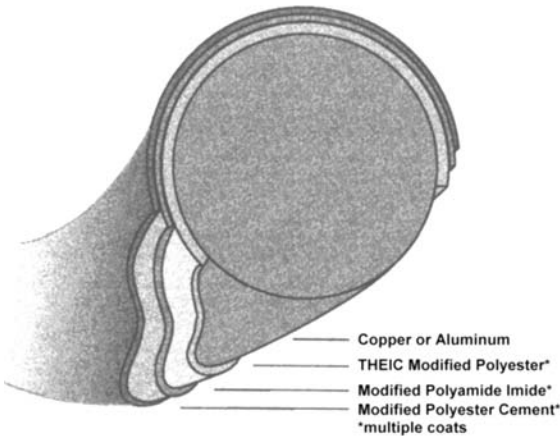


Figure 4.28. Construction of a triple-insulated wire: Bondeze® M. (Courtesy PD Wire and Cable).

Table 4.9. Wire Insulation Coatings and Properties

Polymer Type	Product Tradename	Applications	Thermal Class	Dielectric Breakdown	Insulation Resistance (ohms)	Other Properties
Polyvinyl Formal	Formvar	Oil filled transformers	105	10 kV (RT) 7 kV (105°C)	5×10^{13} (RT) 2.8×10^{13} (105°C)	Excellent hydrolytic stability
Modified Polyester (inner layer), Polyamide-imide (outer layer)	Armored Poly-Thermaleze 2000*	Dry-type transformers hermetic motors, tool motors, auto alternators, stators, solenoids, toroidal TV yokes	200 (Cu) 220 (Al)	11 kV (RT) 7 kV (200°C)	5×10^{13} (RT) 9.2×10^{10} (200°C)	Temp. resistance >200°C
Modified Polyurethane (inner layer), Polyamide Nylon (outer layer)	Nyleze/155*	Coils (particularly random wound) Universal motors	155	8.5 kV (RT) 6.0 kV (105°C)	5×10^{13} (RT) 2.8×10^9 (155°C)	
Modified Polyester (inner layer) Modified Polyamide-imide (middle layer) Modified Polyester cement (top layer)	Bondeze M*	Fractional and integral horsepower motors, universal motor fields and motor stators	180	Same as for Poly-Thermaleze 2000	Same as for Poly-Thermaleze 2000	Bondable version of Thermaleze 2000, high retention of bond strength at 180°C

(cont'd.)

Table 4.9. (cont'd.)

Polymer Type	Product Tradename	Applications	Thermal Class	Dielectric Breakdown	Insulation Resistance (ohms)	Other Properties
Polyesterimide	Thermaleze T*	Motors and coils	180	11 kV (RT) 7 kV (180°C)	5×10^{13} (RT) 5×10^{10} (180°C)	Solderable
Polyarylether-etherketone	PEEK	Motors operating in harsh thermal and chemical environments	220	9 kV (RT) 5 kV (220°C)	3×10^{12} (RT) 4.5×10^9 (220°C)	Very high thermal and chemical resistance, extruded
Polyarylsulfone	PAS	Oil-filled transformers, Class B and F motors	180			Extruded
Aromatic Polyimide	Imideze *	Dry-type transformers, traction motors, DC field coils	240	12 kV (RT) 7 kV (220°C)	5×10^{13} (RT) 8.6×10^{10} (220°C)	Very high thermal and chemical stability, highest overload and cut-through resistance

Note: Data are for comparative purposes; not to be used for specifications.

*All products are registered tradenames of PD Wire & Cable except for PEEK.

(Courtesy of PD Wire & Cable.)

4.12.3 Wire Coating Types

Most of the polymer types discussed in “Chemistry and Properties,” Ch. 2, may be used as wire insulation or as coil impregnating resins. Although they are formulated differently, the basic properties of each type remain the same. Accordingly, polyimides, fluorocarbons, silicones, and polyaryletheretherketone are best suited for very high temperature applications. A list of the major polymer types used for wire insulation is as follows:

- Polyvinyl formal (Formvar)
- Polyimide (Pyre ML, Kapton, tradenames of DuPont)
- Polyamide (Nylon)
- Polyamide-polyimide (amide-imide)
- Polyester
- Polyesterimide
- Oleoresinous enamel
- Polytetrafluoroethylene (PTFE) (Teflon TFE)
- Fluorinated ethylene propylene (FEP)
- Polyurethane elastomers
- Polyvinyl chloride
- Polyethylene
- Polyaryletheretherketone (PEEK)
- Polyarylsulfone (PAS)

Polymer types used for coil impregnation include:

- Polyurethane
- Acrylic
- Epoxy
- Silicones

In general, wire and impregnation coatings consist of high-molecular-weight polymers, either thermoplastic (linear) or thermosetting (cross-linked). The thermoplastics have definite softening or melting points, above which the materials are not usable, especially where local stresses are encountered. Examples of thermoplastics include Teflon, other fluorocarbons, polyamides such as Nylon, polyaryletheretherketone (PEEK), and polyarylsulfone (PAS). The melt temperatures for most of these thermo-

plastics are very high, greater than 200°C and for some greater than 300°C. Thermosetting coatings are tougher, more resistant to abrasion and cut-through, and have improved solvent resistance. Examples include polyesters, epoxies, and polyvinyl formals.

To insure reliability, wire may be coated with several layers of two, or even three, different polymer types. In this way characteristics are also achieved that could not be achieved with any one polymer alone. Thus, polyvinyl formal may be overcoated with nylon to provide the lubricity properties of nylon for greater ease in winding. Polyvinyl formal is frequently overcoated with polyvinyl butyral to render the coating self-bonding either by heat or solvent action, a property that is especially important in fabricating formed coils.

Plain Enamel or Oleoresinous Coatings. The terms “plain enamel” or “oleoresinous varnish” refer to the natural resinous coatings that have been used as standard wire insulation for more than sixty years. They are derived from natural drying oils such as linseed or tung oil and are cured through air oxidation of their inherent double (ethylenic) bonds. The coatings may be enhanced by “cooking in” fossil or synthetic resins to improve their hardness and resistance to solvents. Because of the dark color of the finish wire, such coatings are sometimes referred to as “black enamels.” Oleoresinous coatings are rapidly being replaced by the higher performance synthetic coatings.

Polyvinyl Formal and Modified Polyvinyl Formal Coatings. Coatings based on polyvinyl formal (Formvar) were first introduced in 1938 as magnet wire insulation, but remain in wide use today. The base polymer is synthesized by partially hydrolyzing polyvinyl acetate and then reacting the free hydroxyl groups of the resulting product with formaldehyde to form the six-membered formal structure. The polymer, therefore, contains three basic functional units: vinyl formal, vinyl alcohol, and vinyl acetate, as in Fig. 4.29.

Polyvinyl formal is thermally stable for extended periods of time at 110°C; its thermal endurance curve is shown in Fig. 4.30. Used alone, Formvar has marginal solvent and abrasion resistance, but its properties are greatly improved by modifying the basic resin through reaction with phenol formaldehyde or cresol formaldehyde resins. Both resins condense with the free hydroxyl groups of the polyvinyl formal to produce coatings that are extremely tough and flexible and that possess good abrasion and solvent resistance. Polyvinyl formal can also be modified with resins such as melamine, urea, epoxy, and urethanes.^[59]

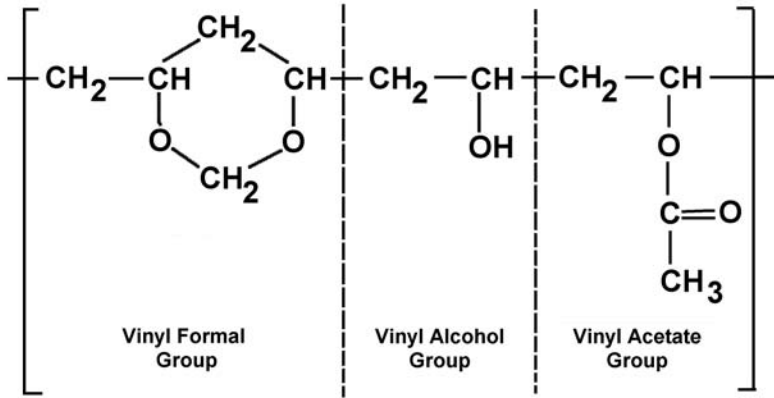


Figure 4.29. Molecular structure for polyvinyl formal resin.

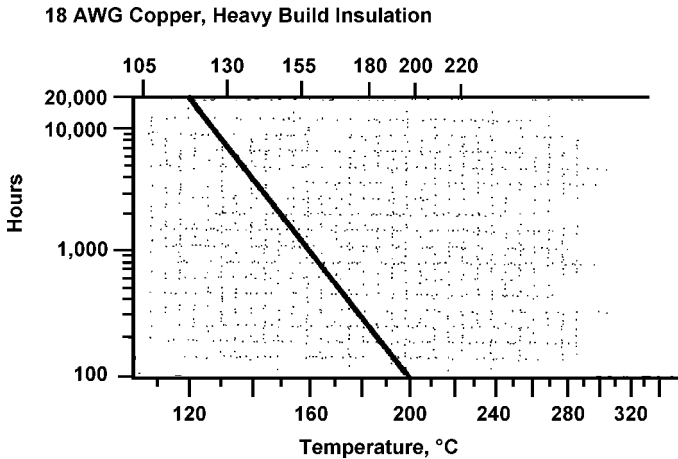


Figure 4.30. Measured thermal endurance curve for Formvar. (Courtesy PD Wire & Cable.)

The modifications with urethanes are especially favored because of their solder-through properties. Dip-tinning or soldering at high temperatures (up to 350°C) may easily be performed without having to previously strip off the insulation. Three-component coatings consisting of polyvinyl formal, polyurethane, and polyester are also easy to solder through and, in addition, have good flow, flexibility, heat shock properties, and good resistance to

solvents and abrasion.^[60] In fact, practically all the solderable magnet wire coatings on the market contain urethane modifications.

Polyurethane Coatings. Polyurethane coatings that are used as wire enamels are generally the reaction products of hydroxylated polyesters or hydroxylated polyethers with tolylene diisocyanate. Admixing these components, however, results in very rapid polymerization—too rapid to be of any practical use. For this reason, polyesters containing excess isocyanate groups are first reacted with phenol to yield adducts that are relatively stable at room temperature. After coating the wire and baking at elevated temperatures, the phenol portion of the adduct is released and the resulting free isocyanate groups then react with the hydroxyl groups of the polyester to form the desired polyurethane coating. This is the ASTM Type 3 polyurethane previously discussed in Ch. 2. Other polyurethane wire enamels consist of reaction products of isocyanates with Formvar and, as mentioned in the previous paragraph, offer good solderability. In fact, the largest share of the solderable insulation market consists of polyurethane systems.^[61]

Polyester Varnishes and Enamels. Polyester varnishes are produced by the condensation of terephthalic acid, a glycol, and a polyol such as glycerine. When the proper ratios are mixed and heated, partial polymerization occurs, leaving the product soluble in solvents. The general structure of a polyester polymer is represented by Fig. 4.31.

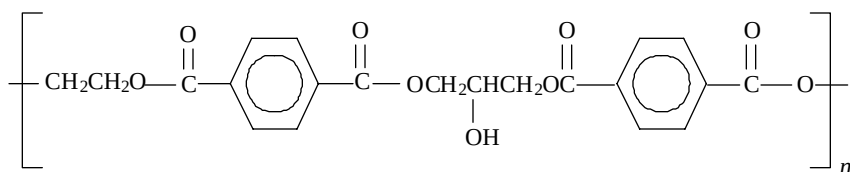


Figure 4.31. General molecular structure for polyester resin.

Polyester coatings may be applied to wire by either an automated or manual dipping operation and subsequently baked at 150°–205°C. They may be used alone or in conjunction with other compatible wire insulation such as nylon polyamides, Formvar, polyimides, or polyurethanes. Polyester wire coatings are noted for their excellent thermal properties which derive from the stability of the ester linkages, the high cross-linking density, and the symmetry of the para-substituted benzene rings. They qualify for Class A (105°C) through Class 200 (200°C) applications.

Polyaryletheretherketone (PEEK). Polyaryletheretherketone is a linear thermoplastic polymer that is difficult to dissolve in any known organic solvent. It must, therefore, be applied to the wire by extrusion whereby it is heated to its softening point and allowed to flow under pressure. The conditions for extrusion are proprietary. The key attributes of PEEK are its high temperature stability (Thermal Class 220) and high chemical and humidity resistance. Its highly aromatic molecular structure provides these excellent properties. The crystalline melting point is 334°C. The thermal endurance curve is given in Fig. 4.32.

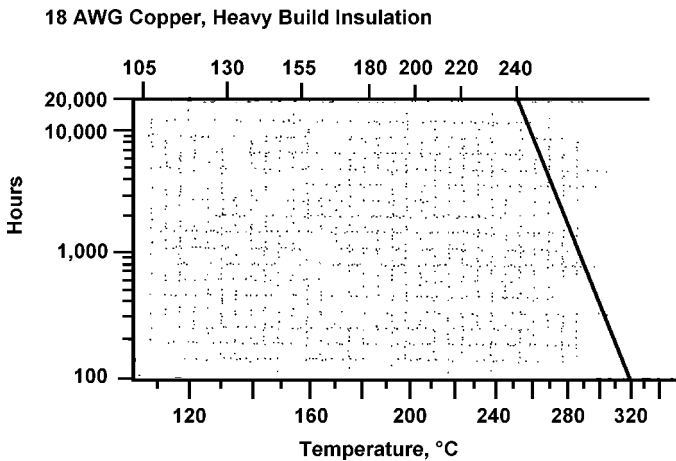


Figure 4.32. Measured thermal endurance curve for PEEK. (Courtesy PD Wire & Cable.)

PEEK's resistance to extreme hydrolysis conditions is unique. When tested in distilled water in a pressure bomb at 260°C and 675 psi for 8 hours followed by 16 hours at room temperature and repeated for a total of 5 days, PEEK retained 56% of its dielectric strength while polyimides failed, and the insulation turned black and became brittle.^[62]

Polyarylsulfone (PAS). Like PEEK, polyarylsulfone is a linear crystalline thermoplastic polymer which is also difficult to dissolve in the known organic solvents. It too must be applied by the extrusion process. Because of its aromatic structure, it has high thermal stability, but not as much as PEEK. Its melt temperature is 254°C and it belongs to Thermal

Class 180. More on the chemistry and properties of polyarylsulfones may be found in Ch. 2.

Polyimide Wire Insulation. Polyimide coatings are extensively used for high temperature wire insulation and for insulation that must withstand high radiation fluxes. Pyre-ML (tradename of Summit Precision Polymers; available from Rea Magnet Wire Co.) polyimide varnish has been in use for many years as a magnet wire insulation for dry-type transformers, dc field coils, and submersible pump motors. It is rated for continuous use at 220°C. The measured thermal endurance for PD Wire & Cable's polyimide Imideze[®] is given in Fig. 4.33. As an overcoating, polyimide provides an extremely tough abrasion-resistant film that also exhibits high resistance to radiation and heat. Polyimide-coated round wire is specified in NEMA MW-16. Polyimide coatings are also used as insulation and impregnants for motor, coils, and relays. Because of their low weight loss at elevated temperatures and their high chemical resistance, polyimide varnishes are useful in encapsulated windings and hermetically-sealed components. Polyimide wire coatings are compatible with numerous phenolic, polyester, and epoxy varnishes and encapsulants and are resistant to most solvents and chemicals. The exceptional toughness, thermal stability, and chemical resistance of cured polyimide, however, becomes a drawback in its ability to be easily stripped from wire in order to perform rework or make electrical connections. Other limitations include its hydrolytic instability at temperatures above 105°C in a sealed system containing moisture. Polyimides under the DuPont tradename of Kapton[®] may also be used as a film to insulate wire.

Impregnating Varnishes. After coils and their cores are assembled, the part (for example, a transformer or toroidal coil) is impregnated with varnish and encapsulated or otherwise embedded in one of a variety of materials (Fig. 4.34). Complete impregnation serves four main functions:

- Additional electrical insulation for the wires
- Better heat dissipation
- Protection from moisture and other contaminants
- Better shock and vibration resistance

The exclusion of air and oxygen by thorough impregnation with organic coatings results in substantial improvements in thermal life. Epoxy impregnation, for example, may upgrade a Class A insulation to a Class B. The cooler operation of coils and transformers has permitted a degree of miniaturization never before possible.

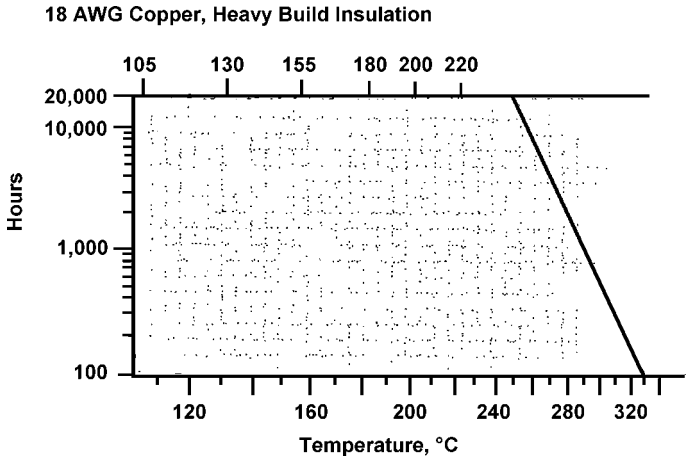


Figure 4.33. Measured thermal endurance curve for Imideze. (Courtesy PD Wire & Cable.)

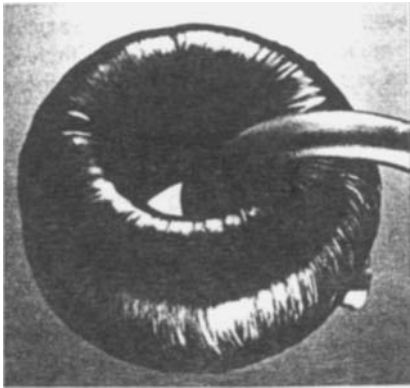


Figure 4.34. Silicone-coated toroidal coil. (Courtesy of Dow Corning Corp.)

4.13 COATINGS FOR SPACE APPLICATIONS

Coatings and other polymeric materials are extensively used in manned and unmanned space vehicles and communications satellites to reduce volume, weight, and cost. In these applications, organic PCB coatings and other plastic materials are exposed to space environments ranging from the rather benign, Low Earth Orbits (LEO) to hostile deep

space and planetary orbits. Their survivability in high vacuum, extremes of low and high temperatures, ultraviolet light, atomic oxygen, micrometeorites, gamma radiation and other forms of high energy ionizing radiation must be known and mitigated.

4.13.1 Radiation Effects

In selecting coatings for space or military applications, such as planetary probes, manned orbiting laboratories, satellites, spacecraft, and missiles, the effects of solar, deep space, and nuclear radiation must be considered. A comprehensive discussion of radiation effects on electronic systems was given by Messenger and Ash.^[63] Radiation effects on coatings and plastics are difficult to evaluate or predict because of the difficulty in reproducing the exact radiation environment which consists of many types of radiation, fluxes, energy levels, high vacuum (space), or high heat (nuclear). In addition, coating formulations are proprietary mixtures of many ingredients, and have a distinctive behavior. Accordingly, generalizations should not be made, except perhaps for pure unformulated resins under controlled radiation test conditions.

A detailed description of the various elements comprising the space-radiation environment has been given by Goetzel, et al.,^[64] and by McIlwain.^[65] In general, space radiation may be classified as solar or penetrating. Solar radiation consists of x-rays, uv light, visible light, and infrared radiation while penetrating radiation consists of high energy ionizing radiation such as protons, electrons, alpha particles, and gamma rays. The most serious radiation exists in the Van Allen belts where high energy ionizing radiation from solar flares has become trapped by the Earth's magnetic field. The inner belt starts at only 200 miles above the Earth, but extends beyond 500 miles. It consists mainly of high-energy protons with energies of 10–100 MeV. The outer Van Allen belt consists mainly of electrons with energies of 1–10 MeV. Both protons, electrons, and other ions from these belts are highly penetrating and pose a danger to astronauts and risk damage to electronic devices, sensors, instruments, and to materials.^{[66][67]}

Transient and Permanent Effects. The effects of radiation on the electrical and mechanical properties of many polymeric dielectric materials have been reported by Pascale et al.,^[68] and Bouquet.^[69] The *radiation hardness* of a material is denoted as the total rad flux required to degrade a specific material parameter to the point where it is no longer useful or becomes a reliability risk. Material parameters normally measured

are tensile strength, elongation, flexibility, adhesion, insulation resistance, and dielectric constant. Radiation effects may be *transient*, those that disappear upon removal of the radiation field, or *permanent*, those that remain after the field has been removed. In either case, catastrophic failure of electronic components and circuits can occur.

Transient effects are usually the result of electron excitation and temporary ionization and will normally affect the electrical properties of the polymer. Electron excitation increases the number of conducting electrons, hence, the electrical conductivity of the polymer—a process similar to photoconductivity induced by light. Where coatings provide insulation between closely spaced conductors or serve as interlayer dielectrics for controlled-impedance circuits, radiation-induced conductivity can cause circuit failures through an accumulation of electrostatic charges.

Besides an increase in electrical conductivity and leakage currents, reduction of breakdown and flashover voltages can also be produced by radiation. Transient effects disappear immediately or slowly after the radiation source has been removed. However, these transient effects are often not large enough to disqualify polymers as protective coatings or as insulation, especially if the design engineer has made allowance for these changes. In most cases, structural changes occur before any permanent electrical changes.

Permanent damage due to radiation is generally the result of chemical changes. Radiation may induce either scission of long-chain polymer molecules or increased cross linking. In the course of either mechanism, ionic and free-radical species are formed that, in turn, degrade the electrical properties of the insulating material. Molecular scission results in reduced mechanical strength, lower softening point, and outgassing of low-molecular-weight species that are formed by decomposition. Increased crosslinking results in increased hardness, loss of tensile and peel strengths, embrittlement, cracking, and loss of adhesion. (Fig. 4.35).

Outgassing Due To Radiation. In addition to the transient and permanent radiation effects described above, there may be side effects on both components and materials caused by gases and other volatiles arising from the decomposition of the plastic. Gases commonly evolved from irradiation include ammonia, water vapor, methane, low-molecular-weight hydrocarbons, carbon dioxide, hydrogen halides, and halogens. Gas evolution can be particularly detrimental for electronic parts that are sealed. First, a build-up of pressure can cause rupture of the seal or package. Secondly, entrapped gases cause corrosion and shifts in electrical parameters.

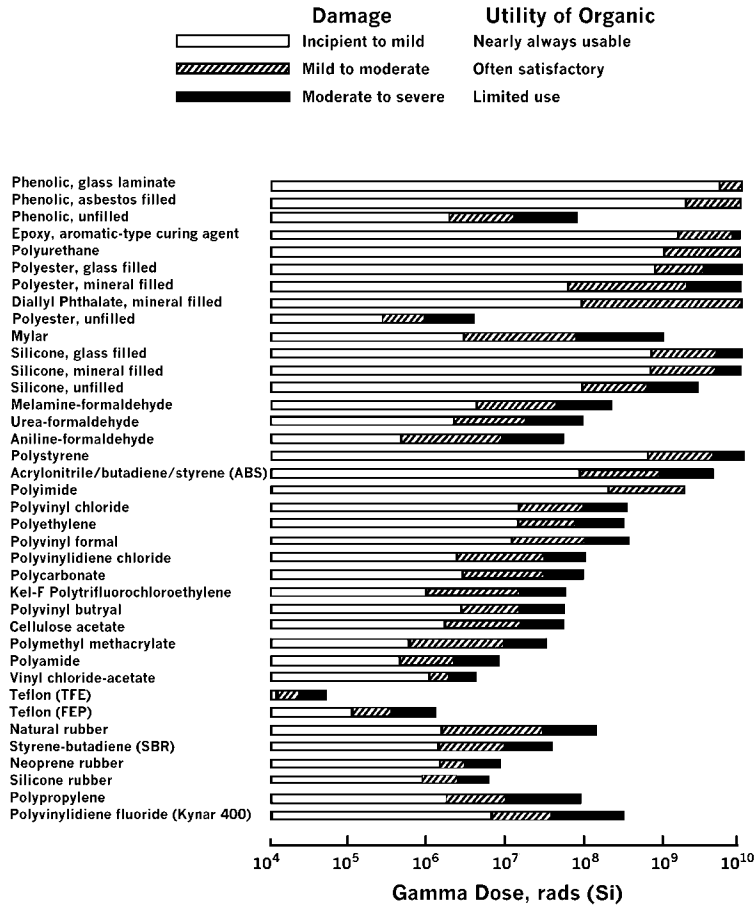


Figure 4.35. Relative radiation resistance of polymer insulation materials based on changes in physical properties.

Outgassing becomes significant at radiation dosages of 10^6 rads and above. Limited data exist for values below 10^5 rads. However, extrapolating data from high radiation doses to lower doses shows that neoprene outgasses to the extent of 7×10^{-4} ml/g at 10^4 rads and Mylar film has very slight outgassing of 7×10^{-5} ml/g under the same conditions^[70] (Fig. 4.36). In general, outgassing at total doses of less than 10^4 rads is negligible for most

polymers and not considered a problem. At higher doses, the severity of outgassing from specific materials must be determined experimentally. Materials evaluated to date show a linear response in the amount of evolved gas versus gamma radiation dosage as shown in Fig. 4.36. A comparison of gas evolution from various polymer materials when exposed to 3 to 7×10^8 rads is given in Table 4.10. Several conclusions may be drawn from this table:

- The more aromatic the polymer structure, the less gas is evolved. Aromatic structures of varying degrees are represented by items 2 to 4, 6, 8, and 9 in the table.
- The nature of the filler has a pronounced effect on gas evolution. As indicated by comparing the paper-filled with the graphite-filled phenol-formaldehyde, paper is a poor material to use as a filler.
- Polyvinyl formals (Formvar), widely used as wire insulation, were among the worst outgassers and should be avoided for radiation-hardened systems. Polyimide (Pyre ML) wire insulation is reported to be very resistant, again because of its highly aromatic structure.

Radiation Effects on Plasticizers and Fillers. Probably the most serious effect of radiation is on the stability of plasticizers in coating formulations. Increased crosslinking caused by irradiation results in polymer shrinkage and squeezing out of the plasticizer. The plasticizer may then agglomerate in droplets throughout the specimen or exude to the surface. The combination of crosslinking and separation of plasticizer increases the rigidity and brittleness of the coating.^[71]

Other formulation ingredients such as driers, pigments, and flame retardants, especially if used in small amounts, are little affected by radiation. Whereas, some finely powdered metal fillers have been known to catalyze radiation damage in polymers, inorganic fillers such as silica and alumina suffer comparatively little deterioration and, in fact, can reduce the total damage to the plastic matrix. Terai^[72] has shown very little effect due to pigments in paints at radiation doses less than 1.5×10^7 rads (gamma), but considerable changes occurred at levels of 8×10^8 rads or greater. At the higher doses, for example, titanium oxide accelerated the damage of nitrocellulose lacquer, whereas, carbon black inhibited damage. At lower levels, no differences were noted with white lead, titanium dioxide, antimony oxide, calcium carbonate, barium sulfate, talc, iron oxide, chromium oxide, carbon black, Hansa yellow, and toluidine red.

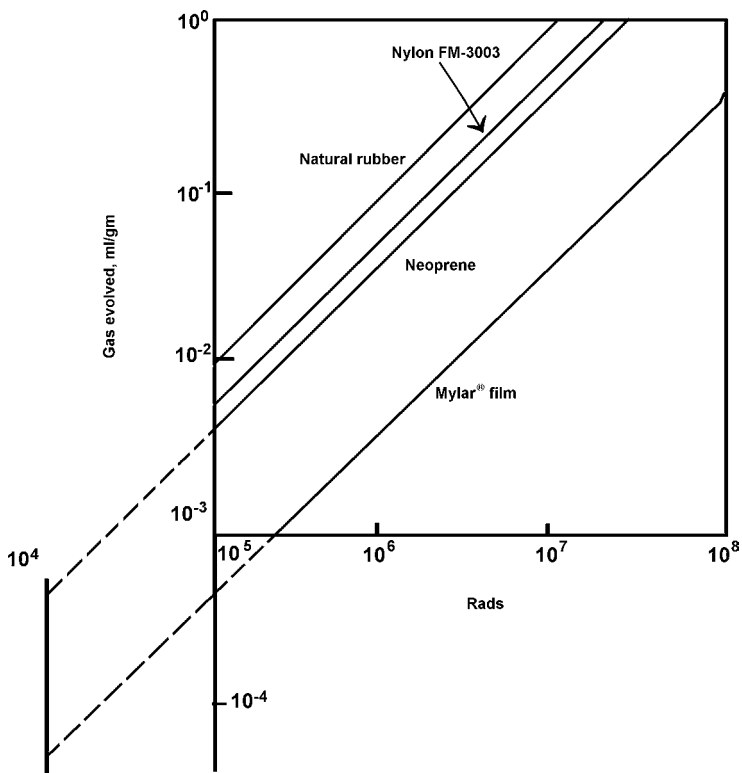


Figure 4.36. Outgassing of plastics resulting from irradiation.^[70]

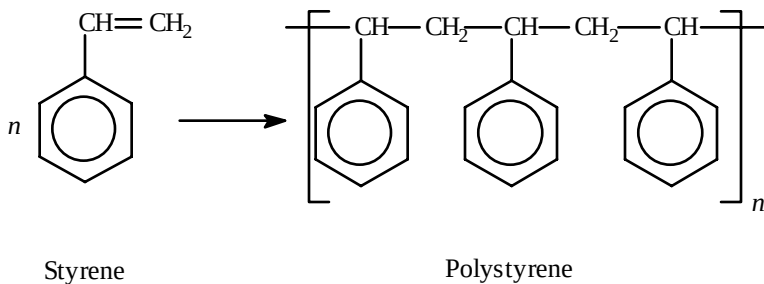
Table 4.10. Gas Evolution from Polymers Irradiated at $3 \text{ to } 7 \times 10^8$ rads

Polymer Type	Gas Evolved, ml/g
1. Polymethylmethacrylate	12.0
2. Phenol formaldehyde, unfilled	1.1
3. Phenol formaldehyde, graphite filled	0.01
4. Phenol formaldehyde, paper filled	6.0
5. Polyamide	11.0
6. Polyester	3.4
7. Polyethylene	38.0
8. Polyethylene terephthalate (Mylar®)	1.2
9. Polystyrene	0.1
10. Polyvinyl formal (Formvar)	37.0

Correlation of Polymer Structures with Radiation Resistance.

As a rule, polymers having highly aromatic benzene-ring type or nitrogen heterocyclic structures are much more resistant to radiation than aliphatic polymers such as polyethylenes or fluorocarbons. Polymers consisting of repeating aromatic or heterocyclic units will display a high degree of radiation resistance. For example, an epoxy cured with an aromatic amine retained 60% of its flexural strength after exposure to 10^9 rads, whereas, the same epoxy resin cured with a low-molecular-weight aliphatic amine retained only 25 to 30% of its flexural strength after exposure to 4×10^8 rads.^{[73][74]} The aliphatic amine-cured epoxies also showed three times greater outgassing than the aromatic-amine-cured epoxies.

Polystyrene, which has a highly aromatic structure, is among the most radiation-resistant plastics known.



As shown in Fig. 4.37, most of the physical properties for polystyrene were unaffected at electron dosages up to 1×10^8 rads. Tear strength was an exception with about 75% retention at the same radiation dosage.^[75]

In spite of their excellent radiation resistance, polystyrenes are not widely used for electronic applications because of their inherent flammability, low thermal stability, high shrinkage, high exotherm during cure, and generally poorer mechanical properties compared with other polymer coatings.

Polyimides, also highly aromatic and heterocyclic polymers, have been reported to withstand up to 100 Mrad of gamma radiation without degradation of mechanical, electrical, or adhesion properties.^[76] Benzocyclobutene, also a highly aromatic structure, withstood a 10 Mrad dose without affecting its flexural strength or CTE properties.^[77] Room temperature vulcanizing silicones are also reported to have radiation stability at 100 Mrads when exposed to a Cobalt 60 source.

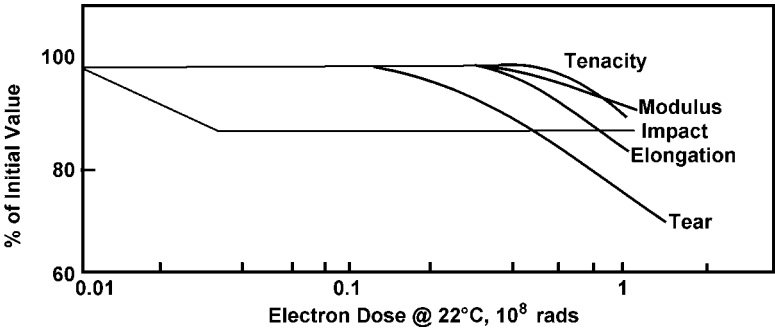


Figure 4.37. Effect of irradiation on the mechanical properties of polystyrene.^[75]

Dielectric materials, such as PTFE and other fluorocarbons used in microstrip antennas and RF cable insulation, are particularly vulnerable to radiation damage on long-term or high-intensity exposures. It is reported that the degree to which PTFE is affected is a function of the amount of energy absorbed, regardless of the type of radiation; beta, gamma, and x-ray energies; all had an equivalent effect.^[78] Fortunately for space applications, the total radiation threshold that polymer materials can tolerate is higher in vacuum than in air, but still, depending on how many years a satellite is to be operational, even these moderate radiation doses may be exceeded. Table 4.11 shows the thresholds for PTFE in air and in vacuum versus the loss of mechanical strength.^[78] The primary failure mechanism for PTFE and related fluoropolymers consists of scission of the polymer chain into smaller fragments.

Table 4.11. Threshold Radiation Doses in rads for PTFE in Air and Vacuum

Parameter	In Air	In Vacuum
Damage Threshold	$2-7 \times 10^4$	$2-7 \times 10^4$
50% Tensile Strength	10^6	10^7 or more
40% Tensile Strength	10^7 or more	8×10^8 or more
Retain 100% Elongation	$2-5 \times 10^5$	$2-5 \times 10^6$

Ultraviolet Irradiation. More work has been performed on the effects of uv radiation of polymer coatings than any other radiation source. This is probably because of the need to test commercial products for the long-term effects of sunlight, but also because of the availability and lower equipment cost for uv sources such as mercury-vapor lamps. Xenon- and carbon-arc lamps such as those employed in the Weather-Ometer[®] (Atlas Electric Devices Co.) are often used, but require more expensive equipment and yield less intense radiation in the low-frequency regions. The Weather-Ometer simulates and accelerates various terrestrial environments by simultaneously exposing parts to xenon-arc radiation, controlled relative humidity, temperature, and water spray. The equipment is extensively used by manufacturers of commercial products such as textiles and paints to determine their light-fastness and long-term durability. Coated panels may be visually examined after exposure or may be tested by infrared spectroscopy to determine changes in polymer structure and degradation.

By exposure to the more intense mercury-arc radiation, a variety of gaseous decomposition products have been identified from some polymers. Some of these, such as carbon dioxide and carbon monoxide, are common to most organic coatings, regardless of their type. Other outgassing products are specific to the polymer structure. For example, nine outgassing products were identified from an alkyd coating after mercury-arc irradiation in air for 6 hours or xenon-arc exposure for 54 hours.^[79] Besides carbon dioxide and carbon monoxide, other gases evolved included formic acid, methanol, hydrocarbons, ethylene, acetylene, and small amounts of acetone and vinyl compounds. Carbon dioxide was the major constituent as with other coatings tested including vinyl, vinyl-alkyd, polyvinyl acetate, epoxy-amine, and epoxy-polyamide. Polyvinyl chloride films released hydrogen chloride on irradiating with mercury-arc source.

4.13.2 Outgassing in a Thermal-Vacuum Environment

Another major concern in using organic materials in space is outgassing and degradation in a thermal-vacuum environment. Outgassed products can condense on optical lenses and instruments or create a corrosive ambient for electronics. The main mode of outgassing consists of the volatilization of low-molecular-weight, high-vapor-pressure species. These may consist of resins and hardeners that have not completely reacted due to insufficient cure or use of nonstoichiometric amounts of reactants. Additives such as plasticizers, flame retardants, diluents, and solvents are

also vulnerable to outgassing. In some cases, outgassing may be due to *sublimation* which is the vaporization of a solid without going through the liquid state, followed by redeposition from the gaseous state onto a cooler surface. At sufficiently high temperatures, all polymers decompose by the rupturing of atomic and molecular bonds and by the release of smaller more volatile fragments.

Outgassed products from plastic materials constitute serious contaminants in both unmanned and manned spacecraft because of one or more of the following reasons; they may:

- Be flammable.
- Be noxious or toxic to astronauts.
- Interact with volatiles from other materials to yield even more toxic or flammable products.
- Corrode thin-film metallizations on electronic devices.
- Deposit onto slip rings, switches, relays, and electromechanical parts causing high contact resistance, electrical opens, or high noise levels.
- Deposit on windows, optical lenses, and display units decreasing their transparency and reflectance.

Because plastics outgas and degrade to varying degrees in a high vacuum space environment, special formulations, curing conditions, and testing must be performed. In addition, for manned spacecraft, the outgassed products must not be toxic. Outgassing data must be known before specifying an organic material for space use. Fortunately, extensive tests have already been performed and data are available from NASA and from numerous contractors and universities who have conducted programs for the Space Shuttle, Space Station, Skylab, and numerous satellites. For example, NASA-SP-R0022A, MSFC-SPEC-1443, and ASTM-E-595 all describe the test methods for total mass loss (TML) and collected volatile condensible material (CVCM) when exposed to a thermal-vacuum environment.^[80] Requirements in these specifications are 1% maximum TML and 0.1% maximum VCM (Volatile Condensible Materials) after the sample has been heated for 24 hours at 125°C and 10^{-6} torr. In a Marshall Space Flight Center specification (MSFC-SPEC-1443), there is also a uv reflectance measurement test for condensibles on a mirror. According to this specification, the reflectance of a mirror coated with aluminum magnesium fluoride or a chromium-plated collector held at 25°C should not change more than $\pm 3\%$ at 200 nm. A fourth measurement of *water vapor regained* (WVR) is

optional. Water vapor regained is the weight gained by the sample after the vacuum bake exposure on allowing the sample to reabsorb moisture in a 50% RH ambient at 25°C for 24 hours. Thus, in specifying conformal coatings for space applications, it is not sufficient to specify only MIL-I-46058C since many of the coatings, polyurethanes, and acrylics, in particular, may outgas over 1% TML, depending on their degree of cure and formulation ingredients. With the imposition of the NASA requirements, suppliers have developed many space-grade coatings that meet or exceed all the requirements. For example, a polyurethane that passes the NASA outgassing requirements and has been used successfully for many years as a PCB conformal coating in space applications is Uniroyal's Solithane 113, an isocyanate resin cured with a polyol (C113-300).

Several simple processes, such as preconditioning the liquid resins and hardeners prior to cure or after curing, may be used to reduce the amount of outgassed material. With the solvent-less coatings, volatiles may be removed by evacuating the resin and hardeners separately at elevated temperature using a rotating evaporator. This relatively inexpensive equipment continuously rotates the liquid resin producing thin layers and exposing a large surface area to vacuum. Low-molecular-weight species vaporize and condense in a second chamber that is cooled (Fig. 4.38).

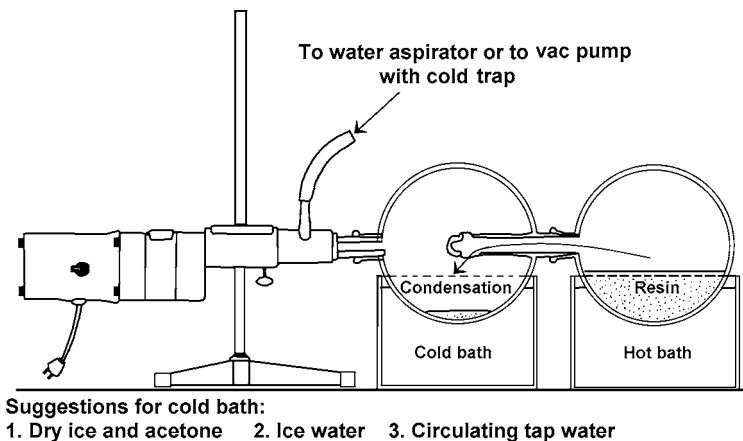


Figure 4.38. Diagram of a laboratory model roto-evaporator.

Preconditioning may also consist of postcuring a coating for a prolonged period of time in an inert ambient or under vacuum. The effectiveness of this approach was demonstrated by Thorne et al.^[81] Postbaking a silicone insulating varnish and RTV silicones at an elevated temperature or for extended periods of time resulted in significant reductions in the amount of outgassing (Figs. 4.39 and 4.40). Outgassing data are given for numerous organic materials in NASA Reference Publication 1124, *Outgassing Data For Selecting Spacecraft Materials*, Revision 4, June 1997.

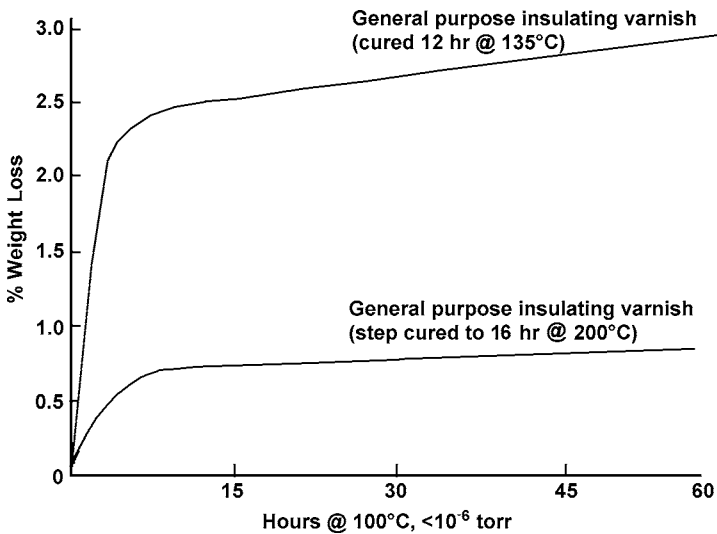


Figure 4.39. Reduction of outgassing from a silicone varnish on increased temperature baking.^[81]

The unique high-purity properties of the parylenes and silicones have made them especially useful as conformal coatings for space applications. Parylene pellicles and parylene-coated parts have been used in the Space Shuttle, Hubble Telescope, Mars Global Surveyor, and many other satellite programs. Other proprietary coating formulations of acrylics, polyurethanes, silicones, and epoxies have passed the NASA outgassing requirements and are listed in NASA-RF1124.

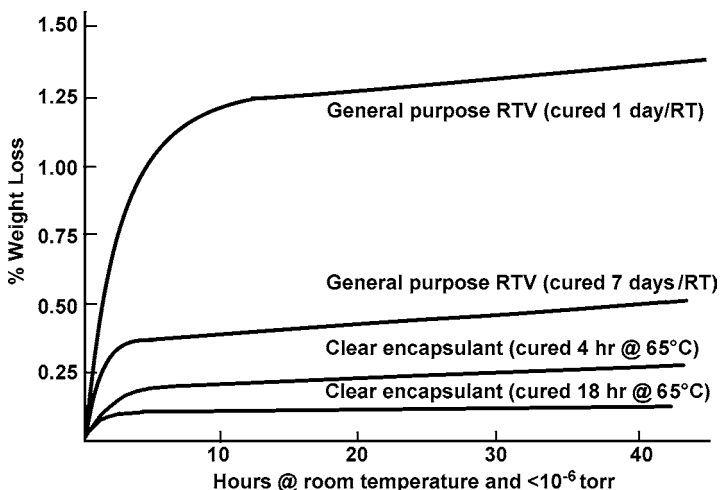


Figure 4.40. Reduction of outgassing from RTV silicones on extended cure.^[81]

4.13.3 Atomic Oxygen

In low Earth orbital (LEO) space environments, organic materials must also be resistant to monatomic oxygen and ultraviolet radiation. Atomic oxygen can physically erode and chemically oxidize the surfaces while ultraviolet radiation can discolor and physically degrade the surface or the entire coating. NASA-TP-1999-209260 provides material selection guidelines to limit atomic oxygen effects on spacecraft surfaces.

4.13.4 Flammability

Flammability of materials is another key concern of NASA, especially for manned spacecraft. Extensive testing of tens of thousands of polymeric materials has been performed by NASA and its contractors and a database (MAPTIS) of flammable and nonflammable materials is available from Marshall Space Flight Center. Most aerospace-grade electrical wire insulation is nonflammable, but may still present a risk due to other factors such as poor flexibility and poor cut-through resistance. Teflon, for example, has poor cut-through resistance while polyimide has a propensity to arc. Flammability is augmented in oxygen-rich ambients. The prevalent use of COTs (Commercial Off-the Shelf) wire and cable insulation is of

concern where there is a risk in using commercial insulation coatings such as PVC, polyethylene, polyamides, and chloroprene that are considered flammable for manned spacecraft. However, flammable insulation may be acceptable on wires in external payloads that are not powered.^[82] All flight hardware now used in NASA manned space programs must comply with the requirements of NASA-STD-6001, *Flammability, Odor, Offgassing and Compatibility Requirements and Test Procedures for Materials in Environments that Support Combustion*. Test #4 of this specification provides details on conducting flammability tests for electrical wire insulation.

4.13.5 Sterilization and Decontamination^[83]

A key objective of the space program is to probe the surface of Mars, asteroids, and other extraterrestrial bodies for living organisms. The issue is how to assure that, in removing and analyzing samples, microorganisms are not in fact introduced from Earth-contaminated hardware. Thus, considerable efforts have been spent on methods for cleaning, decontaminating, and sterilizing, not only the electronic subassemblies and assemblies, but the entire spacecraft prior to leaving the Earth's atmosphere.

The sterilization of spacecraft for planetary missions, particularly for the Mars mission, is considered important in obtaining an unequivocal understanding of the origin of life. Planetary landings have to be isolated from contact with viable Earth microorganisms to prevent uncertainty about the results of experiments and to determine if viable organisms exist or existed on other planets. Thus, sterilization and other bioburden reduction procedures impose yet another requirement on materials and components destined for space use. Materials must withstand the sterilization procedures without physical or electrical deterioration within certain specified tolerances. To qualify for NASA approval in the early missions of the 1970s, materials had to remain stable after ethylene oxide or thermal exposure, the two key sterilization procedures at that time. Surface decontamination entailed exposing the component to six separate cycles of ethylene oxide/Freon mixture. Each cycle consisted of exposure to a mixture of 12% ethylene oxide and 88% Freon 12 at 50% relative humidity and 50°C for 30 hours. Some coatings and plastics were seriously damaged by the Freon solvent portion of the ethylene oxide mixture, particularly silicones that swelled and polysulfides that softened and flowed.^{[84][85]} Internal sterilization was accomplished by thermal exposure: an additional six cycles of 92 hours

each cycle at 135°C. Details of the dry-heat sterilization and ethylene oxide-decontamination procedures were given by Kalfayan.^[86]

Today, sterilization remains a key requirement for most NASA space missions, but the sterilization procedures have changed somewhat. Ethylene oxide is no longer used and the dry-heat conditions have been reduced. The temperature range is typically between 110° and 125°C at a relative humidity below 0.2%. The following equation gives the duration of the process, t , in hours needed to achieve a 10^4 reduction in bioburden as a function of T , the minimum temperature achieved at the high end in the process for the range of temperatures between 110° and 125°C.

$$\text{Eq. (4.1)} \quad t = 5 \times 10^{(125 - T)/21}$$

Individual missions are now divided into five categories according to the likelihood of contamination and the level of concern associated with possible contamination of the target.^[87] For example, the Mars Lander is considered to have a very high probability of contamination because the lander will be in intimate contact with the Martian surface and atmosphere, and the level of concern that contamination will occur is high because of the possibility of past or present existence of life on Mars.

Categories I through IV apply to missions where *forward contamination*, bringing life from Earth to another body, is possible. Category I missions have no planetary protection requirements and apply to missions having virtually no biological contamination concern, such as missions to the Sun or Mercury. Category II missions have minimal biological concerns and also have no bioburden reduction requirements; however, they are required to develop a planetary protection plan and follow that plan. Categories III and IV apply to missions with substantial biological interest or where contamination of a target with high biological interest is likely to occur. Category III applies to missions without direct contact with the target, while Category IV applies to those having direct contact. Category IV is further divided into subcategories A and B. Category IV-A missions have landers or probes without any life detection experiments, while Category IV-B missions have life detection equipments.

The Viking Mars Landers of 1975 set the current standards for the Category IV missions. Each lander was to have less than 1 in 1000 chance of contaminating Mars. In order to meet this specification, the landers were first hand cleaned with alcohol wipes until fewer than 300,000 spores per lander and fewer than 300 culturable bacterial spores per square meter of

the surface of each craft were measured. This level of contamination represents the current Category IV-A requirement. Next, the landers were subjected to a NASA certified process known to reduce the bioburden by a factor of 10^4 so that the landers then each had fewer than 30 viable organisms present per landing event. This level of sterilization represents the current Category IV-B requirement. A Category V mission is one that will return to Earth and where *reverse contamination*, the bringing back of alien life to Earth's biosphere is possible.^[88]

A mission to return samples from Mars is now in the planning stage at Jet Propulsion Laboratory. Planetary protection includes the control of terrestrial microbial contamination associated with robotic space vehicles (such as the Mars Exploratory Rover) intended to land, orbit, flyby or otherwise be in the vicinity of extraterrestrial bodies and control of contamination of the Earth from bioorganisms collected and returned. If the existence or non-existence of living organisms on Mars is to be proven, then all probes, robotics, and spacecraft landing on Mars must be sterilized to assure that any organisms detected cannot be attributed to have come from Earth.

Plastics constitute the largest single class of insulating and protective materials used in electronic packaging for spacecraft. A typical electronic assembly may contain a wide variety of polymeric materials in the form of coatings, adhesives, encapsulants, and laminates. Although the polymer resin itself may be non-nutrient and stable to the sterilization conditions, other ingredients in the formulation—plasticizers, catalysts, excess curing agents, uv stabilizers, pigments, fillers, and solvents—may harbor microorganisms and may not be able to withstand the sterilization conditions without degradation.

The basic polymer or the additives may be subject to partial or complete decomposition at the dry-heat sterilization temperatures. Organic coatings deteriorate and discolor to varying degrees upon thermal sterilization. The thermal sterilization of several circuit board assemblies at 135°C, the temperature originally used, showed several failure modes, one of which was the discoloration of a polyurethane conformal coating. Although this, in itself, would not affect the electrical functioning of the module, it could risk long-term reliability through subsequent corrosion or outgassing. Other failures such as the charring of polystyrene capacitors and electrical opens in the wet electrolytic tantalum capacitors were catastrophic.^[84] (See Table 4.12.) Coating types having low thermal stability such as the polystyrenes, whose maximum service temperature is approximately 85°C, should not be

used. Coatings such as epoxies and polyimides with high thermal stabilities have been found satisfactory. Kalfayan^[86] evaluated several wire enamels and found that the polyimide enamels best withstood both thermal and ethylene oxide exposures.

Table 4.12. Effects of Thermal Sterilization on Electronic Subassemblies^{[84][85]}

Subassembly	System Usage	Effects of Thermal Sterilization
Voltage Regulator	Computer	Polyurethane conformal coating and filleting material discolored; tantalum wet electrolytic capacitors failed; function within tolerance after six cycles; thermal conductive adhesive bond to power transistor separated.
Electronic Power Switch	Flight Control	Polyurethane conformal coating and filleting material discolored; insulation resistance increased; function within tolerance after 3.679 hr poststerilization operation.
Servo Amplifier	Flight Control	Polyurethane conformal coating and filleting material discolored; insulation resistance increased.
Power Supply and Regulator	Flight Control	Polyurethane conformal coating and filleting material discolored; insulation resistance increased; 10 of 17 tantalum wet electrolytic capacitors failed ; one polystyrene dielectric capacitor charred; two zener diodes partially shorted.
Electronic Switch and Sync Signal Demod	Flight Control	Visible cracking of potting material; intermittent electrical discontinuities; physical-stress failure of transistor; solder-lead separation; cracked printed-circuit connector.
Electronic Switch-roll Control	Flight Control	No visible effects function within tolerance after six cycles.
Ref Signal Generator	Navigation and Guidance	Discoloration of CPC chips and fiberglass circuit board; function within tolerance after six cycles.
400 Hz Amplifier	Navigation and Guidance	Discoloration of CPC chips and fiberglass circuit boards; two of five tantalum wet electrolytic capacitors failed, causing secondary failure of three transistors.

4.14 COATINGS FOR AUTOMOTIVE APPLICATIONS

As the usage of electronics in automobiles increases, the protection of these electronics to assure reliable performance under very harsh environments is critical. Three general environments are well known in the automotive industry:

- Passenger compartment
- Under the hood
- On or near the engine

Of these, the least severe ambient occurs in the passenger compartment while the most severe is on or near the engine. Temperatures inside the car can range from -40° to 85°C and relative humidities can vary from near 0 to 100%. Water can condense on electronic surfaces and, combined with water-soluble contaminants, can cause momentary malfunctions and ultimately catastrophic failures. Generally, electronics inside the vehicle are not coated because of the sparsity of proven failures due to unprotected circuits and the added cost of coating. However, this situation is changing with the increasing use of sensors, advanced devices, PCBs having finer conductor lines and closer spacings, and the use of thin-film metallization—all of which are more susceptible to corrosion and transient electrical effects. Where organic coatings are used, those that meet the industry conformal coating specifications, such as acrylics, polyurethanes, epoxies, and silicones are the favorites. Silicones, because of their high thermal stabilities are used in the near-engine circuits, while polyurethanes and epoxies are used for passenger compartment electronics. Applications include sensor circuits for aid in parking, belt-locks, side airbags, and the central locking mechanism. Schenectady-Beck's Bectron PK43, a polyurethane, is used to selectively coat a portion of an airbag electronic module installed in the sidedoor of an automobile.^[89]

The under-the-hood environment is much more severe than the passenger environment. The maximum temperature there can reach 105°C and temperatures can rise quickly from outdoor freezing to super hot. Concurrently, the electronics may be exposed to corrosive materials including gasoline, motor oil, antifreeze, battery acid, brake fluid, and numerous road contaminants. For this environment, thin conformal coatings may not suffice as adequate protection. Thick coatings or coatings combined with encapsulants or potting compounds are generally required. Silicones and

epoxies are favored because of their high temperature and chemical resistances.

An even more severe environment exists on or near the engine where temperatures may reach 125°C and where extremely rapid temperature changes occur. Electronics in this environment must be protected by potting with very high temperature resistant materials such as silicones.^[90]

Even harsher environments occur near the exhaust manifold and catalytic converter where temperatures reach 150°C, near the brake system where maximum temperatures may reach 205°C, and where electronic modules, if used, are exposed to hydraulic oil and greases.

4.15 COATINGS FOR ELECTROMAGNETIC INTERFERENCE (EMI) SHIELDING AND ELECTROSTATIC DISCHARGE (ESD)

Metal-filled electrically conductive organic paints and coatings are used on electronic chassis and enclosures to absorb and attenuate electromagnetic energy, thus, shielding the internal electronics. Electrically conductive coatings are also used to dissipate electrostatic charges (ESD) that build up on plastic or glass parts, to ground surfaces, and to prevent corona discharge. Conductive coatings allow static charges to be distributed evenly over the surface and allow charges to be bled off to ground. Generally, a surface resistance of $<10^5$ ohm/sq is required, but the most effective compositions have surface resistances of 0.03 to 1.0 ohm/sq/mil. Besides these electrical requirements, EMI shielding coatings must meet a combination of other requirements among which are:

- Ability to be sprayed or otherwise deposited in uniform thicknesses of 1 to 2 mils.
- Good adhesion to a variety of metal, plastic, and glass surfaces of which enclosures may consist. Examples of plastics used for enclosures include ABS, Noryl^{*}, polystyrene, and polycarbonate.

*Noryl[®] is a registered tradename of General Electric.

- Rapid room-temperature or low-temperature cure or dry in a reasonable time of 30 to 60 minutes.
- Noncorrosive, especially to aluminum under salt fog and humid environments.
- Abrasion resistant.
- Resistant to jet fuel (JP4), hydraulic fluids, oils, and greases that may be encountered in aircraft applications.
- Electrically stable at temperature extremes.

There are numerous one-part and two-part EMI/ESD compositions on the market that can be cured or dried at room temperature or cured at moderate temperatures. Most of the compositions are sprayable or brushable. Polymer binders include acrylics, polyurethanes, epoxies, silicones, and blends such as vinyl-acrylics and acrylic-urethanes. Fillers include silver, copper, silver-plated copper, blends of silver and silver-plated copper, nickel, and ferrous metals. Table 4.13 presents properties of some commercially available EMI coatings.

Commercial applications of coatings for both EMI and ESD include plastic enclosures for notebook and desktop PCs, routers, servers, medical electronics, and telephone handsets. With the proliferation of wireless electronic devices, EMI shielding has become critical to their performance. Wireless transmitters and transceivers radiate electromagnetic signals. Emissions result from both electric and magnetic fields surrounding current-carrying conductors or wires. These signals radiate into surrounding areas and couple with nearby signal lines, cables, and other conductors. Even though PWBs and PWAs can be designed to minimize or avoid EMI, it becomes increasingly difficult as frequencies increase beyond 800 MHz and into the GHz regions in which most wireless devices operate. At high frequencies, the wavelengths are so short that many circuit conductors have lengths that make them act as efficient quarter- or half-wavelength antennas. Thus, enclosures with EMI shielding become essential.^[91]

MIL-HDBK-263 (ESD Control Handbook for Protection of Electrical and Electronic Parts, Assemblies, and Equipment) provides guidelines for the design and application of materials and methods to obviate or mitigate electrostatic effects. The EMI shielding effectiveness of a commercial silver-plated copper/acrylic formulation is shown in Fig. 4.41, as an example.

Table 4.13. CHO-SHIELD* Coatings for EMI/ESD Shielding

CHO-SHIELD® Composition	Metal Filler	Polymer Binder	Applications	Properties	Surface Resistance, ohms/sq/mil	Useful Temp Range, °C
4900	Silver	Acrylic	Antistatic protection, grounding surface	One-part spray	0.05	-54 to 93
4914	Nickel	Acrylic	Antistatic use on ABS, Noryl and polyester	One-part spray high solvent resistance	2.0	-54 to 85
4916	Nickel	Acrylic	Effective on ABS, Noryl, polystyrene and poly- carbonate	One-part RT curing, provides 40–50 dB EMI shielding	<1.0 at 2 mils	-54 to 85
2001	Copper	Urethane	Corrosion resistant conductive flange coating	Three-part system, stable to jet fuel, hydraulic fluids, high abrasion resistance	0.1	-65 to 85
596	Silver	Epoxy	EMI, antistatic, corona shielding, use on glass or plastic	Two-part, spray or brush, RT or heat cure, 60–80 dB attenuation at 30 MHz to 1 GHz	0.06	-65 to 125
610	Silver- plated copper	Epoxy	Resistant to harsh environments	Two-part system, RT or heat cure	0.15	-65 to 125
4076	Nickel	Poly- urethane		One-part spray, good adhesion to most surfaces	0.5	-54 to 85

(cont'd)

Table 4.13. (cont'd.)

CHO-SHIELD® Composition	Metal Filler	Polymer Binder	Applications	Properties	Surface Resistance, ohms/sq/mil	Useful Temp Range, °C
2052	Silver-plated copper	Acrylic	EMI shielding of commercial electronic products such as computers, routers, servers, medical electronics, and telephone handsets	One-part, non-aqueous, sprayable, abrasion resistant, adheres well to plastics	0.04 @ 2 mils	-40 to 100
2054	Silver-plated copper	Acrylic-urethane	EMI shielding of commercial electronic products such as computers, routers, servers, medical electronics, and telephone handsets	One-part, water based, low VOC, sprayable, adheres well to plastics	0.03 @ 1.5 mils	-40 to 75
2056	Blend of silver and silver-plated copper	Acrylic	EMI shielding of commercial electronic products such as computers, routers, servers, medical electronics, and telephone handsets	One-part sprayable system, adheres well to plastics	<0.03	-40 to 100

*CHO-SHIELD® is a registered tradename of Chomerics, Div. of Parker Hannifin Corp. (Courtesy Chomerics, Div. of Parker Hannifin Corp.,

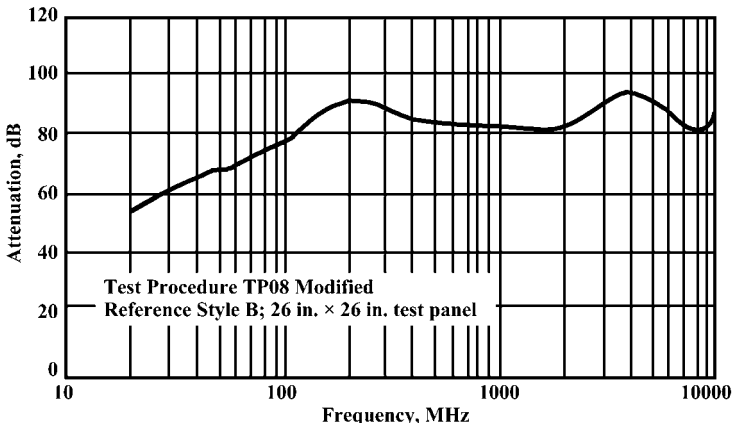


Figure 4.41. Electromagnetic interference shielding effectiveness of CHO-SHIELD® 2056 coating. (Courtesy Chomerics, Div. of Parker Hannifin Corp.)

4.16 COATINGS FOR MEDICAL APPLICATIONS

Understandably, coatings used for medical applications, especially on or in the body, must meet very stringent requirements and in most cases must be approved by the Food and Drug Administration. Among these requirements are:

- High purity and inertness of the coating material. The coating should not produce or release any by-products such as catalysts, plasticizers, or solvents or other materials that may be toxic or corrosive.
- Biocompatibility and biostability. The coating material must be compatible with body fluids and tissues and must not degrade, soften, lose adhesion, or flake on long exposure to the body environment. If used in a blood environment, it must have anticoagulant properties or must be surface treated to produce anticoagulant properties.

- Integrity. The coating must be pin-hole free and must conform to the substrate and coat around and beneath closely spaced components.
- Uniformly thin and low weight. The coating must be as thin and lightweight as possible and still perform its intended function.

Coatings in medical applications are being used in short-term expendable hardware such as catheters, brain probes, needles, guide wires, and for long-term applications such as pacemakers and defibrillators. They are also finding new uses in protecting electronic circuits that control dispensing of medicines within the body, biosensors, and implantable devices. In all cases, the coating serves to shield the electronic circuits from body fluids and provide lubricity. The most widely used coatings for these applications are the parylenes and silicones.

4.17 TAMPER-PROOF COATINGS

A unique and specific application for coatings involves tamper-proofing of electronic circuit boards and assemblies. Secure systems for military and space electronics must prevent access to stored information and prevent reverse engineering. Even some commercial and consumer products such as toys and smart cards may require such protection, e.g., preventing competitors from determining a circuit design or the nature of an IC chip.

To be effective, tamper-proof coatings must first be opaque to prevent visual examination and hard enough to prevent microprobing. Furthermore, they must be difficult to remove by the normal thermal, chemical, or mechanical means without destroying the underlying circuitry and secure devices. Hence, highly cross-linked thermosetting polymer structures that are resistant to high temperatures are better than linear thermoplastic polymers that melt at low temperatures. Polymers that have a high T_g are better than those having a low T_g . Adhesion to all surfaces should be so strong that the coating cannot be separated from the surfaces without the surfaces themselves being destroyed in the process. The coating should also be formulated to prevent non-invasive detection methods such as x-ray and neutron-ray examination. In addition to all these requirements, any coating or process used must still be compatible with the operation and

reliability of the electronic circuits. Often multilayers of several different coating materials including ceramics are used in order to achieve all the desired requirements.

4.18 TEMPORARY COATINGS

Some coatings, such as solder or plating resists and photoresists, are used temporarily during processing. These coatings are usually used to shield critical portions of the circuitry during subsequent processing, such as soldering or laser ablation, or to selectively mask portions of a surface in the photofabrication processing of microcircuits and thin-film circuits.

4.18.1 Maskants Used During Soldering or Laser Processing

Permanent maskants, previously described, are generally used for PWBs as solder maskants but, in some cases, removable maskants are more appropriate. For example, in assembling hybrid microcircuits, in which both wire bonding and solder attachment processes are used, the soldering processes are performed first, but the remainder of the circuit must first be protected from solder splatter and flux residues. Polyvinyl alcohol and polyvinylacetate coatings provide this protection and are subsequently removed by dissolving in water or alcohol. Urethane/acrylate formulations that cure on exposure to 365 nm wavelength radiation may subsequently be removed either by peeling or dissolving in water.

In the formation of microvias in polyimide film or in other substrates by laser ablation, carbonaceous, non-volatile residues deposit on adjacent surfaces. Here too, water-soluble coatings such as PVA have been used to shield adjacent surfaces, for example, in the processing of Tape Automated Bonding (TAB) devices.^[92]

4.18.2 Photoresists

Photoresists are a major class of temporary organic coatings essential in the fabrication of all microelectronic devices and thin-film circuits. Advances in photoresists together with optical tools have enabled the continued shrinking that has been occurring in device dimensions from

5 μm in the late 1960s to approximately 0.1 μm today. During this period, chemists have synthesized unique photosensitive polymers to satisfy the resolution, light sensitivity, and processing requirements for each successive generation of semiconductor and integrated circuit chips. Concurrently, physicists have optimized the optics and optical tools. The process by which photoresists are used to etch intricate and precise lines, spacings, and vias in metals and dielectrics has been a key factor in the rapid development of microelectronics from the early 1960s until today.

Photoresists are organic compositions consisting of radiation-sensitive polymers or polymer precursors together with additives such as photoinitiators dissolved in one or more non-aqueous or aqueous solvents. They are of two types: those that on exposure to uv light or other radiation source polymerize or crosslink to form a hardened coating that is resistant to etching solutions (*negative types*) and those that on exposure to light or other radiation source decompose into constituents that are easily washed away with a developer solution while the remaining coating becomes hardened and further polymerized by the same developer (*positive types*).

Negative photoresists were the first compositions used to pattern semiconductor devices and thin-film microcircuits and still comprise the largest segment of the photoresist industry because they are also widely used in the fabrication of PCBs. Early formulations from Eastman Kodak consisted of cinnamic acid esters that polymerized by a free-radical addition mechanism on exposure to uv light.^{[93]–[96]}

Positive photoresists, first introduced by Azoplate in the 1970s, are based on an entirely different chemistry than negative resists. Positive photoresists have replaced negative types for high resolution circuits, but advances are still being made in the chemistry of the negative resists to enhance their ability to produce very fine circuit features.^[97] In general, uv light in the 200 to 450 nm wavelength is used, with 300–450 nm used for most applications while 200–300 nm deep uv is used to obtain higher resolutions. Deep-uv negative resists have been reported to produce 150 nm lines and 230 nm spacings.^[98]

Generally, the photoresist is first applied over the entire surface of a substrate (for example, by spin coating), baked at a low temperature (soft bake) to remove solvents, then exposed to the radiation source through a separate mask which may consist of either a Mylar film or a glass plate having opaque and transparent regions corresponding to the image to be produced. This mask is referred to as the artwork, photo-tool, or hard mask. After exposure to light, the photoresist is developed, a process by which it is immersed in or sprayed with a chemical solution that dissolves the

unexposed portions of the photoresist (in the case of negative resists) or dissolves the exposed portions (in the case of positive resists). The remaining photoresist may then be hard-baked to render it more resistant to the subsequently used etching solutions. In using a negative resist, the mask must have a negative image of the pattern to be produced. Figure 4.42 illustrates the steps in etching a thin film of gold on an alumina substrate using a negative photoresist and a negative image mask. The pattern produced is the opposite of the image on the mask.

In a positive photoresist, the areas exposed to uv light are degraded or decomposed and consequently readily dissolved and removed. The chemistry is such that the remaining (unexposed) areas are hardened and rendered resistant to etching solutions simultaneously by the same solution (developer) that is used to dissolve the exposed areas. Hence, a positive image on the mask results in the same pattern on the substrate. The steps in etching metallization using a positive resist are shown in Fig. 4.43. In all, four combinations are possible, depending on whether a positive or negative resist is used with a positive or negative mask (Fig. 4.44). The chemistry of photoresists is quite varied and complex and has been extensively described in numerous articles and books.^{[8][99]–[101]}

Besides uv and deep uv, other radiation sources and lithographic processes are being used to produce even finer dimensions.^{[96]–[98]} Among these are: electron beam lithography ($<1\ \mu\text{m}$ resolution), x-ray lithography ($0.02\ \mu\text{m}$ resolution), and ion-beam lithography ($<1\ \mu\text{m}$ resolution). The resolution of features is ultimately limited by the wavelength of the exposing radiation and the chemistries of the resist materials.^[102] These factors are critical in fabricating semiconductor devices where submicron dimensions are required. However, for PCBs whose geometries are on the order of mils, uv photolithography is the most commonly used process. These resists may also be negative or positive.^[103]

Photoresists are generally liquid compositions that are applied by spin coating onto circular wafers or, by roller-coating or screen printing on large panels for printed wiring boards. The introduction of dry-film Riston[®] photoresists by DuPont in 1968 was a great advance in uniformly coating large PWBs, producing finer lines and spacings, and improving yields. Pinholes and touch-up, previously required with the liquid photoresists, were virtually eliminated since the dry-film was processed under clean room conditions and protected by a polyester support film and a separator sheet that are removed just prior to use. The dry-film resist is then laminated to the

circuit board, exposed and developed. Riston photoresists are now available as both negative and positive types having various resolution capabilities from several mils to below 0.1 mil.

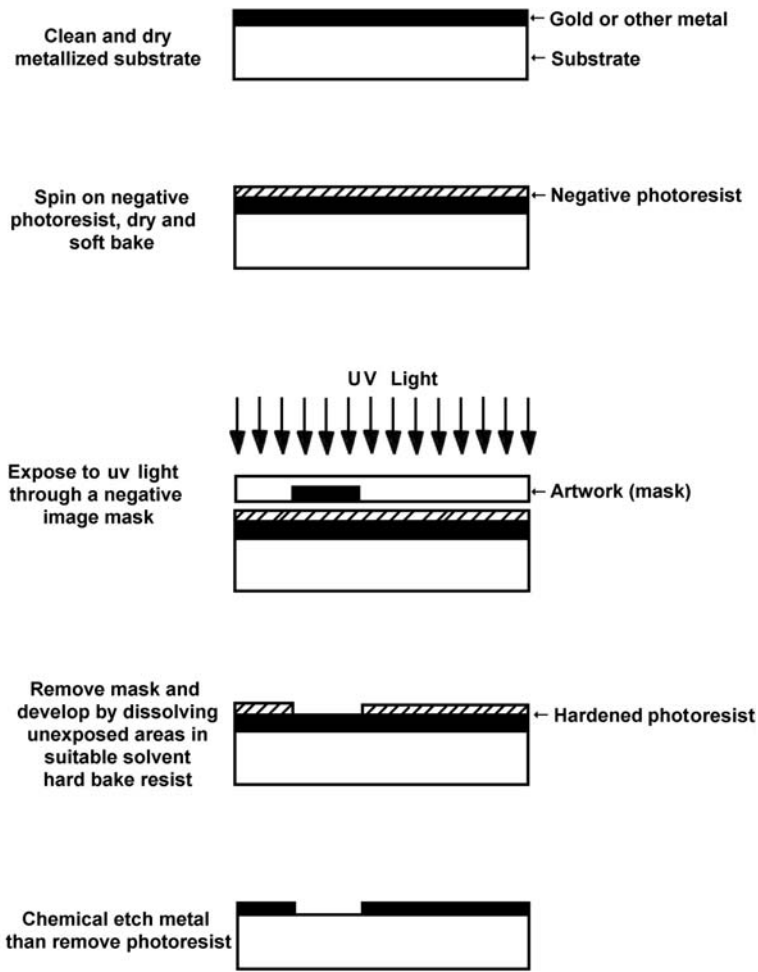


Figure 4.42. Photolithography steps using a negative photoresist.

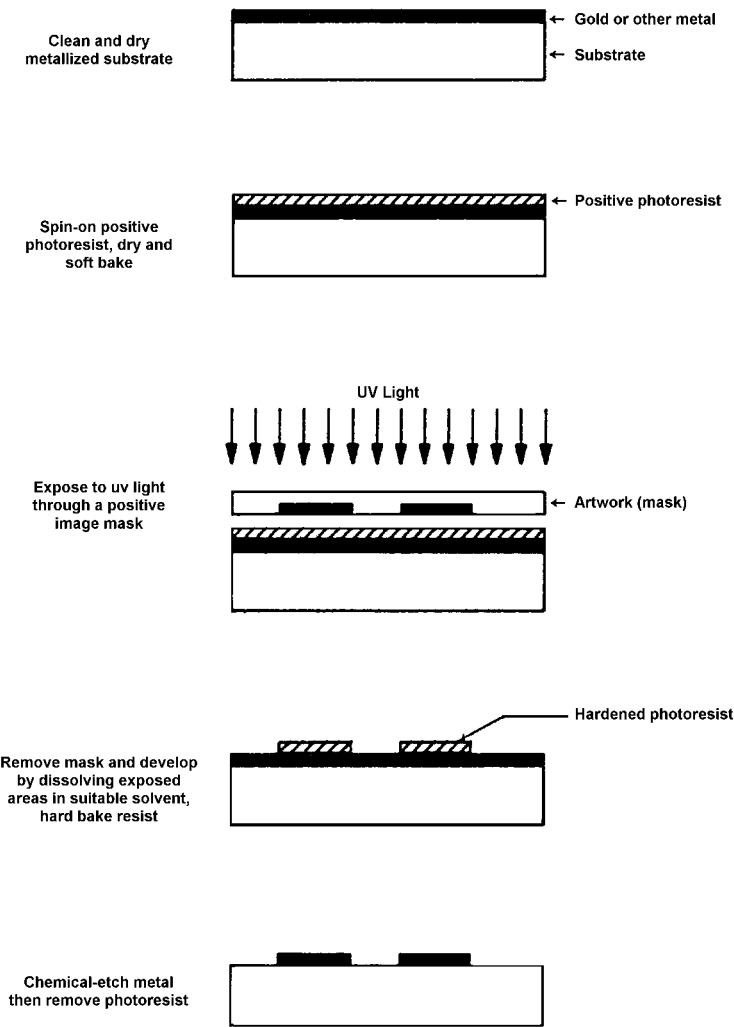


Figure 4.43. Photolithography steps using a positive photoresist.

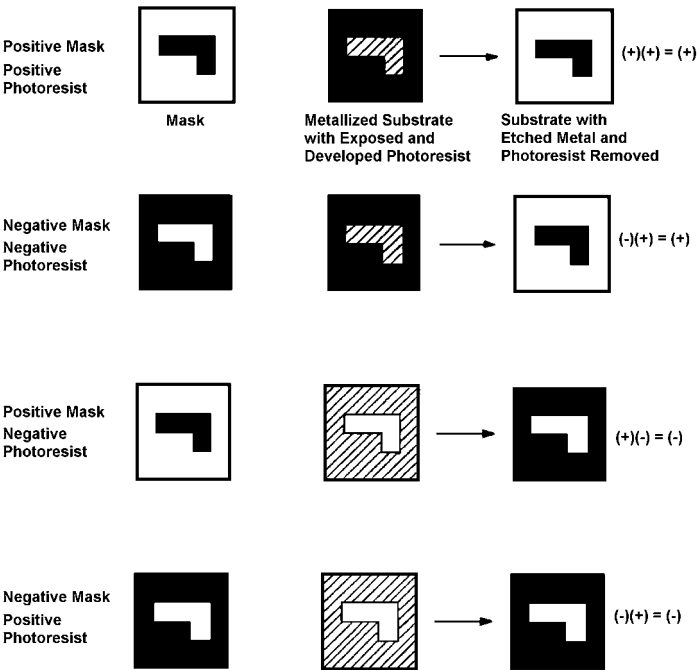


Figure 4.44. Mask/photoresist combinations.

A recent development is the deposition of liquid photoresist by an electrophoretic process. This process also permits the coating of large flat panels, but has the added advantage of being able to coat irregular shapes and three-dimensional surfaces. A positive-acting photoresist is electro-deposited from an electrolytic aqueous bath in a fashion similar to the electroplating of metals. The photoresist consists of positively charged particles that are attracted to a metallized surface (such as a copper-clad PWB laminate) that is rendered cathodic through an applied potential of 60 to 100 volts. It is reported that thin uniform coatings of 0.2 mils can be deposited and can conformally coat all metal surfaces.^[104]

4.19 POLYMER THICK FILMS

Polymer thick films (PTF), also referred to as inks or pastes, are treated here as polymer coatings because they are basically filled polymers that can be screen-printed to produce films that are between 1 and 1.5-mils thick after curing. Polymer thick films have specific electrical functions depending on the nature of the filler, and are useful in fabricating printed circuits, and in protecting electronics from ESD, EMI, and corrosive ambients. Methode Electronics was among the first companies to develop and supply PTFs in the early 1960s and continues to be a major supplier, although other companies such as DuPont are also active in this field.

Like cermet thick films, PTFs are screen-printable pastes that can form conductors, resistors, capacitors, and dielectric layers. However, unlike cermet pastes, PTF pastes contain polymer resins that remain an integral part of the final thick film. The key advantage of PTFs over cermet thick films is that they are processed at relatively low temperatures (95–165°C), namely at temperatures required to cure the resin. Cermet thick films, on the other hand, require firing temperatures of 850–950°C to completely burn off the organic binders, melt the glass frit, and sinter the ceramic particles together. Because of their low processing temperatures, PTFs can be applied to plastic substrates such as polyesters, polyimide (Kapton), and epoxy-glass (such as FR4). They can also be applied to flexible substrates to form flex circuitry. A further benefit of PTFs is the low cost of both material and processing. Polymer thick films have received wide acceptance in commercial electronics, notably for flexible membrane switches, touch keypads, automotive dashboard circuits, telecommunications circuits, and sensors. Other applications include EMI shielding on PCBs, replacing one or more copper foil/laminate layers, crossovers and jumpers for low-voltage circuits, as a filler for throughholes in lieu of plated throughholes, heating elements, electrodes for tantalum capacitors, and carbon-loaded phenolics as variable resistors for potentiometers. With PCBs, the key advantage of PTFs is that thick-film resistors can be batch screen-printed, avoiding costs of attaching and soldering discrete resistors. To complement the PTF conductors and resistors, dielectric pastes are also available and useful in fabricating multilayer interconnect substrates.

On the negative end, PTF circuits are generally limited to commercial applications, to low-voltage circuits, and to relatively low temperature (less than 90°C) applications.

Polymer thick films pastes are formulated with three main ingredients: a polymeric material, a functional material (metal, metal oxides, glass, or carbon), and a solvent, although some are 100% solids types. The polymer matrix of PTFs can be cured at relatively low temperatures, provides integrity to the film, and provides adhesion to the substrate. A variety of polymer resin binders may be used. For flexible printed circuits and membrane switches, thermoplastic flexible polymers such as acrylics, polyesters, or vinyl copolymers are used. For rigid substrates in addition to the thermoplastic binders, thermosetting polymers including epoxy and phenolic may be used.

The solvent is used to dissolve the resin and control the viscosity and flow properties of the paste so that it can be easily screen printed. The solvent should have a moderately high boiling temperature to prevent evaporation during screen printing, yet be completely evaporated during drying and curing.

Generally, PTF pastes are screen printed through 200–280 mesh stainless steel screens having emulsion thicknesses of 0.5 to 1 mil. Thicknesses of the wet (uncured) pastes are approximately 1.5 mil while thicknesses of the cured pastes may range from 0.8 to 1 mil, depending largely on the size of the screen mesh. Line widths and spacings are approximately 7–10 mils.

4.19.1 Polymer Thick Film Conductors

The functional material in PTF conductor pastes is a metal powder that combines high electrical conductivity, good solderability, and low cost. The most widely used metal fillers for low-resistivity conductors are silver, silver alloys, and copper. Commercially available conductor pastes are primarily silver compositions though a few silver-palladium pastes are available. Silver-carbon and carbon fillers are used for medium to high resistivity conductors. The amount of filler may range from 60–80%, but 66–77% is typical. Cure temperatures range from 95°C for 5–20 minutes to 180°C for 30 minutes, depending on the formulation, and may be performed in either a convection oven or infrared furnace. Curing in air is generally satisfactory except for some high temperature curing compositions where circuit materials such as copper may degrade through oxidation. Curing at temperatures above 250°C for extended times may also result in decomposition of the polymer matrix and adversely change electrical and physical

properties of the final film. In such cases, curing is best performed in a nitrogen ambient. In general, resistivities decrease somewhat at higher curing or drying temperatures, for example, see Fig. 4.45 for DuPont’s 5007 paste.

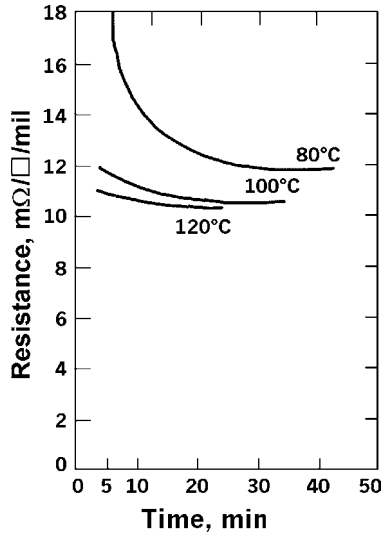


Figure 4.45. Sheet resistivity vs drying conditions for DuPont 5007 PTF conductive paste. (Courtesy of DuPont.)

Some silver-based PTF conductors are solderable using conventional tin-lead or tin-lead-silver solders, but the contact time with the molten solder is critical and must be minimized. Extended contact causes leaching of the silver and loss of adhesion. Accordingly, some PTF suppliers do not recommend soldering to their conductors. However, one silver-coated copper PTF is reported to be solderable.^[105] Some characteristics of PTF conductors are given in Table 4.14. The silver-based conductors were subjected to the environmental tests listed in Table 4.15 and were found to change less than 10% in electrical and physical properties.^[106]

Table 4.14. Typical Properties for Some DuPont PTF Conductors

PTF Number	Filler	% Solids	Sheet Resistivity M Ω /sq/mil	Viscosity, Pa·s	Operating Temp. °C max.	Cure Conditions
5028*	Silver	73–79	7–10	25–45	90	120°–140°C/5 min
5000*	Silver	50.5–52.5	8–14	8–16	70	120°C/8–10 min
5007*	Silver	70–74	12–15	20–40	70	120°C/8–10 min
5025*	Silver	60.3–61.7	8–15	20–30	90	120°C/5–6 min
5089*	Silver/Carbon	42–46	50–80	220–260	70	120°C/5–6 min
5524*	Silver/Carbon	66–72	25–30	200–270	90	120°C/5–6 min
CB230**	Silver-coated copper	NA	65–75	65–75	125	170°C/30 min
CB200*	Copper	NA	20–30	75–85	120	160°C/30 min
CB028*	Silver	69–71	7–10	15–30	85	160°C/60 min

*Solderability of these conductors is not recommended.

**Solderable.

Note: CB materials are used primarily on circuit boards such as FR4. *(Courtesy of DuPont.)*

Table 4.15.Environmental Tests for PTF Silver-based Conductors

Test	Test Conditions
Thermal Shock	+85°C to -40°C, 30 min each cycle, 5 cycles
Dry Heat	+85°C, 20 days
Humidity	+60°C, 95% RH, 1,000 hrs (MIL-STD-202E, Method 103, Cond. A)
Salt Spray	+35°C, 5% salt, 10 days (ASTM B-117)
Silver Migration	1 Vdc/mil gap, +40°C, 90% RH, 500 hrs, tested on 40- and 7-mil gaps
Sulfur Dioxide	+45°C, 90% RH, 500 hrs in a 9-liter chamber containing 500 mg of flowers of sulfur
(Courtesy of DuPont.)	

Conductive carbon-filled PTFs are also available and used as overprint layers on silver-conductive PTF and on copper conductors. As an overprint on silver-filled PTFs, carbon-filled PTFs offer environmental protection and protection from silver tarnishing while still maintaining a low contact resistance. Sheet resistances of various compositions range from 15 to 25 ohms/sq/mil.^[107] As a low-cost alternative to gold plating, carbon-filled PTFs provide protection from oxidation to copper pads and tabs and give them a hard wear-resistant surface.^[108]

4.19.2 Polymer Thick Film Resistors

Polymer thick film resistors are formulated similar to PTF conductors except that, instead of metals, resistive fillers are used as the functional component. Resistive fillers consist of carbon or graphite compositions. Resistor values may be varied by changing the particle size and concentration of the filler, the type of polymer binder used, and the cure schedule. Resistor pastes having sheet resistivities ranging from 10 ohms/sq/mil to over 1 MΩ/sq/mil are commercially available; however, the lower sheet resistance pastes have much better stabilities. Different sheet resistances can be produced by blending a resistor paste of relatively low resistivity with varying amounts of a dielectric paste. Figure 4.46 shows how sheet resistances from 1kΩ to 700 kΩ can be obtained by blending DuPont 7082, a carbon-filled PTF paste, having a sheet resistivity of 400 ohm/sq/mil, with DuPont 3571, a PTF dielectric paste.

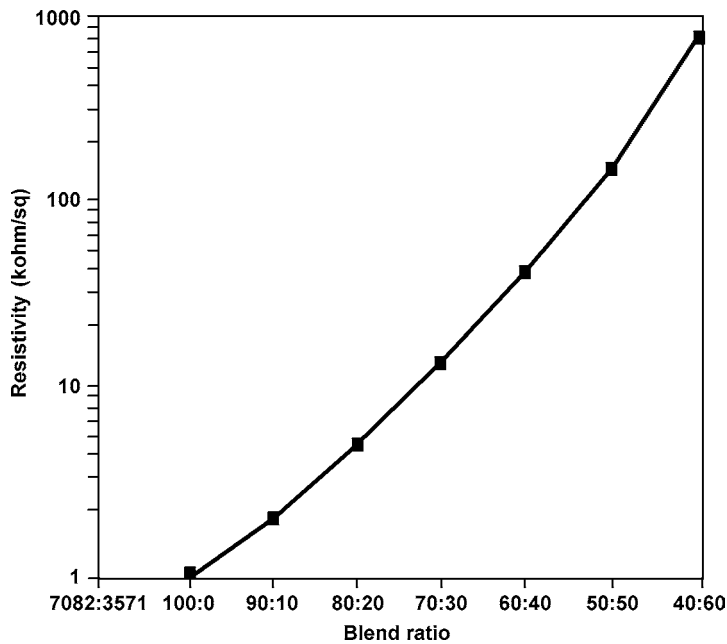


Figure 4.46. Resistivities of blend ratios of PTF 7082 with PTF 3571 (thickness extrapolated to 10 μm). (Courtesy of DuPont.)

Reported Temperature Coefficients of Resistance (TCRs) are ± 100 to ± 200 ppm/ $^{\circ}\text{C}$ for the 100-ohm to 100-k Ω resistor pastes, ± 500 ppm/ $^{\circ}\text{C}$ for the 1 M Ω pastes, and ± 800 ppm/ $^{\circ}\text{C}$ for the 10 M Ω pastes when measured at 125 $^{\circ}\text{C}$.^[109] Resistor tolerances as screen-printed range from $\pm 10\%$ to $\pm 20\%$ but, after laser trimming, can be reduced as low as $\pm 1\%$. Power dissipation is reported to be approximately 5 W/cm².

Because of their low-temperature-curing properties, PTF resistors may be used on a wide variety of substrates including low-cost plastic laminate PCBs such as FR-4 epoxy, polysulfone, and phenolic molded plastics as well as higher cost boards such as polyimide. In contrast, cermet resistors can only be processed on ceramic substrates because of the high temperatures required to fire them (850 $^{\circ}\text{C}$ or greater). Because of their low

processing temperatures and low cost, PTF resistors have found wide applications in automotive sensors. Among the uses are sensors for throttle positioning, windshield wiper controls, light dimmers, sensors for sensing and measuring fluid levels and pressures, and seat, radio, and cruise control circuits.

Polymer thick film resistors are not recommended when high precision, thermally stable resistors are required. Resistance values for PTF are much more sensitive to the nature of the substrate than are values for cermet resistors. Early applications of PTF resistors were plagued by large variations in resistance values that occurred during temperature cycling, elevated temperature burn-in, and aging and were discouraged in military and high-reliability products. It was soon discovered that the glass transition temperature (T_g) of the substrate had a pronounced effect on resistor stability. At and above the T_g , the molecular structure of the plastic laminate relaxes and experiences a sharp increase in expansion. A thermal mismatch that degrades the resistor both physically and electrically then occurs between the resistor and the substrate. It is, therefore, important to select a substrate that has an expansion coefficient matching that of the resistors over the temperature range that the circuit will be operated and tested. A T_g that is higher than any temperature that the circuit will be subjected to is desirable. Other substrate properties that have been found critical in achieving reproducible and stable resistance values include low porosity, high surface smoothness, and absence of moisture, contaminants, and outgassing products. Still another limitation of PTF resistors is the change in resistance values with temperature due to the thermally induced changes in the polymer matrix. Cermet resistors on ceramic substrates exhibit much higher thermal stabilities and higher voltage ratings than PTF resistors. It is reported that cermet resistors change less than 1% with 1,000 volts applied (200 V/mm) for over 100 hours. Polymer thick film resistors on ceramic substrates are more stable than on printed circuit boards such as FR-4 but, in both cases, can only survive 100 volts for 100 hours with 1–5% resistance change.^[110] Typical properties for some PTF resistors are given in Tables 4.16 and 4.17.

Table 4.16. Typical Properties for Some DuPont PTF Resistors

PTF Number	Filler	Percent Solids	Sheet Resistivity, ohm/sq/mil	Viscosity, Pa·s	Operating Temp., °C max.	Cure Conditions
7101	Carbon	35–37	20–30	10	70	120°–130°C/5 min
7102	Carbon	34.5–37.5	35 (max)	60–125	90	120°–130°C/5 min
7103	Carbon	35-38	35–40	85–125	90	120°–130°C/5 min
7861D	Carbon	N/A	<80	30–100	70	120°C/10 min
7082	Carbon	28–30	400	150–250	90	120°C/10 min

(Courtesy DuPont.)

Table 4.17. PTF Resistor Characteristics

Effects of Temperature Exposure			Environmental Effects		
Characteristics	Level of Exposure	Typical Result	Characteristics	Level of Exposure	Typical Result
High Temperature Storage	1,000 hrs at 85°C	<-5% Change	Moisture	1,000 hrs at 45°C	+5% Change (Change Stabilizes)
Temperature Cycling	-55° to 105°C, 5 cycles	0.5% Change	Substrate	Standard PC	Each substrate yields its own typical resistance values
Low Temperature Storage	5,000 hrs at -2°C	No Change	Solvent	Standard solvent used for cleaning PC boards	Slight, reversible changes in resistance
Exposure to Soldering	Commercial wave solder	-1% Change	Lubricant	Standard lubricants for variable resistance switches	No effect
Thermal Shock	MIL-STD-107	<1% Change			
TCR	MIL-STD-202, 304	Approx. 250 ppm			

(cont'd.)

Table 4.17. (cont'd.)

Electrical Properties		Wear Properties		
Characteristics	Typical Performance	Characteristics	Typical Performance	
Resistor Range	0 to 10 MΩ	Contacts	Four basic features: 1. Contact design 2. Number of contact points 3. Contact force 4. Material used for fabrication	
Resistor Tolerance	Screened, ±10 to 20% Trimmed, ±1%	Travel	Linear or rotary. Contacts can slide directly on resistive material or on conductive trace coming from it.	
Noise	Typically low; e.g., 10 k/sq = 6 dB	Life Cycling	Pressure	Cycles
Power Rating	Up to 5 watts/cm ²		5–10 grams	2 million
Voltage Coefficient	-.0015%/volt		40–50 grams	250,000 to 500,000
Linearity	2% as screened; 0.5% with special handling		100–150 grams	10,000 to 50,000
Short Term Overload	2.5 times rating, 5 seconds, change under 0.5%	Lubricant	A suitable lubricant will prolong life and enhance performance.	
Derating	Derates linearly 70° to 150°C			
(Courtesy of Methode Electronics, Inc.)				

4.19.3 Polymer Thick Film Dielectrics

Several PTF dielectrics are commercially available that may be used as insulating layers in fabricating multilayer interconnect substrates or as overcoatings for resistors and conductors. In addition to the polymer matrix, these PTFs contain glass, aluminum oxide, or silicon oxides as fillers. Vias of 15–20 mils in diameter may be formed by screen printing. The processing steps and conditions for dielectric PTFs are similar to those for PTF conductors and resistors, for example, screen printing through a 200–280 mesh stainless-steel screen, curing for 30 minutes at 150°–175°C or, if infrared heating is used, for 10 minutes. Some compositions are uv curable. Volume resistivities are greater than 1×10^{12} ohm-cm and dielectric constants range from 4 to 8 at 1 kHz, depending on the composition. Breakdown voltages greater than 1,000 V/mil have been reported. Typical properties for some DuPont PTF dielectrics are given in Table 4.18.

Table 4.18. Typical Properties for Some DuPont PTF Dielectrics

PTF	% Solids	Dielectric Constant	Break-down Voltage	Viscosity, Pa·s	Operating Temp., max.	Cure Condition
3571	30–33	4–5	<500 V/mil	1.9–3.0	90°C	120°–130°C/5 min
5018	N/A	<5 at 1 kHz	>1000 V/mil	35–55	approx. 70°C	uv curable
(Courtesy of DuPont.)						

REFERENCES

1. Coombs, C. F., *Printed Circuits Handbook*, 4th Ed., McGraw-Hill (1996)
2. Licari, J. J., and Etchason, P., High Reliability Polyurethane Insulative Coating for Circuit Board Protection, *Insulation* (Jun. 1962)
3. Bent, W. R., and Turbini, L., Evaluating the Effect of Conformal Coatings in Reducing the Rate of Conductive Anodic Filament Formation, *APEX*, San Diego (Jan. 2002)
4. Beccasio, A. J., Conformal Coatings for Printed Circuit Assemblies, ASTIA Document AD-273080 (Nov. 1961/Jan. 1962); *Insulation* (Dec. 1963)

5. Weigand, B. L., et al., Manufacturing Technology for Conformal Coatings, Technical Report, AFWAL TR-80-4139 (Sep. 1980)
6. McGuinness, E. W., Improved Reliability for Printed Circuits with Protective Coatings, Soc. Plastics Engrs., Tech. Paper 7 (Jan. 1961)
7. Licari, J. J., and Hughes, L. A., *Handbook of Polymer Coatings For Electronics*, Noyes Publ., Park Ridge, NJ (1990)
8. Licari, J. J., and Enlow, L., *Hybrid Microcircuit Technology Handbook*, 2nd Ed., Noyes Publ., Westwood, NJ (1998)
9. Wilson, J. R., Packaging COTS Chips for Environmentally Demanding Applications, *Military and Aerospace Electronics*, 12(4) (Apr. 2001)
10. Wafer Applied Seal for PEM Protection, 3rd Semiannual Workshop, Los Angeles (Feb. 2001)
11. Ahn, S., Kwon, Y., and Shin, K., Popcorn Phenomena in a Ball Grid Array Package, *Proc. 44th IEEE Electronic Components and Technol. Conf.*, Washington, DC (May 1994)
12. Werbaneth, P., Ross, S., and Rousey-Seidel, M., Polyimide for Flip Chip Packaging, *Advanced Packaging* (Feb. 2002)
13. Hall, S., and Schuckert, C. C., Single Mask Wafer Overcoat Process Using Photodefinable Polyimide, *Solid State Technol.* (Oct. 1999)
14. Hiro, M., and Schuckert, C. C., Thicker Film Photodefinable Polyimides, *Advanced Packaging* (Oct. 2000)
15. Walgren, Use of Epoxy Resins in High Reliability Transformers, *Electronic Equip. Engineering* (Jan. 1956)
16. Hanson and Tuzinski, Strain Gauge Evaluation of Flexible Epoxy Resins, *NEMA-AIEE, 2nd Natl. Conf. Application Electr. Insulation*, Washington, DC (1959)
17. MacLeod, R. W., Final Protection of Printed Wiring Modules by Organic Materials, *Ann. Symp. Inst. Metal Finishing, Printed Circuit Group*, Bristol, England (Sep. 1968)
18. Schwartz, S., (ed.), *Integrated Circuit Technology*, McGraw-Hill, NY (1967)
19. Silicoat Technical Data Sheet, Transene Co., www.transene.com
20. Work performed by D. Smith and J. J. Licari while at the Microelectronics Division of Hughes Aircraft (1992)
21. Licari, J. J., *Multichip Module Design, Fabrication, and Testing*, McGraw-Hill (1995)
22. Levinson, L. M., et al., High Density Interconnects Using Laser Lithography, *Proc. NEPCON* (1989)
23. Carlson, R. O., et al., A High-Density Copper/Polyimide Overlay Interconnection, *Proc. Int. Electronics Packaging Soc.*, Dallas, TX (1988)

24. Fillion, R. A., and Neugebauer, C. A., High Density Multichip Packaging, *Solid State Technol.*, Hybrid Supplement (Sep. 1989)
25. Ostmann, A., Neuman, A., Jung, E., Boettcher, L., and Reichl, H., Chip in Polymer: The Next Step in Miniaturization, *Advancing Microelectronics* (May/Jun. 2002)
26. Manufacturing Technology for VLSIC Packaging, Final Report, Naval Command, Control and Ocean Surveillance Center, Contract N66001-88-C-0181, Hughes Microelectronics (Jun. 1993)
27. Adema, G., Berry, M., and Turlik, I., Via Formation in Thin Film Multichip Modules, *Electronic Packaging and Production* (Nov. 1992)
28. Hiro, H., and Schuckert, C. C., Thicker Film Photodefinable Polyimides, *Advanced Packaging* (Oct. 2000)
29. Nader, A. E., et al., Photodefinable Polyimides Designed for Use as Multilayer Dielectrics for Multichip Modules, *Proc. Int. Conf. on Multichip Modules*, Denver, CO (1992)
30. Heistand, R. H., et al., Advances in MCM Fabrication With Benzocyclobutene (BCB) Dielectric, *Int. J. Microcircuits and Electronic Packaging*, 15(4) (1992)
31. Nargi-Toth, K., and Conrad, J., Photodefinable Dielectric Materials for High Density Printed Wiring Board Applications, *IPC Printed Circuits Expo* (Mar. 6, 1996)
32. Fisher, J., Increasing Wireability, *Printed Circuit Fabrication*, 18(7) (Jul. 1995)
33. Brannon, J. H., et al., Excimer Laser Etching of Polyimide, *J. Applied Physics*, 58(5) (Sep. 1985)
34. Tessier, T. G., et al., Via Processing Options for MCM-D Fabrication: Excimer Laser Ablation vs. Reactive Ion Etching, *Proc. EIA/IEEE, Electronic Components Technol., Conf.*, Atlanta (1991)
35. Smith, A. H., Phase Mask Machining for High Throughput Via Formation, *Proc., 2nd Int. Conf. Multichip Modules*, Denver, CO, (Apr. 1993); Personal communication with P. Trask of Litel Instruments (Jul. 5, 2002)
36. Licari, J. J., Varga, J. E., and Bailey, W. A., Polyimide Supported Microramps for High-Density Circuit Interconnections, *Solid State Technol.*, 19(7) (Jul. 1976)
37. Augustsson, T., et al., Low Cost Branching Devices Based on Multi-Mode Interference (MMI) Waveguide Structures in BCB, *6th Int. Conf. on MicroElectro, Optic, Mechanical Systems*, Potsdam, Germany (1998)
38. Booth, B. L., Polymers for Integrated Optical Waveguides, *Polymers for Electronic and Photonic Applications*, (C.P. Wong, ed.), Academic Press (1993)

39. Danielsson, H., Lead-free Soldering Causes Reliability Risks for Systems with Harsh Environments, *Advancing Microelectronics* (May/Jun. 2002)
40. Lau, J. H., (ed.), *Ball Grid Array Technology*, McGraw-Hill (1995)
41. Badihi, A., Ultra-Thin Wafer Level Chip Size Package, *IEEE Trans. on Advanced Packaging*, 23(2) (May 2000)
42. Elenius, P., Barrett, S., and Goodman, T., Ultra CSP - A Wafer Level Package, *IEEE Trans. on Advanced Packaging*, 23(2) (May 2000)
43. Kelkar, N., Mathew, R., Takiar, H., and Nguyen, L., MicroSMD - A Wafer Level Chip Scale Package, *IEEE Trans. on Advanced Packaging*, 23(2) (May 2000)
44. Norris, A., and Pernisz, U., Silicone Packaging Materials with Low Alpha Particle Emissions Prevent Soft Errors in Memory Devices, *Chip Scale Review* (Jul.-Aug. 2000)
45. White, M., and Serpiello, J., et al., The Use of Silicone RTV Rubber for Alpha Particle Protection on Silicon Integrated Circuits, *Proc. 19th Reliability Physics Symp.* (Apr. 1981)
46. Darrin, A. G., Le, B., and Kadesch, J., COB Comes On Board, *Advanced Packaging* (Jul./Aug. 1997)
47. Licari, J. J., and Jones, E. W., A Non-hermetic Packaging Technology for Low-Cost, Low-Weight Multichip Modules, AFRL-VS-TR-1999-1107, Final Report (Aug. 1999)
48. Weigand, B. L., and Licari, J. J., Verification of Selected Solvent-Soluble Coatings Using Production Hybrid Microcircuits, AFWAL TR-80-4048 (1980)
49. Weigand, B. L., Licari, J. J., and Perkins, K. L., Manufacturing Technology for Conformal Coatings, AFWAL TR-80-4139 (1980)
50. Licari, J. J., Perkins, K. L., and Barnett, B. F., Solder Mask/Conformal Coating Systems for Improved Maintainability of PWBS, IPC-TP-304, *Institute of Printed Circuits*, San Francisco (1979)
51. David, R. F., and Bakhit, G., Block Co-Polymer Coating of Hybrid Microcircuits, *Proc. Electronic Components Conf.*, Orlando, FL (1983)
52. King, J., Qualification of Dow Corning Q3-6527 as a Particle Getter, Singer Internal Report YS57A834 (1985)
53. King, J., Use of Silicone Gel Particle Getters for Microcircuits Packaging, *Proc. ISHM* (1985)
54. Beach, W. F., and Austin, T. M., Update: Parylene as a Dielectric for the Next Generation of High-Density Circuits, *SAMPE J.*, Vol. 2, p. 25 (Jun. 1988)

55. Suryanarayana, D., and Farquhar, D., Underfill Encapsulation For Flip-Chip Applications, *Chip on Board Technologies for Multichip Modules*, (J. H. Lau, ed.), Ch. 12, VanNostrand Reinhold (1994)
56. Tong, H. M., et al., Effects of Parylene Coating on the Thermal Fatigue Life of Solder Joints in Ceramic Packages, *IEEE Trans. on Components, Hybrids, and Mfg. Technol.*, 16(5) (Aug. 1993)
57. *Modern Plastics Encyclopedia*, McGraw-Hill, New York (1991)
58. Croop, E. J., *Materials and Processes Handbook*, (C. Harper and R. M. Sampson, eds.), 2nd Ed., Ch. 6, McGraw-Hill (1993)
59. Cohen, S. M., Kass, R. E., and Lavin, E., Chemical Interactions in the Poly(vinylformal)-phenolic Resin System, *Ind. Eng. Chem.* 50:229 (1958)
60. Lavin, E., Markhart, A. H., and Ross, R. W., Recent Developments in Magnet Wire Based on Formvar, *Insulation* (Apr. 1962)
61. Sollner, G. N., et al., Review of Solderable Magnet Wire Insulation, *Proc. of the 17th EEIC* (1983)
62. Product Data Sheet No. MW-00010, PD Wire & Cable.
63. Messenger, G. C., and Ash, M., *The Effects of Radiation on Electronic Systems*, VanNostrand Reinhold (1986)
64. Goetzel, C. G., Rittenhouse, J. B., and Singletary, J. B., *Space Materials Handbook*, Addison-Wesley (1965)
65. McIlwain, C. E., The Radiation Belts, Natural and Artificial, *Science* 142:355 (1963)
66. Van Allen, J. A., et al., Observations of High-Intensity Radiation by Satellites, *Alpha and Gamma*, JPL, 28:588–592 (1958)
67. Van Allen, J. A., and Frank, L. A., Radiation Around the Earth to a Radial Distance of 107,400 km, *Nature*, 183:430 (1959)
68. Pascale, J. V., Herrmann, D. B., and Miner, R. J., High-Energy Radiation Resistance of Plastics, *Modern Plastics* (Oct. 1963)
69. Bouquet, F. L., and Winslow, J. W., *IEEE Trans. Nuclear Sci.*, 31:1387 (1984)
70. Levine, J. H., Radiation Effects: Considerations, *Advances in Electronic Circuit Packaging*, (G. A. Walker, ed.), Vol. 2, Plenum Press (1962)
71. Bolt, R. O., and Carroll, J. G., (eds.), *Radiation Effects on Organic Materials*, Academic Press (1963)
72. Terai, I., Damage to Various Films by Gamma Irradiation, *Paint, Oil, Chem. Rev.*, 121(2) (Jan. 6, 1958)
73. Aitken, I. D., and Ralph, K., Effects of Radiation on Cast Epoxy Resin Systems, British Report AERE R-3085 (Feb. 1960)

74. Mixer, R. Y., and Parkinson, D. B., *Nuclear Radiation Effects on Structural Plastics and Adhesives*, Stanford Research Institute, Report WADC-TR-56534, Part iii (Aug. 1957)
75. LeClair, H. G., and Cobbs, W. H., Jr., Effect of Radiation on Plastic Packaging Films, *Ind. and Engineering Chem.*, 50(3):323 (Mar. 1958)
76. Jensen, R. J., Douglas, R. B., Smeby, J. M., and Moravec, T. J., *Proc. VHSIC Packaging Conf.*, Houston, TX, p. 193 (1987)
77. Messner, G., Turlik, I., Balde, J., and Garrou, P., Thin Film Multichip Modules, *ISHM Monograph*, p. 145 (1992)
78. Kumar, A., Gauging the Effects of Nuclear Radiation on Microstrip Antennas in Space, *Microwaves and RF* (Aug. 2000)
79. Hearst, P. J., Volatile Degradation Products of Organic Coatings Irradiated in Air, *J. Paint Technol.*, p. 39 (Mar. 1967)
80. Standard Methods for Total Mass Loss and Collected Volatile Condensable Materials from Outgassing in a Vacuum Environment, ASTM E-595.
81. Thorne, J. A., Whipple, C. L., and Boehm, A. B., Space Environmental Effects on Silicone Insulating Materials, *6th Electrical Insulation Conf.*, IEEE Publication 32C3-60 (Sep. 1965)
82. Griffin, D., NASA Spacecraft Fire Safety Workshop (Jun. 2001)
83. Portions of this section were written and contributed by Mr. Brian McCool, summer student at JPL from the U. of Texas and Dr. Karen Buxbaum, Supervisor, Biotechnology and Planetary Protection at JPL.
84. Lee, S. M., Licari, J. J., and Fewell, R. O., Sterilization Effects on Microelectronics, *NEPCON*, Long Beach, CA (Jan. 31, 1967)
85. Lee, S. M., and Licari, J. J., Effects of Decontamination and Sterilization on Spacecraft Polymeric Materials, JPL Contract 951566, NASA Report NAS7-100 (Jan. 1968)
86. Kalfayan, S. H., Campbell, B. A., and Silver, R. H., Effects of Ethylene Oxide-Freon-12 Decontamination and Dry-heat Sterilization Procedures on Polymeric Products, JPL Technical Report 32-1160 (Sep. 15, 1967)
87. Evaluating the Biological Potential in Samples Returned from Planetary Satellites and Small Solar System Bodies, Planetary Protection Policy, NASA and COSPAR, <http://www.nas.edu/ssb/sssbapd.htm>
88. Rohatgi, N., Koukol, R., and Barengoltz, J., *Planetary Protection Design Guide Book: Sample Return and In-situ Life Detection Missions*, JPL D-18635, Revision 3, Chs. 7 and 13 (Oct. 31, 2001)
89. Werner, V., and Prester, F., *10th Meeting Electrical Insulation Systems*, Congress Centre, Hamburg, Germany (1999)
90. Ward, D. K., Automotive Perspective, Paint, Spray, Dip, Pot or Seal the PCB, *Advanced Packaging* (Aug. 1999)

91. Quesnel, N. J., New EMI Shielding Approaches Optimize Wireless Designs, Div. of Parker Hannifin Corp., <http://www.chomerics.com> (2002)
92. Lizotte, T., Cleaning Laser Debris from TAB Circuits, *Advanced Packaging* (Jan. 2002)
93. Minsk, L. M., Light Sensitive Unsaturated Esters of Polyvinyl Alcohol, U. S. Patent 2725372 (Nov. 1955)
94. Minsk, L. M., Photosensitization of Polymeric Cinnamic Acid Esters, U. S. Patent 2670285 (Feb. 1954)
95. Unruh, C., et al., Vinyl Cinnamal Acetophenone Polymers, U. S. Patent 2716102 (Oct. 1955)
96. Williams, J., Photoprocess Using Light Sensitive Polymeric Quaternary Salts, U. S. Patent 2908667 (Oct. 1959)
97. Shaw, J. M., et al., Negative Photoresists for Optical Lithography, *IBM J. Research and Development*, Vol. 41 (1997)
98. JSR Microelectronics Data Sheets.
99. Moreau, W. M., Azide-Sensitized Resists, *Semiconductor Lithography*, Plenum Press, NY (1991)
100. Thomson, L. F., Wilson, C. G., and Bowden, M. J., (eds.), *Introduction to Microlithography*, Amer. Chem. Soc. (1983)
101. Elliott, D. J., *Integrated Circuit Fabrication Technology*, 2nd Ed., McGraw-Hill, New York (1989)
102. Reichmanis, E., The Chemistry of Polymers for Microlithographic Applications, *Polymers for Electronic and Photonic Applications*, (C. P. Wong, ed.), Academic Press, San Diego (1993)
103. Lai, J. H., *Polymers for Electronic Applications*, CRC Press, Boca Raton, FL (1989)
104. Schmitt, T., and Goldman, P., New Design Applications Made Possible by Utilizing a Positive-Acting Electrophoretic Photoresist, *IMAPS SoCal '02 Symp.*, Pasadena, CA (May 2002)
105. CB230 Copper Conductor, DuPont Data Sheet (Jan. 2001)
106. 5007 Silver Conductor, Polymer Thick Film Composition, DuPont Technical Data Sheet H-54869 (Apr. 1994)
107. Flexible Goldstone Conductive Carbon Overprint, Methode Electronics Product Data Sheet, #6175 Series (1998)
108. Goldstone® # 3100 Carbon Based Polymer Overprint, Methode Electronics Product Data Sheet (1997)
109. Martin, F. W., and Shahbazi, S., Polymer Thick Film For Reliability Applications, *Hybrid Circuits J.*, ISHM-UK, No. 3 (Autumn 1983)
110. Data Sheet for High Voltage Divider Networks, Methode Electronics (1998)

5

Reliability Assurance and Testing

The main reason for coating electronic devices and assemblies is to safeguard the reliability of the system; if not properly chosen, applied, and tested, a coating can also adversely affect reliability. The key elements to assure reliability include:

- Initial selection and qualification of the coating for the intended application.
- Adequate receiving inspection to assure the quality and reproducibility of the coating.
- Clearly defined application dimensions such as thickness, coverage, and meniscus.
- In-process testing to assure proper application and curing.
- Final inspection and testing.
- A Physics of Failure (PoF) analysis and corrective active program.

Reliability is assured by considering it in the initial design, for example, by assuring the compatibility of all the materials used with the electrical functioning of the part and by knowledge of and avoiding potential failure modes and mechanisms that can occur. Also, when failures occur,

an effective reliability and corrective action program should be in place. This program consists of a plan for determining the failure modes and mechanisms and taking corrective actions.

5.1 INITIAL QUALIFICATION

For high-reliability military applications, the qualification tests of MIL-I-46058 have been the mainstay for decades. Although this specification has recently been inactivated for new designs, the test procedures and the specified limits are still valid and useful. Accelerated temperature/humidity tests are used to measure electrical properties on test patterns representative of the circuit. A Qualified Product List (QPL) is available for five major polymer coating types. Although military environments are quite strict, the requirements for other products, even some commercial products, may be even more severe. Hence, MIL-I-46058 has been used as a basic specification, with superimposed tests for the application-specific requirements. For example, the qualification for space applications must include the added requirements of high vacuum, outgassing, atomic oxygen, and radiation. The automotive industry also has its own qualification criteria because of harsh under-the-hood, near-engine environments. Qualification and performance of conformal coatings for printed circuit assemblies have also been addressed by the IPC in IPC-CC-830A^[1] and IPC-HDBK-830.^[2] Qualification tests for deposited interlayer dielectrics for multichip modules are defined in IPC-DD-135^[3] and qualification of solder maskants in IPC-SM-840C.^[4]

5.2 RECEIVING INSPECTION

Once qualified and approved for use, each batch of coating material should be procured to meet a specification that assures its reproducibility and quality. Viscosity and percent solids (for a solvent-based system) are two relatively easy, low-cost tests. In the past, some suppliers have been known to make what they considered small changes in the formulation without notifying the user. For example, substitutions have been made for the type of solvent, diluent, or hardener; any one of which could affect adhesion,

curing conditions, and the ultimate physical and electrical properties. To assure that no changes have occurred in the chemical composition of the coating, an infrared spectrum of a small sample can be taken and compared with the infrared spectrum that was originally run at the time the material was qualified. Any shifts in absorption bands or appearance or disappearance of absorption bands in the IR spectra indicate chemical changes due to alteration of the original formulation.

5.3 IN-PROCESS INSPECTION AND TESTING

The reliability of coated assemblies also depends on monitoring processing conditions such as cleaning and drying, curing temperature and time, clean room conditions (temperature, humidity, and particulates), thickness, and coverage. Test patterns can be processed prior to or at the same time as the production lots and withdrawn at critical process steps to measure, for example, adhesion, thickness, and to inspect for discoloration, blistering, dewetting, or other flaws. Insulation resistance patterns may also be used for quality control of cleaning, drying, and coating processes by measuring the surface insulation resistance (SIR) of closely-spaced conductor traces. The SIR patterns range from simple trumpet Y patterns to the more detailed IPC-B-25 patterns^[5] used for printed circuits assemblies and to the very fine-line interdigitated comb patterns on silicon chips used for thin-film microcircuits (*cf.* ATC and Moisture Sensor chips described in Sec. 5.8.3).

5.4 FINAL INSPECTION AND TEST

Final inspection of coated modules consists largely of visual inspection at 10–30 times magnification. Most coatings are formulated with a small amount (0.1 to 0.5%) of a fluorescent dye indicator. Inspection under uv light discloses areas that have been left uncoated, but generally cannot detect pinholes or small uncoated areas. Inspection criteria for conformal-coated printed wiring assemblies are found in MIL-C-28809^[6] and IPC-A-610.^[7]

Besides final visual inspection, nondestructive screen tests and, on a sampling basis, destructive physical analysis (DPA) tests can be performed on coated modules or on test coupons prior to shipment. Such tests may include accelerated thermal exposure, temperature cycling, thermal shock, mechanical shock, and temperature/humidity exposure followed by electrical measurements.

5.5 RELIABILITY PREDICTION

There is no simple method or equation to calculate the long-term reliability of a coating or of a coated electronic part, especially under combined thermal, mechanical, humidity, electrical stresses, and sometimes under other environments such as contamination and radiation. Nevertheless, for specific stress-related failure mechanisms such as those that are temperature-dependent, by plotting the time-to-failure or the time required for 50% degradation (median life) of a selected critical property at several elevated temperatures, it is possible to extrapolate data to obtain life expectancies at lower operating temperatures. The Arrhenius equation and variations of it provide models for such accelerated aging. By plotting the degradation of a selected parameter such as tensile strength, elongation, or flexibility as a function of several elevated temperatures and calculating the activation energy, it is possible to calculate rates of degradation reactions. In a real situation, however, temperature is not the only stress factor. Generally, electronic circuits, during storage and operation, must withstand simultaneous variations in temperature and humidity under conditions of powered or non-dissipating bias. To accelerate these conditions, the 85°C/85% RH or the HAST stress conditions, with or without electrical bias, are widely used in predicting life expectancies of plastic-encapsulated electronic parts. From his work at BT Labs, Sinnadurai developed the S-H model for damp heat acceleration of aging and calculated the life expectancies of plastic-encapsulated devices (PEDs) at 20 years for various temperature-humidity environments from HAST testing at 108°C/90% RH.^[8] For example, PEDs would have to survive 2,000 hours of HAST at 108°C/90% RH to be equivalent to 20 years in a severe tropical environment of 35°C/90% RH.^[9]

An understanding of the potential failure modes and mechanisms that can occur during various exposures can be of practical use to avoid

potential failures. Hence, a basic understanding of material properties and the interactions of materials with each other and with electronics are important in predicting their behavior under operating conditions. Accelerated tests and stress testing to failure followed by DPA are useful in characterizing potential failure modes and mechanisms, in comparing the performance of several systems under the same conditions, and in selecting an optimum set of materials and conditions.

The (PoF) analysis approach^{[10]-[12]} for design and assessment of electronic hardware has been the focus of intensive studies at the CALCE Electronic Products and Systems Center, University of Maryland. The PoF approach is based on the understanding that failure of electronic hardware arises because of fundamental thermodynamic aging/degradation processes that are related to the construction (geometry and material) of the hardware and to the life cycle loading conditions (physical stresses) that the hardware experiences.^[13] Knowledge of these aging and failure processes allows for proactive consideration of reliability in the design process and establishes a scientific basis for evaluating new materials, structures, and electronics technologies. Physics of failure encourages innovative, cost-effective design through the use of realistic reliability assessment. Key steps of the PoF approach include:

- Estimating the stresses at potential failure sites, caused by life-cycle loading conditions. This includes chemical, electrical, physical, mechanical, structural, and thermal stresses. The stresses can be estimated either by computer-aided modeling and simulation of the product or by measuring the stress values on representative hardware, using appropriate sensors.
- Identifying potential failure mechanisms (e.g., chemical, electrical, physical, mechanical, structural, and thermal processes leading to failure), failure sites (e.g., die, component package, component interconnects, board metallization, and external connections), and failure modes (e.g., electrical shorts, opens, or deviations that result from the activation of failure mechanisms) expected because of the identified stresses.
- Identifying the appropriate failure models for each relevant failure mechanism and site, including inputs associated with material characteristics, damage properties,

relevant geometry at failure sites, manufacturing defects, and environmental and operating loads.

- Determining the variability for each design parameter when possible.
- Estimating the effective reliability metrics (such as time-to-failure and failure-free operating periods).
- Accepting the design if the estimated time-to-failure meets or exceeds the requirement.

The PoF approach has been demonstrated to identify design deficiencies, to improve designs, to establish effective accelerated stress tests and screens, and to assess the remaining life of the hardware.^{[14][15]}

5.6 FAILURE MODES AND MECHANISMS

Most failure modes associated with electronic devices and equipment have been well characterized and documented.^[16] This section covers those failures and failure mechanisms that are most directly associated with the coating and the coated electronic assembly.

5.6.1 Visual Defects

Defects that are visible in coatings immediately after application, after drying and curing, or that occur after exposure to accelerated environments are indications that the coating will not perform its intended function. A discussion of these defects follows.

Blisters and Bubbles. Blisters or bubbles may form in a coating or solder maskant immediately after curing or on subsequent moisture exposure. Blistering, also referred to as vesication, is most likely the result of moisture entrapment, or worse still, of moisture combined with ionic or non-ionic residues. Epoxy and polyimide circuit board laminates especially can absorb and retain large amounts of moisture. Furthermore, epoxy, polyimide, and other polar substrates have an affinity for salt-like contaminants which are hygroscopic, absorbing even more moisture. Fingerprints, for example, contain salt residues and, if not removed prior to coating, cause blistering especially on humidity exposure. Thus, moisture and solvents must be thoroughly removed by drying or vacuum baking a part before a coating

is applied. Cleaning printed wiring boards or plastic-encapsulated modules with water, although desirable from an environmental and economic standpoint, runs the risk of water absorption and difficulty in its removal. To avoid blistering, solvent-based coatings should be applied in thin layers and should be thoroughly dried or vacuum baked to assure the removal of solvents.

Dewetting. The coating may not wet and adhere well to all surfaces to be coated due to the inherent nature of the surface or to surface-tension-altering residues such as greases, oils, and other contaminants that have not been completely removed. Surfaces such as fluorocarbons (Teflon) and silicones have low surface tensions, and thus do not wet or adhere well to other coatings.

Flaking and Cracking. Flaking and cracking are the result of stresses, embrittlement due to overcuring or runaway temperatures during cure, or large differences between the expansion coefficients of the coating and the substrates. Cracking of a cured coating generally occurs because of shrinkage during polymerization or rapid solvent evaporation from a solvent-based coating. Figure 5.1 shows the extensive cracking that occurred after solvent evaporation from a silicone coating. The cracking and stresses were so extensive that they severed several interconnect wires.



Figure 5.1. Integrated circuit showing wire breakage due to shrinkage stresses after coating with a silicone varnish.

Orange Peeling or Mealing. Orange peel, also known as mealing, is a form of delamination or blistering that covers a large area and follows a pattern tracing the irregularities of the surface or beginning at the edge of the substrate. Mealing can be caused by applying too thick a coating, by trapped solvent or contaminants, or incorrect drying or curing conditions.

Discoloration. Discolorations may or may not be serious. Most slight discolorations do not affect the electrical or mechanical properties of a coating. For example, in reworking by soldering through polyurethane or acrylic coatings, some localized discoloration occurs, but is not considered serious. However, charring of a coating indicates extensive decomposition usually due to high-temperature exposure that causes carbonization of the coating. The charred or carbonized areas can be a reliability risk, since being electrically semiconductive can result in leakage currents. In these cases, either lower temperatures must be used during subsequent processing or a higher-temperature-stable coating should be used.

Thickness and Edge Coverage. Uniform thickness and complete edge coverage are essential for near-term and long-term reliability of the coating. If too thick a coating is applied in a single step, several potential reliability problems can arise, for example, stresses and cracking can develop on curing. Thick layers of solvent-based coatings are also likely to entrap solvent during curing or drying, causing subsequent blistering. Thick moisture-cured polyurethanes are also known to blister. Thick sections of air-curable polyurethanes generate a surface appearance called “alligator skin” that slows down or prevents the deeper portions from curing. If thick layers of a solvent-based coating are required, it is best to apply several thin layers with curing or drying between depositions to facilitate solvent removal. If a thick coating must be deposited in one step, it is best to use a 100%-solids coating. To achieve a 100% solids coating and still maintain a moderate viscosity, solvents may be replaced by reactive diluents, especially in the case of epoxies.

If too thin a coating is applied, sharp edges may not be completely covered, providing sites for stress corrosion. One must be particularly careful in using solvent-based coatings since a thinning occurs at sharp edges and at 90° corners. If edges can not be avoided in the initial design, they are best protected by applying a thick coating or applying a thick coat in several thin layers. Coatings are available that are formulated with thixotropic additives, such as silica powder, to control their flow properties. Only parylene coatings, because they are applied by vapor deposition, are able to completely coat all surfaces with extremely thin coatings.

5.6.2 Moisture and Contaminant Effects

With all plastics, ionic contaminants together with the moisture contained in coating materials or penetrating through the coatings, constitute the greatest reliability risk for both semiconductor devices and assembled circuits. Unprotected electronic assemblies exposed to accelerated humidity and temperature generally fail because of moisture penetration that, together with ionic residues, cause degradation of electrical insulation properties, electrical shorts or opens, and chemical corrosion. Failures may occur by electrochemical corrosion, metal migration, or both.^[17] In all cases, the rates of reaction are accelerated by the presence of an electrolyte which may consist of a plastic or ceramic surface having absorbed or adsorbed water. Highly polar polymers that contain water and contaminants are excellent electrolytes.

The many reactants that are used in the synthesis of a resin, catalyst, or hardener may produce ions which, unless special steps are taken to remove them during or after their synthesis, remain and are carried over into the final cured coating. As an example, over twelve steps are required in the synthesis of most diglycidylether-Bisphenol A (DGEBA) epoxies and both sodium and chloride ions are generated from the sodium chloride by-product. Chloride ion concentrations from commercial-grade epoxies can be as high as 600 ppm. Ionic impurities may also be generated from additives used in formulations such as fillers, fire retardants, and flow-control agents. Glass fillers, in particular, can be a major source of sodium ions. A third source of ion contaminants arises from metal or glass kettles, mixers, and other equipment used in processing the resins. It has been shown that epoxy coatings mixed in metal containers acquire trace amounts of the metal.

In addition to inherent ionic impurities, reactive outgassing products can evolve from plastics under ambient conditions, but more so upon thermal aging or irradiation. In early work, the outgassing of ammonia from certain amine-cured phenolic compounds and the ammonia's conversion to ammonium ions in the presence of moisture was reported to cause inversion layers and an increase in leakage current in microdiodes.^[18] Katsev, et al.,^[19] also reported on the deleterious effects of ammonia and other amine compounds on transistors. The detrimental effects of other outgassing products such as benzene and carbon dioxide have also been reported.^[20] The collector-to-base current (I_{CBO}) for bare chip transistors was measured while the transistors were reverse biased and exposed to benzene vapor, moisture vapor, and carbon dioxide. Not surprisingly, the largest increase

in I_{CBO} occurred with devices exposed to moisture, followed by benzene, and carbon dioxide (Table 5.1). In all cases, vacuum baking restored the original values.

Table 5.1. Effect of Gas Ambients on Reverse Leakage Current of Dual PNP Signal Transistors^[20]

Condition	Collector-to-base Current (I_{CBO}) at 20 volts Reverse Bias, nanoamp	
	Transistor A	Transistor B
Initial value	3.0	2.5
After exposure to benzene vapor and reverse bias on transistor A only	2,400	
After exposure to water vapor and reverse bias on transistor A only	10,000	
Vacuum bake at 300°C and no bias	2.5	2.5
Bias on transistor B in vacuum		3.0
After exposure to carbon dioxide and bias on transistor B only		650
Vacuum bake at 300°C		3.0

Improved purification methods and process controls now produce polymer coatings and encapsulants that can be used directly and reliably on active devices. Purified, semiconductor-grade polymers are now available having sodium and potassium ion contents of less than 5 ppm and chloride ions of less than 10 ppm. Coatings can also be filtered through 0.1 to 0.2 μm filters to remove particulates. However, to maintain these low levels, the user should store and apply the materials in a clean-room environment.

The application of a high-purity conformal coating over a well-cleaned and dried electronic assembly greatly improves the reliability and performance of the assembly and extends its useful life. This is particularly true for printed wiring assemblies where severe environments, as encountered in military, automotive, and space applications where the life expectancy must be ten years or greater, and where the cost, with assembled components, may run into the tens of thousands of dollars. However, conformal coatings are seldom used for low-cost consumer applications such as television, computers, cell phones, and other electronics used in benign environments.

Corrosion of Solder. An example of the effects of moisture on an uncoated printed circuit board is shown in Fig. 5.2. Excessive corrosion occurred on solder-attached leads and solder-plated conductors after only two days exposure to 95% RH. A similar board coated with 1.5-mil-thick polyurethane survived six months of 95% RH without corrosion or electrical malfunction^[21] (Fig. 5.3). Figure 5.4 compares the corrosion effects on an uncoated circuit board after 50 hours of salt spray exposure with the protection afforded by a 1-mil-thick polyurethane coating under the same conditions. Thus, for the required protection against humidity and salt spray, a coating, encapsulant, or a hermetic enclosure is required.

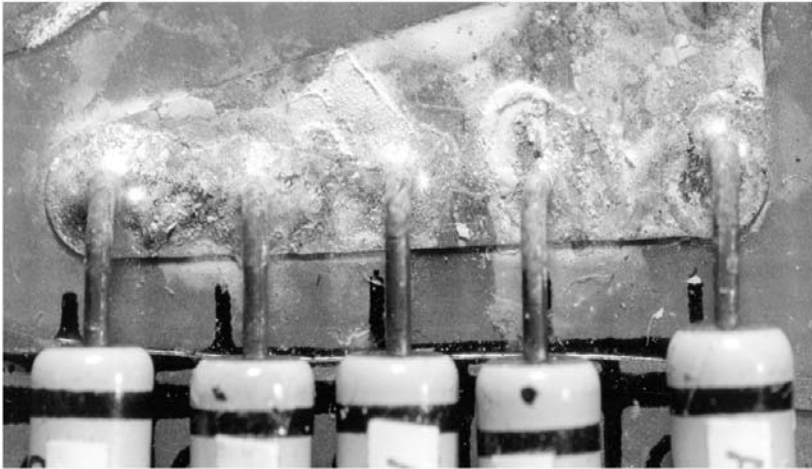


Figure 5.2. Uncoated section of circuit board after 2-day humidity exposure.

The amount of moisture that a plastic printed circuit board or a coating can absorb or permeate is a function of the basic polymer; fillers; reinforcements, such as glass and its adhesion to the basic polymer; other additives and ingredients of the formulation; and the degree of cure or polymerization. In addition, hygroscopic residues such as airborne salts and minerals, acid pollutants, and flux residues draw more moisture into or onto the board. Coatings, to some extent, can extend the life of an electronic assembly, but should not be considered a cure when they are applied to a surface that already contains moisture and ionic contaminants.

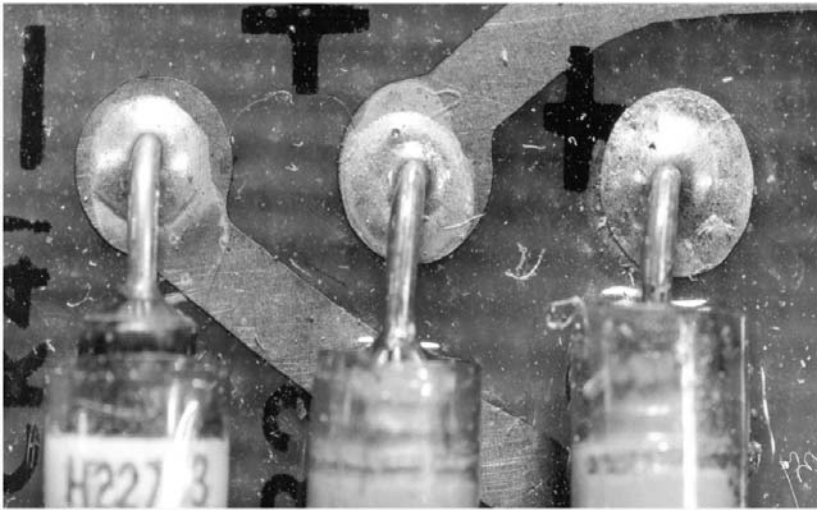


Figure 5.3. Circuit board coated with 1.5 mils polyurethane survived six months of humidity cycling.

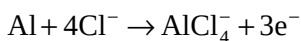
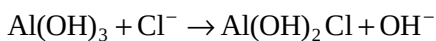
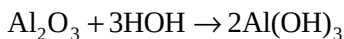
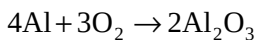


Figure 5.4. Effects of 50 hr salt spray on uncoated circuit board (left) and coated board (right).

Corrosion of Metal Thin Films. Failures due to electrolytic corrosion include the dissolution of thin-film metallizations such as nichrome resistors and aluminum conductors, increases in reverse leakage currents, electrical shorts or opens, and general degradation of electrical parameters. An electrochemical cell can form between two dissimilar metals regardless of whether a bias is applied. Sodium, potassium, and chloride ions that may not present a problem under dry, low-temperature conditions, become mobile with moisture and temperature and penetrate to the active semiconductor junctions. The contaminants may be inherent in the coating itself or may be trace residues that have not been sufficiently removed during cleaning of the assembly prior to coating. Contaminants residing in the coating result in degradation of electrical properties especially in the presence of moisture and at elevated temperatures. In addition, residues remaining on the surface result in a loss of adhesion to the coating, again exacerbated by moisture.

The catastrophic effect of fingerprints left on thin-film metallized substrates prior to coating is shown in Fig. 5.5. Thin-film nichrome resistors contaminated with salt residues from fingerprints applied prior to polyurethane coating corroded and showed drastic changes in resistance values after three-days storage over water in a desiccator with 10 volts bias applied. Cleaned and coated test parts under identical test conditions showed no physical or electrical degradation. Some nichrome resistors actually disappeared when tested in humidity with an applied bias. Apparently, an electrolytic cell was created in which the resistors ionized and went into solution.

Like nichrome, thin-film aluminum metallization is particularly susceptible to attack by trace amounts of chloride ions that act in a catalytic manner. The monolayer of oxide that naturally exists on an aluminum surface hydrolyses with moisture, then reacts with the chloride ions, and in the reaction sequence generates more chloride ions as follows:



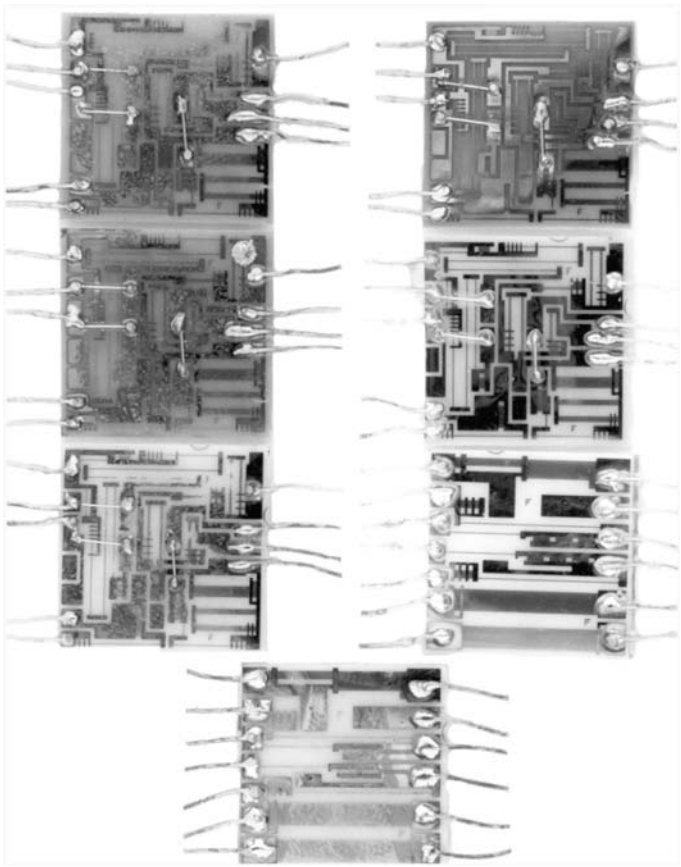


Figure 5.5. Effect of fingerprints on coated and uncoated nichrome resistors; Right: Cleaned and coated with polyurethane, Left: Coated with polyurethane, but not cleaned, Bottom: Not cleaned, not coated.

Thus, the initial chloride is not consumed, but is regenerated to continue the reaction, ultimately consuming all the aluminum. Figure 5.6 shows the extent of corrosion and etching of the thin-film aluminum metallization of an integrated circuit due to the penetration of moisture and the presence of ionic residues in an early-vintage, plastic-encapsulated device. In wire-wound resistors or thin-film resistors, voltage gradients, together with ionic conductivity, cause dissolution of metal from the anodic areas, decreasing the cross-sectional areas of the resistive metal and increasing resistor values. Under more severe conditions, etching of the metal continues until the metal is completely removed and an electrical open occurs.

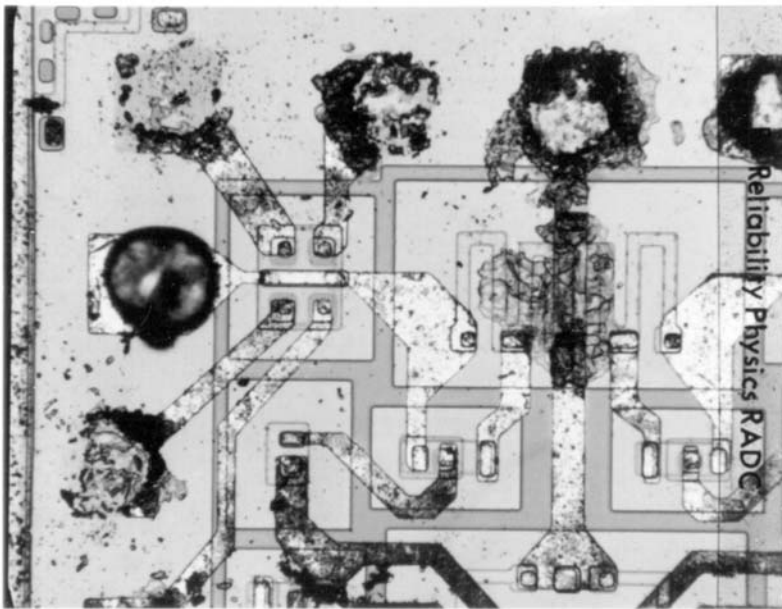


Figure 5.6. Corrosion of aluminum near ball bonds of an IC due to moisture penetration and ionic contaminants.

Corrosion Testing. The corrosion properties of polymer coatings may be evident during the testing of devices under normal operating conditions or may be determined under accelerated conditions by one of several rapid screening tests. According to one of these tests, strips of

transparent Mylar film that have previously been metallized are used as test vehicles. The Mylar strips may have vacuum-deposited, thin-film aluminum, copper, nichrome, or other metal to simulate materials used in actual devices. The metallized samples are coated, then placed in test tubes containing small amounts of water, sealed, and heat-aged in an oven. Any corrosion effects due to the coating generally appear after several days of exposure, although the test may be continued until corrosion occurs, if at all.

Another test^[22] consists of embedding or coating a fine copper wire and measuring the increase in resistance of the wire after various periods of exposure to temperature and humidity. The extent of corrosion is a function of the increase in resistance of the wire above what occurs on an uncoated sample. The extent of protection from corrosion provided by the coating is also measured by the decrease in resistance relative to the bare wire. Although this method was developed to evaluate magnet wire and wire coatings, it is useful in evaluating coatings and plastics, in general. A comparison of the corrosive or protection effects of epoxies, epoxy-polysulfides, and polyesters is shown in Fig. 5.7.^[23]

Ion Permeation. The most deleterious ions to semiconductor reliability are sodium and chloride, but potassium and ammonium ions have also been reported to cause failures and should be controlled and minimized. These ions may be inherent in the coating as part of its synthesis, may be introduced through additives, or may permeate from external sources such as fingerprints, salt spray, or perspiration. Ionic residues are particularly deleterious to electrical functioning in the presence of moisture or elevated temperatures under which conditions their mobility increases. It is well known that ions migrating to the surface of semiconductor devices result in leakage currents.

A relatively simple test for determining the total ionic content of a coating involves digesting a weighed amount of the cured coating in a pulverized state in a known volume of deionized water at some elevated temperature then measuring the resistivity of the water extract. Specific ions may be analyzed from the water extracts directly or from the solid residues remaining after evaporating the water.

5.6.3 Metal Migration

Two mechanisms for metal migration or metal growth have caused electronic failures in which an entire system has failed. Metal migration may

result from an electrochemical cell that forms between two electrodes, from metal whisker growth, or from diffusion and chemical reactions of metal ions in a metal/polymer interface. Polymer coatings can suppress these phenomena, but the best approach is to avoid the causative conditions through proper materials selection and circuit design.

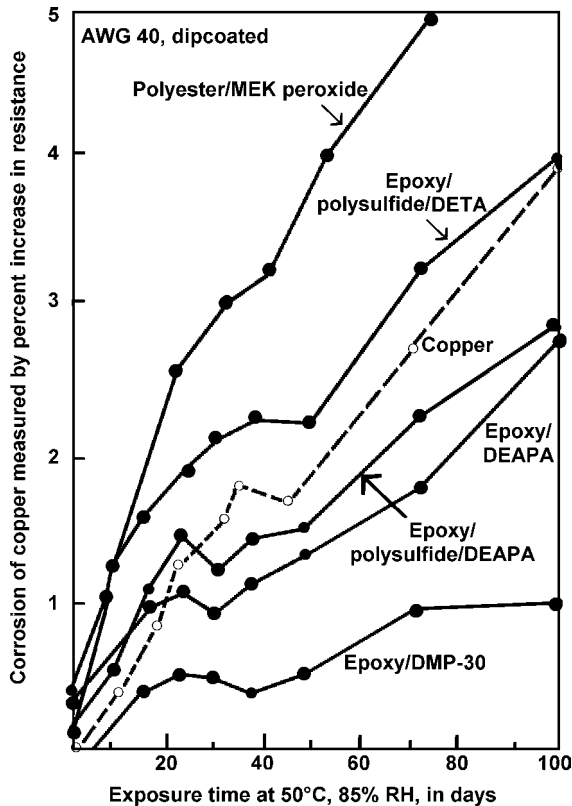


Figure 5.7. Corrosive effects of polymer coatings on copper wire.^[23]

Silver Migration. Metal migration, notably silver migration, can occur between closely spaced conductors and can result in a reduction of insulation resistance, an increase in leakage current, and eventual electrical shorting, arcing, or dielectric breakdown. Metal migration has been known and studied for over thirty years and has been the cause of many catastrophic microcircuit failures.^{[24][25]} Metal migration has been dominant with silver and silver-bearing alloys, but may occur within almost any metal. Even

gold, under conditions of bias, ionic contaminants, and moisture, has been reported to migrate.^[26] It is generally reported that three conditions must exist for metal migration to occur: a dc or ac potential, some ionic residues on the surface of or within a dielectric, and condensed moisture.

Basically, metal migration is an electrochemical phenomenon.^[27] Silver, the metal having the highest propensity for migration, is oxidized at the anode (positively biased conductor line) to form positively-charged silver ions. These ions are then attracted to the negatively-biased conductor (cathode). On their journey across or through the dielectric, the ions are accelerated by the presence of moisture and ionic contaminants. A chemical reaction usually occurs between the metal ions and the hydroxyl ions generated from the water; for example, silver forms silver hydroxide which appears as a milky-white smudge between the conductors. This reaction can either accelerate or suppress the migration depending on the solubility of the hydroxide that is formed. If the hydroxide is soluble in the medium, it will quickly dissociate freeing the metal ions so that they can continue their migration to the cathode, as in the case of silver. If, however, the hydroxide or oxide formed is insoluble, the migration of the metal ions will be arrested or slowed, as with copper. The insoluble hydroxide forms a passivating barrier that can essentially stop the migration. If the positively-charged ions are unobstructed and arrive at the cathode, they pick up electrons and are reduced back to metal. The metal builds on itself and grows as filaments backward toward the anode. Thus, in essence, a two-dimensional electrolytic cell has been formed. Because these metal filaments have the appearance of tree branches they are referred to as *dendrites* and the process is known as *dendritic growth*. A model for silver migration is shown in Fig. 5.8.

Although both organic and inorganic coatings will greatly suppress and even arrest metal migration by preventing moisture from condensing onto the surface, some proven design rules should be followed, among which are:

- Avoiding the use of pure silver and using noble metals such as gold, platinum, palladium, or alloys of silver with platinum or palladium.
- Designing the circuit to avoid biases between critical components.
- Using low-porosity, hydrophobic dielectrics and substrates. The substrates need to be tested for insulation resistance at elevated temperature or under moist conditions, at

which the ions are most likely to be mobilized. A high insulation resistance of $>1 \times 10^{11}$ ohms under these conditions assures low ionic mobility within the dielectric.^[28]

- Handling, storing, and sealing the circuits in a dry inert environment.
- Assuring that the circuits are ultraclean and free of ionic contaminants.
- Overcoating the circuits with a high-purity polymer or inorganic coating to prevent moisture from condensing onto the surface.

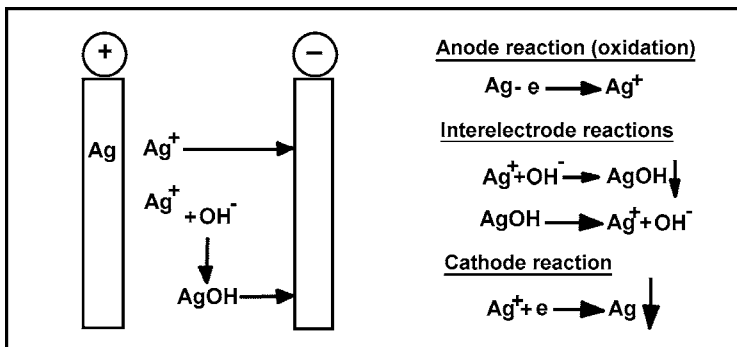


Figure 5.8. Model for silver migration mechanism.

Conductive Anodic Filaments. Under high humidity, a failure mode known as *conductive anodic filaments* (CAF) has been reported to occur in epoxy-glass printed wiring boards between oppositely biased copper conductors. It has also been shown that CAF is augmented by exposure to elevated humidity and temperature in the presence of hygroscopic flux residues. The CAF mechanism is somewhat similar to that for silver migration except that copper ions generated at the anode form oxides, hydroxides, chlorides, and other compounds that continue to grow from the anode towards the cathode. X-ray dispersion analysis of the filament materials indicated copper with chlorine and/or sulfur, the latter being residues from processing of the circuit boards.^[29] The presence of glycols or amines from the fluxes, combined with marginal adhesions between the

glass reinforcement and the epoxy resin of the printed wiring board, have been reported to accelerate CAF formation. Conformal coatings, by reducing the moisture penetration, can slow down the rate of CAF formation and extend the life of the circuit,^[30] but most of them do not prevent CAF.

Tin Whisker Growth. Differing from silver migration and CAF, tin whisker growth does not require moisture, ionic contaminants, or even an electric potential. Pure tin forms single crystals that grow as fine needles or nodules and eventually cause electrical shorts. The tin whisker phenomenon was first reported in 1947^[31] and has been studied extensively over the years.^{[32][33]} Even though it is well recognized as a risk, pure tin is still used and failures continue to occur. With recent emphasis on the elimination of lead from solders, the industry is reverting to the use of pure tin and non-lead solders, bringing the tin whisker problem to the forefront again.^[34] A recent study showed that conformal coated tin-plated surfaces did not prevent tin whiskers from forming, but there was some benefit in the extended time it took before the whiskers penetrated through the coating.^{[35]–[37]} An added benefit to conformal coating a circuit is that if tin whiskers from another portion of the package, for example from a tin-plated lid, break off, the coating shields the active circuits from the tin particles.

Interdiffusion. In some cases, metals diffuse through a polymer coating during its cure or subsequently during thermal exposure. The migration of metal affects the electrical properties of the dielectric and possibly its adhesion. A classical example, one that has been thoroughly studied, is the migration of copper into the interface of a copper-polyimide multilayer structure, as in a MCM-D module. A chemical mechanism is most likely in which the polyamic acid resin (polyimide precursor) dissolves or reacts with some interfacial copper forming a copper carboxylate salt and generating copper ions. The copper (Cu^+) ions migrate into the polymer and subsequently decompose to form cuprous oxide (Cu_2O) during the high temperature imidization reaction. Nodules of copper oxide at the copper-polyimide interface have been verified by numerous analytical methods including microdiffraction analysis, electron microscopy, and XPS.^{[38]–[41]} The copper migration problem was resolved by depositing a thin chromium or titanium diffusion barrier between the copper and polyimide.^[42] The barrier layer provides the further benefit of enhancing the adhesion between copper and the polyimide layers.^[43] Another solution to the copper/polyimide problem involved using a non-polyamic-acid precursor such as a preimidized oligomer that cures through acetylenic end-groups by addition polymerization. In this case, there is no possibility for the copper carboxylate reaction to occur. Other dielectrics such as BCB have also been found to be

compatible with copper. No copper migration in a BCB/Cu interface was detected by TEM after 1,000 hours of 85°C/85% RH exposure.^[44]

5.7 TEST PROCEDURES FOR CONTAMINANTS AND CLEANLINESS ASSURANCE

Electronic assemblies may, if not adequately cleaned, contain both ionic and non-ionic (organic) residues and no single test is available that can measure the removal of both. If both types of contaminants are known to be present, separate tests for ionic and non-ionic contaminants must be performed. Ions may also be inherent in the coating or dielectric materials that are used for protection and insulation or may subsequently penetrate the coating from ambient or processing conditions.

5.7.1 Tests for Ionic Contaminants Inherent in Polymers or on Surfaces

Ions may be inherent in the polymer resin, hardeners, and catalysts, or in additives such as fillers. Ions may also be absorbed and retained from chemicals used in printed circuit board processing such as plating, etching, photoresists, and soldering. Regardless of their source, the presence of ions, particularly chloride, sodium, potassium, and ammonium ions, affect the reliability of a coated assembly. Over the years, improvements have been made by plastics manufacturers in purifying their products, but the risk remains. Several tests have been developed to measure the ionic contents of polymer materials and the effect these ions have on semiconductor devices. Direct tests involve extracting a weighed pulverized sample of the plastic with a measured volume of deionized water of known resistivity. The sample is digested in boiling water for 24 hours, then filtered, and the water extracts analyzed by measuring the their resistivity. The amount by which the resistivity is decreased is a measure of the total ions extracted and is indicative of the purity of the material. A correlation was also found between the water-extract resistivities of a number of silicones and the failures that occurred when MOS devices were coated with these silicones and aged at 125°C for over 1,000 hours with applied power. Those with the highest

water-extract resistivities (highest purity) performed the best (see Table 5.2).^[23] The water extracts may subsequently be analyzed for specific ions and compounds by one of several techniques including atomic absorption spectroscopy and ion chromatography. Potentiometric or gravimetric titration with silver nitrate solution for chloride ions may also be used. The sample is powdered and extracted with deionized water, and the extract titrated with a standard solution of silver nitrate.^[45]

Table 5.2. Typical Failure Data for Silicone-coated MOS Devices (static tested at 125°C/150 milliwatts)

Sample	Water extract Resistivity, Ω -cm	Sample Size	Failures* after 1000 hrs	Failures* after 2000 hrs
Silicone A	80,000	7	3	
Silicone B	180,000	13	2	
Silicone C	190,000	7	3	
Silicone D	300,000	11	1	
Dow Corning DC-51	360,000	10	0	0
Dow Corning XR-62044	660,000	10	0	0
Deionized water (reference)	600,000 to 900,000			
*Failure indicators: threshold voltage, breakdown voltage, leakage current				

A recent report showed that by treating a plastic with water under pressure at temperatures as high as 160°C the amounts of ions extracted increased. Hagge^[46] reported 5 to 10 times higher chloride ions extracted at 160°C compared to 120°C for the same material. This sharp increase was attributed to reaching or exceeding the T_g of the polymer, at which temperature the polymer molecules loosen, allowing trapped ions to be freed (Fig. 5.9).

However, one must distinguish between the extractable mobile ion content of a cured plastic and ions that are formed by conditions that completely breakdown the polymer structure. Covalently-bonded chlorine atoms, for example in Parylene C, are not mobile ions and extracting with water at reasonable temperatures up to the boiling point of water will not

produce chloride ions. The same compound subjected to the bomb extraction process at 160°C may very well decompose and hydrolyze to produce ions.

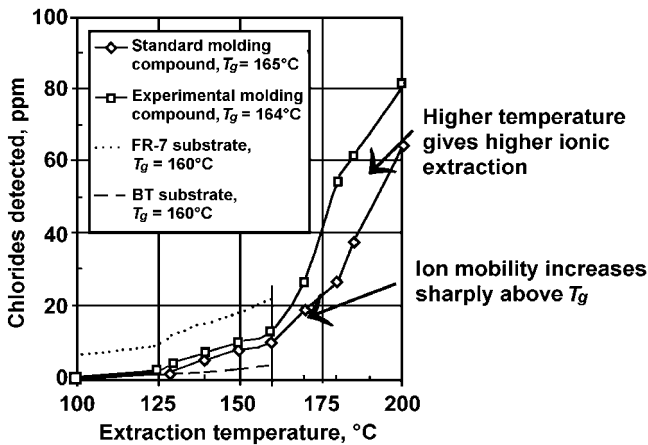


Figure 5.9. Effect of temperature on extracted chloride ions.^[46]

5.7.2 Tests for Surface Ionic Contaminants

The effectiveness of cleaning a printed wiring board prior to applying solder maskant or after assembly prior to coating can also be determined by resistivity measurements of water/isopropyl alcohol washings. Several instruments are available to measure resistivities of extracts and to report the readings as micrograms per square centimeter of equivalent sodium chloride (NaCl). IPC-TM-650 2.3.5^[47] describes test methods that use equipment such as the Omegameter* (Fig. 5.10) or Ionograph*. Requirements using the Omegameter are given in MIL-PRF-55110F.^[48] These are: less than 1.56 $\mu\text{g}/\text{cm}^2$ equivalent NaCl for the printed wiring board prior to solder resist application and less than 2.2 $\mu\text{g}/\text{cm}^2$ prior to conformal coating. The Omegameter consists of a tank filled with 75/25

*Omegameter® and Ionograph® are registered tradenames of Specialty Coatings Systems, a Cookson Co.

isopropanol/water solution into which the part is submerged. The resistivity is measured and the sodium chloride equivalents are automatically calculated. The extracted ions are then removed from the solution by circulating it through ion-exchange resin filters. Many cleaning consoles are now equipped to measure resistivities of water/alcohol extracts either in a static or continuous manner.



Figure 5.10. Omegameter® for testing cleanliness of electronic parts prior to coating. (Courtesy Specialty Coating Systems, a Cookson Co.)

Resistivity is a measure of the total amount of ionic residues. To determine the exact nature and quantities of contaminants, analytical separation and identification procedures such as ion chromatography, atomic absorption spectroscopy, flame photometry, or ESCA (Electron Spectroscopy for Chemical Analysis) must be used.^{[49][50]}

5.7.3 Surface Insulation Resistance (SIR)

Relatively simple electrical test patterns in which the surface insulation resistance (SIR) between closely spaced conductor lines can be measured are useful in monitoring the degree of cleanliness, especially for the removal of ionic residues. Test coupons consisting of Y patterns, interdigitated comb patterns, or the IPC-B-25A test coupon (Fig. 5.11) consist of closely spaced conductor lines of different widths and spacings formed on a printed circuit board. Similar patterns of thin or thick films may be formed on ceramic boards to simulate hybrid microcircuits and other ceramic-based electronics. The IPC-B-25A is a multipurpose test board that can be used to evaluate the efficiency of cleaning processes as well as the reliability of conformal coatings, dielectric coatings, and solder maskants under various humidity and temperature conditions. The IPC-B-25A coupons are also used to test and qualify coatings for resistance to electromigration and thermal shock (Method 2.6.7.1).^[47] Artwork for both the one-sided test pattern^[51] and one- and two-sided patterns^[52] are available from IPC for those wishing to fabricate the coupons themselves or pre-fabricated coupons may be purchased from several suppliers.^[53]

Salt residues are generally hygroscopic and more prone than organic residues to ionize in a humid environment, to become mobile, and to create high leakage currents. A clean dry surface will give high resistance values that are reproducible, while a surface that still contains traces of ionic species will show low and erratic resistance values. Separate test coupons may be included during a production run or the production circuit boards may be designed to contain a small pattern at the edge of each board that can be tested and later removed.

Surface resistances are based on accurate insulation resistance measurements with a known applied bias across the conductor lines while exposed to controlled simulated or accelerated environmental conditions. Typical SIR conditions consist of exposure to 85°C at 85% RH with an applied bias of 100 Vdc for 170 hours. Minimum requirements depend on the

intended application. In general, a minimum of 1×10^8 ohm is specified for most applications while over 1×10^{14} ohms may be specified for high-frequency applications. The minute changes in leakage currents can be measured with a high-sensitivity ammeter and the resistance calculated from Ohm's Law or the resistance can be read directly using a high-resistance meter. An automatic SIR tester (Sirometer) is available from Specialty Coating Systems.

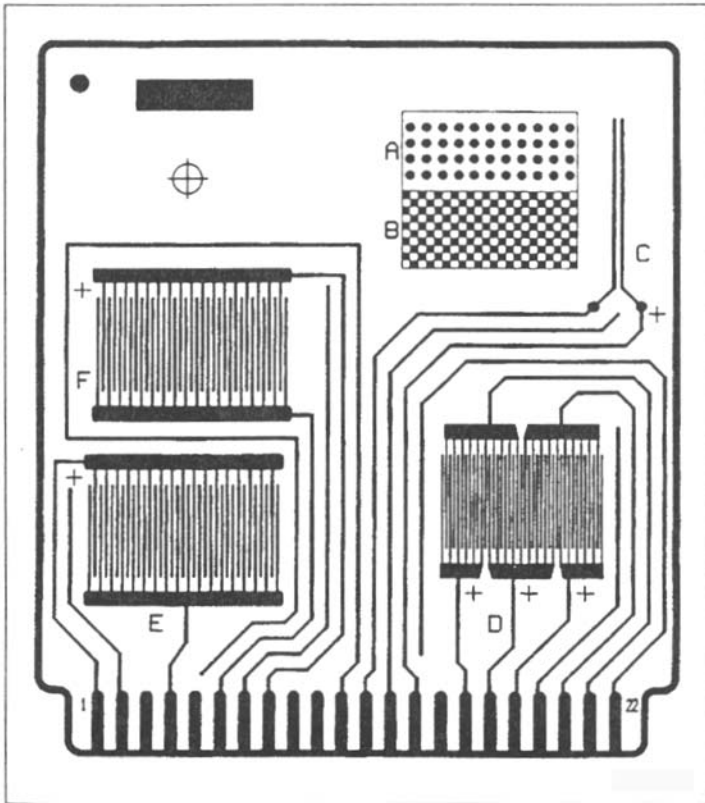


Figure 5.11. IPC-B-25A multipurpose test board.^[1]

Further information on SIR may be found in IPC-9201 *Surface Insulation Resistance Handbook*^[54] and in IPC-TR-468 *Factors Affecting Insulation Resistance Performance of Printed Boards*.^[55]

In summary, the SIR test is useful in:

- Determining the corrosive effects, if any, of conformal coatings or solder maskants on copper conductors or solder-coated copper conductors.
- Evaluating the ability of a coating to protect a circuit from accelerated conditions of humidity, temperature, and bias.
- Evaluating the effectiveness of a cleaning solvent or cleaning process for removing ionic or hygroscopic contaminants from a surface.

5.7.4 Reverse Bias Leakage Current

A highly sensitive test for trace amounts of ions consists of measuring the leakage current of a reverse-biased semiconductor junction at elevated temperatures. Semiconductor devices containing mobile ions form inversion layers and exhibit high reverse leakage currents. The inversion layer is formed if ion contaminants on the surface or in the passivation layer become mobilized at elevated temperatures and aligned by the application of an electrical field. Stress test conditions generally used are 150°C and 20 volts reverse bias.

5.7.5 Tests for Non-ionic (Organic) Residues

A quick semi-quantitative test for the presence of non-polar hydrophobic surface contaminants such as greases or oils involves the water break-free test. This test consists of placing a drop of deionized water on the surface of the circuit board or device. If the water beads, it indicates that hydrophobic (oils, greases, organic materials) contaminants are still present. If the water spreads and wets the surface, it is a good indication that all grease-like residues have been removed (Fig. 5.12). The test can be quantified to some extent by measuring the contact angle of the water bead using a goniometer. At the extremes, a contact angle of 180° indicates complete non-wetting while a 0° angle indicates complete wetting. The absence of ionic water-soluble or hydrophilic residues, however, cannot be assured by this test since they will also cause the water drop to spread. The contact angle measurement has been used to select an optimum cleaning solvent or cleaning process. Silicon substrates contaminated with organic residues showed a water-drop contact angle of 45° to 90° while a cleaned

surface resulted in good wettability and a contact angle of 10° .^[56] The beneficial effects of plasma cleaning copper, aluminum, and epoxy surfaces was also demonstrated by decreases in the contact angle.^[57] Measurement of the contact angle has also been used to study the effectiveness of uv/ozone cleaning of a solder maskant used in BGA packages fabrication prior to overmolding with epoxy. Ahn, et al.,^[58] showed a relationship between the contact angle and the exposure time to uv/ozone (Fig. 5.13). Improved adhesion was demonstrated after one minute of exposure due to the removal of surface contaminants but, at 10 minutes, adhesion degraded

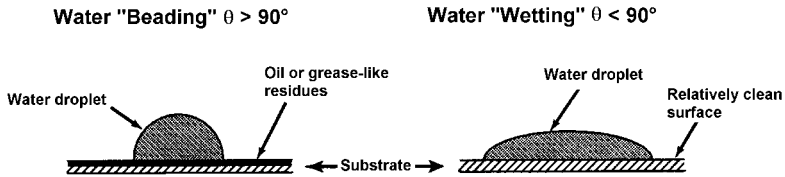


Figure 5.12. Water break-free test for hydrophobic surface contaminants.

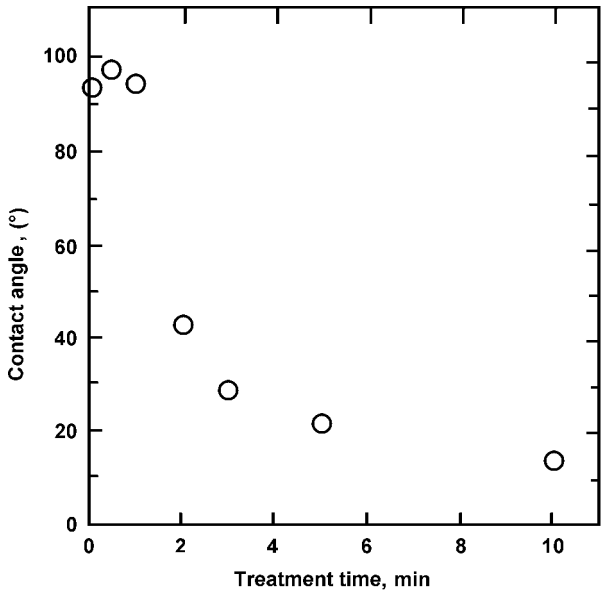


Figure 5.13. Contact angle vs uv/ozone cleaning time for solder maskant.^[58]

due to the initiation of a second mechanism of solder maskant decomposition.

A variation of the water-drop test involves spraying a dry surface with a fine mist of deionized water (Atomizer Test). If the surface is clean and free of organic films, the water droplets will spread immediately to form a continuous water film whereas, on a contaminated surface, the droplets will remain as droplets.

In order to determine the exact nature of organic residues, acetonitrile, a strong polar solvent, can be used to extract the organic contaminants and infrared spectroscopy then used to identify the compounds. Once identified, their sources can be determined and steps taken to prevent further contamination.

5.8 ACCELERATED STRESS AND ENVIRONMENTAL TESTS

To ensure maximum reliability of devices, circuit boards, and other electronic assemblies, defense contracts have specified that hardware meet the accelerated environmental tests called out in specifications such as MIL-STD-810, MIL-HDBK-2036, and MIL-STD-202. In addition to the humidity/temperature cycling test, these specifications define salt-spray, abrasion, impact, fungus, and many other tests. Table 5.3 lists tests defined in MIL-STD-202. These tests are classified into three groups: Environmental, Physical, and Electrical and may be applicable to coatings alone or to coated electronic components.

Because of concern over using polymer coated or encapsulated microcircuits in high-reliability applications, even more severe accelerated tests have been devised along with ultrasensitive electronic test chips and circuits. These new tests were necessary to more quickly predict life expectancies for parts under actual operating environments and to gain information on failure modes and mechanisms in attempts to synthesize or reformulate materials that would avoid failures.

5.8.1 Accelerated Humidity-Temperature Tests

A widely used and accepted test for the qualification of plastic-coated or plastic-encapsulated microcircuits is the steady-state exposure of

parts to 85% RH at 85°C, generally for 1,000 hours with a bias. This test is referred to as the 85/85 test and defined in JEDEC Standard No. 22B, Method A101-A.^[59] The test may also be performed without bias.

Table 5.3. MIL-STD-202 Test Methods

Test	Method
Environmental Characteristics (100 class)	
Salt spray (corrosion)	101D
Humidity (steady state)	103B
Immersion	104A
Barometric pressure	105C
Moisture resistance	106F
Thermal shock	107G
Life (at elevated temperature)	108A
Explosion	109B
Sand and dust	110A
Flammability (external flame)	111A
Seal	112E
Physical Characteristics (200 class)	
Vibration	201A
Random drop	203B
Vibration, high frequency	204D
Life, rotational	206
High impact shock	207A
Solderability	208H
Radiographic inspection	209
Resistance to soldering heat	210E
Terminal strength	211A
Acceleration	212A
Shock, specified pulse	213B
Random vibration	214A
Resistance to solvents	215J
Particle impact noise detection (PIND)	217

(cont'd.)

Table 5.3. (cont'd.)

Test	Method
Electrical Characteristics (300 class)	
Dielectric withstanding voltage	301
Insulation resistance	302
DC resistance	303
Resistance-temperature	304
Capacitance	305
Quality factor (Q)	306
Contact resistance	307
Current-noise test for fixed resistors	308
Voltage coefficient of resistance	309
Contact-chatter monitoring	310
Life, low-level switching	311
Intermediate current switching	312

A much more severe accelerated test is the HAST (Highly Accelerated Stress Test) whereby the parts are subjected to elevated temperature and humidity while under 2 atm of pressure in an autoclave, with or without an applied bias. This test is described in JEDEC Standard No. 22B, Method A110.^[60] The unbiased test is referred to as the pressure cooker test (PCT) and defined in JEDEC Standard 22, Method A102-B.^[61] Early studies were performed at 121°C, 85–95% RH and 2 atm pressure,^[62] but subsequently higher temperatures, e.g., 130° and even 140°C, were used in comparing plastic encapsulated microcircuits with their ceramic hermetic counterparts. One must understand, however, that at such high temperatures, pressure, and moisture most polymer materials undergo new failure modes and mechanisms that are catastrophic and that extrapolations to long-term life expectancies or correlations with the 85/85 test cannot be made. For example, at the T_g , molecular movement and expansion occur in polymers creating stresses and probably an increase in moisture absorption. The test is also not meaningful for applications such as in-body electronics where such drastic conditions would never be encountered. Both HAST and PCT, however, are useful in comparing the performance and failure modes and mechanisms of various plastics.

5.8.2 Hydrolytic Stability

Some polymers, even after achieving a full cure, have been known to soften and even liquefy at elevated temperature and high humidity conditions—a process referred to as *reversion*. This failure was noted primarily with some early polyurethane and silicone formulations and is due to hydrolysis and reversion of the polymer into small monomer or oligomer units. Although not a prevalent failure mode today, it is always best to conduct a relatively simple accelerated test to assure reliability. IPC-TM-650, Method 2.6.11 describes such a test method whereby a circuit board laminate coated either with a conformal coating or a solder mask is exposed in a desiccator to a relative humidity created from a saturated solution of potassium sulfate maintained at various time-temperature conditions: up to 28 days at 97°C for a solder maskant and 120 days at 85°C for a conformal coating. The relative humidity achieved from the saturated potassium sulfate solution is approximately 98%. After the specified time period, the coating is visually examined for any degradation and the surface is swabbed with absorbent cotton to check for any softness or tackiness.

Ambients of constant relative humidities can be generated using saturated solutions of various inorganic salts contained in a desiccator at constant temperatures.^[63] (See also Ch. 6.)

5.8.3 Moisture and Stress Test Chips

Several electrical test chips have been developed to measure moisture resistance and stress effects of polymer coatings. These chips are being used to evaluate and compare the reliability of coatings and encapsulants. Among them are:

- A Moisture Sensor Chip (MSC), designed by AvanTeco (Whittier, CA) and Revtek (Torrance, CA), that is based on the rapid, but irreversible silver migration phenomenon that occurs between thin-film silver conductors in the presence of moisture and an applied bias.
- A series of Assembly Test Chips (ATC) designed by Sandia National Laboratories (Albuquerque, NM) that provide quantitative data for interline leakage currents and resistor changes due to moisture and ion contaminants.

- Humidity sensors based on capacitance changes occurring in porous aluminum oxide or silicon oxide films when exposed to moisture.
- A CMOS stress-sensor chip designed and developed by Sandia National Laboratories based on piezoresistive stress cells.

Design and Characteristics of the Moisture Sensor Chip (MSC). The MSC is based on the phenomenon of silver migration, previously described, whereby closely spaced conductor traces of thin-film silver will short out in a matter of minutes in the presence of condensed moisture, traces of ionic residues, and a small applied bias, generally 2–15 Vdc. Although other metals besides silver migrate in an electrical field under these same conditions, silver migrates orders of magnitude faster.

Catastrophic failures occur when sufficient water and ions are present. Before complete failure, increases in leakage current occur and can be measured. If silver migration occurs on these chips, even though other circuit devices or the entire module remain functional, the circuit should be considered at risk since silver migration is proof that moisture has penetrated to the active devices and interconnect surface.

The MSCs were designed under a NASA program.^{[64]–[66]} The chips consist of interdigitated comb patterns of various spacings photoetched from vapor-deposited silver (Fig. 5.14). Each chip (1.57×1.72 mm) contained four comb pattern designs with spacings of 2, 5, 17, and 25 μm , representing the most moisture sensitive to the least sensitive, respectively (Fig. 5.15 a and b). Only two leads are necessary for each of the sensor elements. Prior to assembly, the sensors must be well protected. They should be stored in dry nitrogen to prevent premature reaction with ambient moisture and over lead acetate paper to getter any ambient sulfur compounds that may also react with the silver sensor. The chips can be used as part of a reliability program to test and compare the barrier properties of coatings, but are not intended to quantitatively measure moisture. They act as a fuse; once they have failed they cannot be used again. According to an Air Force-sponsored study,^[67] the test chips were assembled into 8-lead DIPs (Dual In-Line Packages), coated with various coatings and combinations of coatings, electrically tested, exposed to 500 hours of 85% RH and 85°C, and retested. The parts that passed were then subjected to the pressure cooker test, JEDEC Standard JESD22-A102-B^[61] for various

periods of time until significant failures occurred.^[68] Other accelerated humidity-temperature conditions such as HAST can also be used.

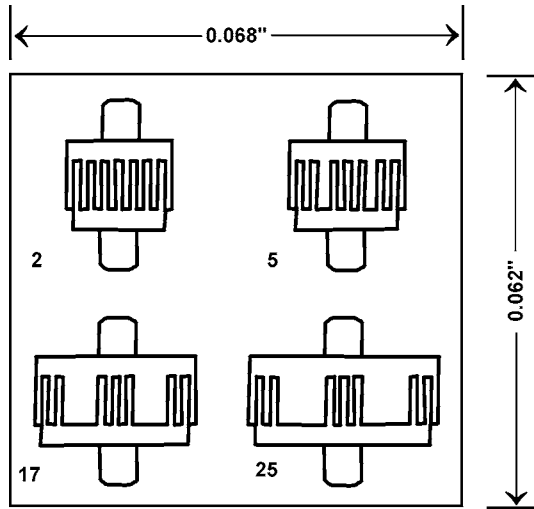
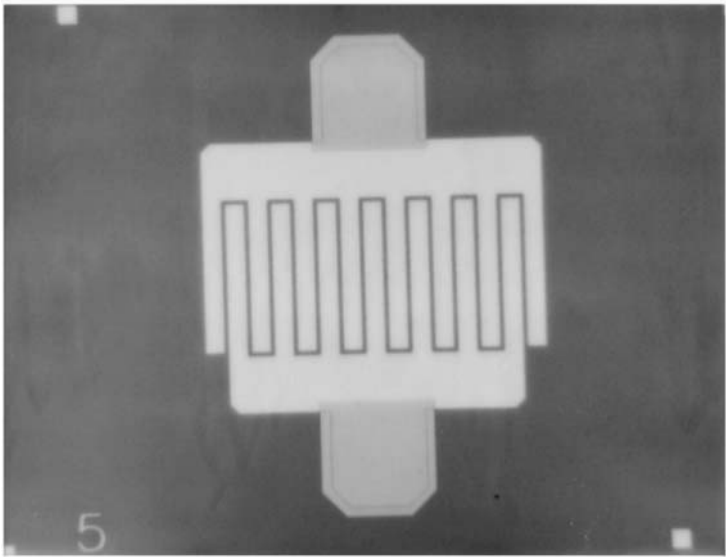
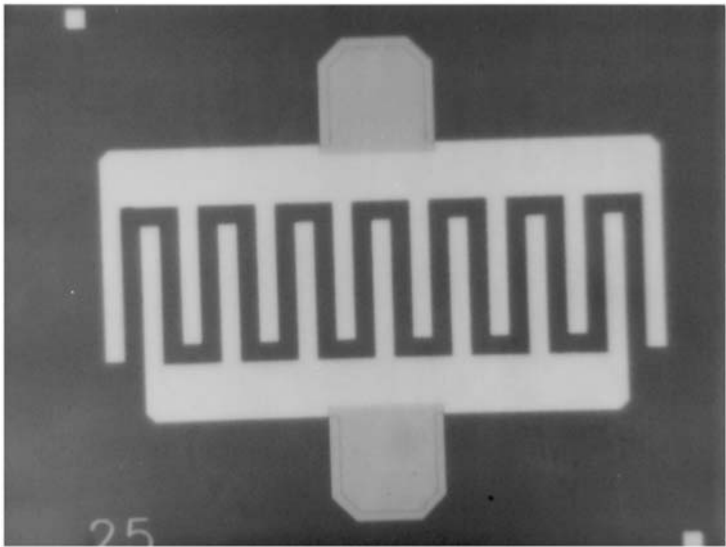


Figure 5.14. Topography of Moisture Sensor Chip.

Design and Characteristics of ATC Chips. The design of the first generation ATC chip, the ATC-01, has been described in several articles and presentations by personnel of Sandia National Laboratories.^[69] The ATC-01 chips are 6.5 mm (254-mils) square and have photodelineated thin-film aluminum traces (1 μm) formed as triple track (TT) resistors having various widths and spacings (Table 5.4). There are 88 external bond pads, each 100 μm (4-mil) square on 200 μm (8-mil) centers. The topography is shown in Fig. 5.16. Other structures include ladder structures, edge crack monitors, and van der Pauw sheet resistance structures. Electromigration structures are also available in the center of the chip. As the aluminum resistors corrode, the device resistance increases in a stepwise fashion. By monitoring the resistance versus time, information about corrosion kinetics and corrosion rate variance may be obtained. The chip also contains some parallel straight line corrosion detectors and a van der Pauw structure that can be used to monitor the Al sheet resistance during the corrosion test.



(a)

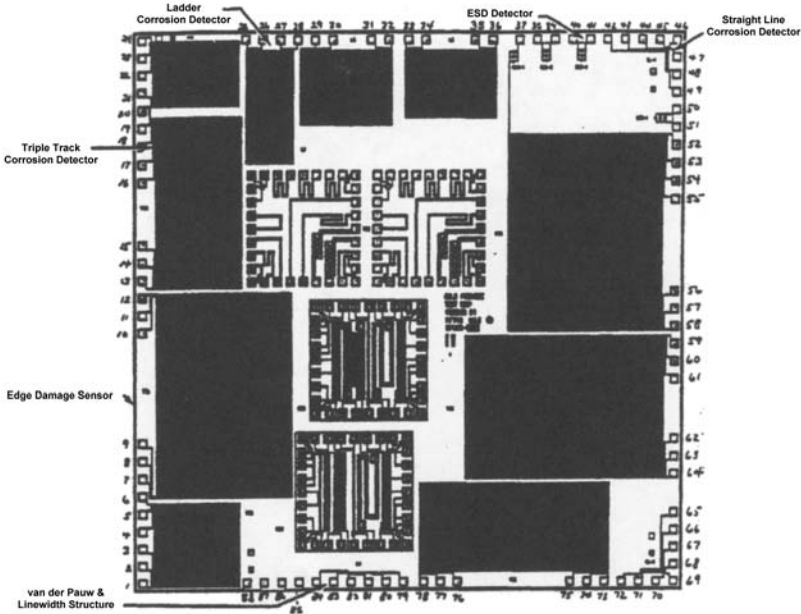


(b)

Figure 5.15. MSC showing interdigitated silver patterns ($\times 100$); (a) $5\text{-}\mu\text{m}$ spacing between conductors, (b) $25\text{-}\mu\text{m}$ spacing between conductors.

Table 5.4. Design Parameters of ATC-01 Triple Track (TT) Resistors

	Line Widths (μm)	Line Spacing (μm)
1	1.25	1.25
2	2.00	2.00
3	2.00	4.00
4	4.00	4.00
5	5.00	6.00
6	6.00	4.00
8	1.25	2.00



Overall layout of ATC-01. The structures with interior bond pads are for electromigration measurements. The large black structures are triple track (TT) and ladder (L) corrosion test structures with densely packed fine Al conductor lines. Starting in the lower lefthand corner and going clockwise, these structures are: TT8, TT6, TT2, TT1, L1, L2, L3, TT4, TT5, and TT3.

Figure 5.16. Topography and layout of ATC-01 chip.

Humidity Sensors Based on Capacitance Changes. Subsequent to the ATC-01 chip, new ATC chips that provide improved and more quantitative data have been designed and made available by Sandia National Laboratories.^[70]

The ATC-02 chip, for example, in addition to the triple track corrosion test structures contained in the ATC-01 chip, contains polysilicon heaters and anodized aluminum (aluminum oxide) moisture detectors designed to function at low moisture levels of 100 to 1000 ppm. The moisture detectors are thin-film capacitors formed by anodizing rectangular Al metal pads leaving some unanodized Al to serve as the bottom electrode. A thin palladium film is then deposited over the porous oxide to serve as the upper electrode. Water vapor readily penetrates the Pd film and condenses in the porous oxide, thus changing its dielectric constant and increasing the capacitance (Fig. 5.17).

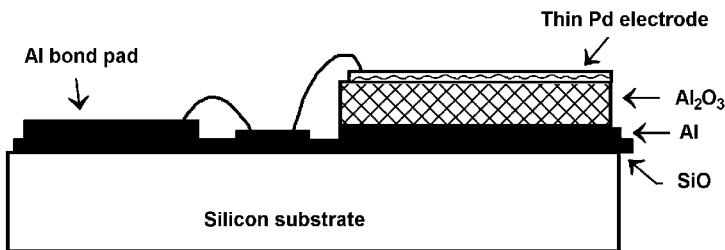


Figure 5.17. Cross-section of anodized aluminum moisture sensor capacitor.

Stress Sensor Chips. The beneficial use of coatings as stress buffers has already been discussed in Ch. 4. However, coatings may contribute stresses of their own and affect the reliability of a circuit. High stresses can be imparted to electronic components due to shrinkage of the resin during cure or by mismatches in the coefficients of thermal expansion between the coating and the variety of metal and ceramic surfaces to which it adheres. Both shrinkage and CTEs vary widely among polymers and depend on the type of polymer and volume percentage and type of filler used. In general, increasing the filler content reduces shrinkage and thermal expansion. Other factors known to affect the percent of shrinkage include the cure temperature, degree of polymerization, geometry of the part, and the amount of polymer used. A poor combination of materials, processes,

and design can create stresses sufficiently high to cause fragile or thin sections of a circuit to reach their ultimate strength and break. Figure 5.1 (see Sec. 5.6) shows an silicone-coated integrated circuit whose flying lead wires were severed by shrinkage produced from solvent evaporation and curing of the coating.

The failure was caused primarily by applying too thick a layer of an unfilled solvent-based coating. A thinner application of the same coating plus a gradual or stepwise increase of the cure temperature would have minimized the stresses and avoided the failure.

Polymer systems involving more than one coating type may present problems if the inner coating has a higher CTE than the outer one. An increase in temperature will obviously cause the inner coating to exert pressure against the confining outer shell. An example is the use of an inner unfilled silicone coating and an outer epoxy shell as in some resistor and semiconductor devices. Stress problems can be avoided by using a thin inner silicone coating or by providing space between the inner coating and the outer plastic into which the silicone can expand.

Stress Testing. Numerous methods exist for testing the mechanical integrity of plastic packaged devices. Among these are vibration, centrifugal-force, thermal shock, temperature cycling, and impact tests. Most of these procedures are detailed in military or industry specifications. An inexpensive and rapid method to measure stresses that a plastic or coating imparts to a device consists of embedding resistance strain gauges or pressure transducers in the plastic and plotting the stresses as a function of temperature.^{[71][72]} Temperature cycling accelerates any stress effects, especially those arising from large differences in expansion coefficients between material interfaces.

Another test consists of recording the temperature of thermometers that have been calibrated to measure stress rather than temperature. A linear relationship has been found between temperature readings and the pressure exerted on the bulb of the thermometer. In practice, the thermometers are embedded in the plastic and readings taken at various temperatures.^[73]

In testing rigid molding or encapsulating compounds, the Olyphant washer test is well established and is fairly standard in the industry. According to this test, a complex metal washer (a machined-steel insert) is embedded in the plastic. High shrinkage or stress from the plastic during its cure or subsequently on temperature cycling results in cracking of the plastic around the washer especially at the sharp corners.

Stress Sensor Chips. Recent developments have been made in quantitatively measuring stresses on specially designed semiconductor chips. Sandia National Laboratory’s ATC-04 is a second generation CMOS chip specifically designed to measure mechanical stresses and thermal resistance. It contains an array of 25 stress sensing cells. Each cell is comprised of four n-type and four p-type piezoresistors for stress measurements and a diode for temperature measurement. The use of four resistors of each doping type, two parallel to the chip edges and two on 45° diagonals facilitates obtaining the maximum amount of information from planar stress sensors on silicon. The chip also contains four polysilicon heater elements for thermal resistance tests and two ring oscillators to measure the chip functionality during accelerated testing. Figure 5.18 shows the layout with locations of the stress sensor cells, oscillators, and heaters. [74] The ATC-04 chips can be characterized electrically before applying a coating, after coating, and after exposure to various accelerated tests to determine the effectiveness of the protective coating or encapsulant.

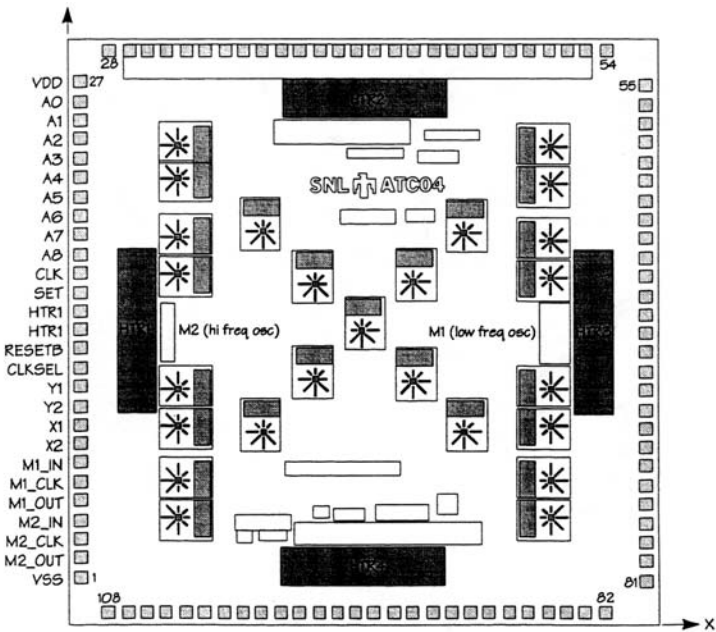


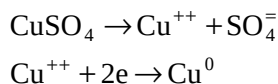
Figure 5.18. Basic ATC-04 layout.[74]

5.9 TESTS FOR COATING INTEGRITY

A coating's ability to prevent moisture and contaminants from penetrating to the active device surfaces depends on its completeness of coverage and integrity, that is, its lack of pinholes, microcracks, and other imperfections. Five tests may be used to measure film integrity; two are based on an electrochemical cell formation, one on a simple chemical etching method, one on a change in reflectance measurement, and the last on a dye penetrant test. Except for the reflectance and dye penetrant methods, the coatings must be deposited onto a metal or metallized base for testing.

5.9.1 Electrochemical Tests

For the electrophoretic test, the coating is deposited and cured onto a metal substrate, then immersed into an aqueous solution of copper sulfate while a negative bias is applied to the metal (Fig.5.19). Any pinholes or discontinuities in the film become sites for the reduction of copper ions to metallic copper which are then visible as dark brown specks according to the following reactions:



The test serves as both a qualitative and semi-quantitative measurement for pinholes in a film.

A second electrochemical test involves rendering the metal substrate, onto which the coating is deposited, anodic while it is immersed in methanol. Any entrance of methanol through a pinhole results in electrolysis of the methanol and evolution of hydrogen gas that becomes visible as tiny bubbles^[75] (Fig. 5.20).

5.9.2 Chemical Test

In yet a third method, the coating is deposited onto an aluminized transparent plastic substrate or glass which is then either immersed or sprayed with a dilute solution of hydrochloric acid. Any pinholes serve as sites for the hydrochloric acid to contact and etch the aluminum which then can be visually detected through the transparent areas (Fig. 5.21).

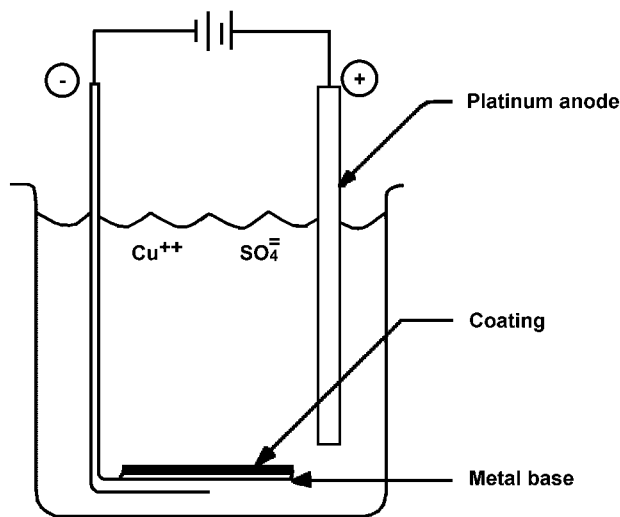


Figure 5.19. Electrophoretic pinhole detection test.

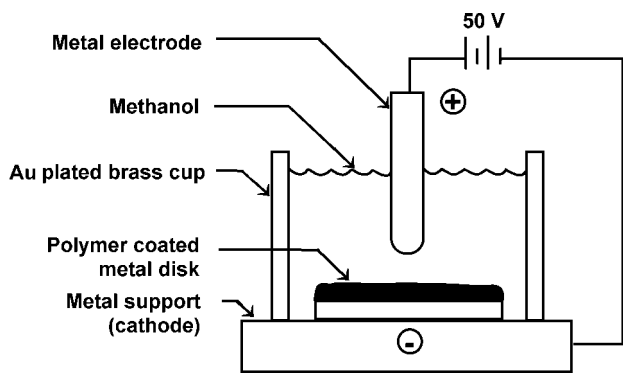


Figure 5.20. Pinhole detection test by hydrogen gas evolution.

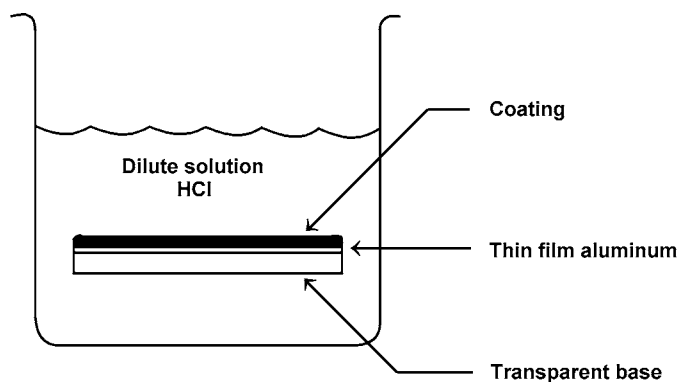


Figure 5.21. Hydrochloric acid etch test for measuring film integrity.

5.9.3 Optical Reflectance Test

A reflectance method may also be used to measure the degree of porosity of an organic coating according to ASTM 3258. The coating is applied to a non-porous surface and measured for reflectance. A colored penetrating dye is applied and the excess wiped off after which the reflectance is measured again. The difference between the two readings indicates the degree of porosity; the smaller the difference, the lower the porosity of the film and the greater its ability to resist penetration.

5.9.4 Surface Discontinuities

Microcracks and discontinuities in the surface of a coating or in other plastic or ceramic materials that are not detectable by microscopic examination may be detected by a dye penetration test. According to this method, a solution of a colored visible or a fluorescent dye (such as Zyglow or Yellow Dye G) is applied to the surface and allowed sufficient time to penetrate through any cracks. To accelerate the penetration, the part may be immersed in the dye solution and either vacuum or pressure applied. The superficial dye solution is then washed off and any dye remaining in the discontinuities will be visible under ordinary light or under a black-lamp. Specimens may also be cross-sectioned and the depth of dye penetration observed. Some dye penetration results for test specimens of Kovar wire embedded in various epoxies are shown in Fig. 5.22. The photos show

complete, partial, and no penetration depending on the adhesion and integrity of the epoxy-to-wire interface. Figure 5.23 shows the high penetration of dye solution along the leads of an early-vintage plastic-encapsulated IC. Because cross-sectioning after a dye penetration test is destructive, the test is best used on a sampling basis for quality control; for initial selection and qualification of a plastic encapsulant, coating or primer; or for failure analysis. MIL-STD-883, Method 1034 describes specific conditions for the test.

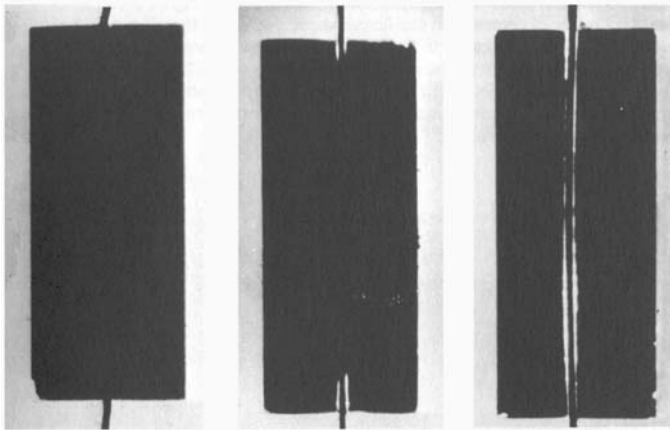


Figure 5.22. Dye penetration along wire leads; (left) no penetration, (center) partial penetration, (right) complete penetration.

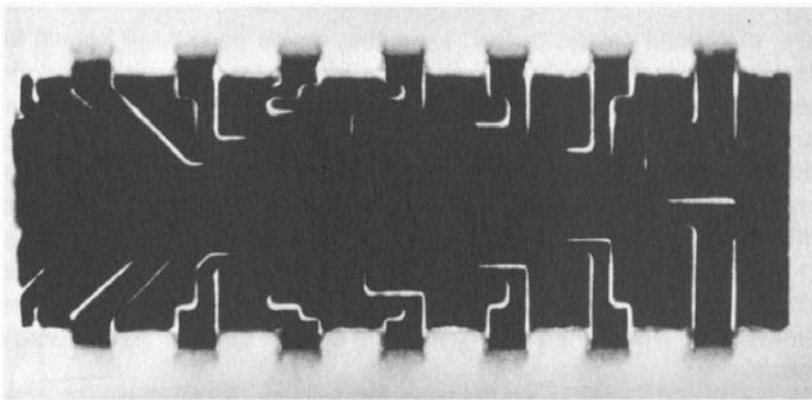


Figure 5.23. Dye penetration along the lead-to-plastic interfaces of an integrated circuit package.

5.9.5 Internal Discontinuities

The dye penetrant test is useful only for detecting surface discontinuities or internal discontinuities that emanate from or are connected to the surface. To detect internal discontinuities such as voids, delamination, or internal cracks, surface acoustic microscopy (SAM) is widely used (Ch. 6). SAM is a non-invasive, non-destructive method that has become very valuable in examining the integrity of CSP, PEMs, PBGAs, and a host of other new packaging constructions being developed for microelectronics.

5.10 ADHESION

Coated substrates can fail mechanically by one or more of three mechanisms involving adhesion:

- Adhesion failure by delamination of the coating from the substrate
- Cohesive failure due to fracture within the coating
- Substrate failure due to fracture or deformation of the substrate

In many cases, it is the toughness or resistance to fracture of the adherents and interfaces that determines whether imposed stresses can be withstood and adhesion preserved. Several quantitative and semi-quantitative tests can be used to evaluate adhesion of coatings.

5.10.1 Tape Pull Test

The most widely used test to determine the degree of adhesion of a coating involves applying and pulling a tape from a coated substrate. The test is simple and quick, easy to perform, and requires no capital equipment; however, at best, it is semi-quantitative. ASTM D3359 *Standard Test Methods for Measuring Adhesion by Tape Test* defines the procedure; an X mark is scribed through the coating to the substrate using a razor blade or other cutting device. A pressure-sensitive tape is then firmly applied over the scribed surface and pulled rapidly at an angle approximating

180 degrees. The degree of adhesion is then rated on a scale from 1 (coating removed from most of the area of the X mark under the tape) to 5 (no peeling or removal of coating). The test is destructive and should be used on a test coupon that is processed at the same time as the coated part.

A variation of this method involves scribing through the coating to form a crosshatch pattern. The recommended tape is Permacel 99 from Permacel Corp., New Brunswick, NJ.

5.10.2 Scratch Adhesion Test

Another destructive test widely used on a test coupon processed at the same time as the coated part utilizes a diamond probe as defined in ASTM D2197 *Standard Test Method for Adhesion of Organic Coating by Scrape Adhesion*. The scratch test provides a rapid indication of hardness and adhesion of a coating, but is not quantitative. There are several drawbacks. It is sometimes difficult to produce delamination due to the tendency for ploughing, especially with soft coatings. Also, the loading intensity to produce adhesion failure is often too high to correspond to actual situations and the failure may be the result of substrate deformation rather than to intrinsic adhesive properties.

5.10.3 Contact Fatigue Adhesion Test

There are adhesion tests that are more accurate and quantitative than either the tape or scrape tests, but they are more suited to laboratory and research and development projects. Among these is the contact fatigue adhesion test.^[76] Micro-impact testing, a repetitive contact method simulates the fatigue conditions that coatings experience in actual service. Time to failure and the overall change in probe depth during testing are measures of the resistance of the coating to fracture. Figure 5.24 shows two contact fatigue tests for a 15- μm PET (polyethylene terephthalate) coating on a plastic substrate. Delamination of the coating (adhesion failure) occurred after 200 seconds of sample oscillation (at 30 Hz) as noted by the rapid displacement.

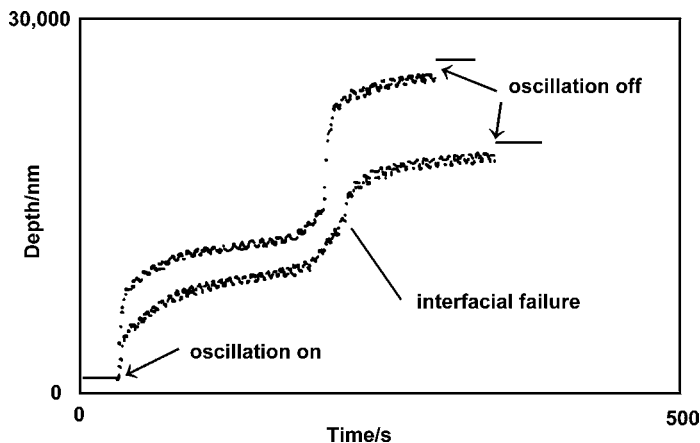


Figure 5.24. Contact fatigue curves for PET coating on a polymer substrate.^[76]

REFERENCES

1. IPC-CC-830A, Qualification and Performance of Electrical Insulating Compound for Printed Board Assemblies, *IPC* (Jul. 1999)
2. IPC-HDBK-830, Guidelines for Design, Selection and Application of Conformal Coatings, *IPC* (2002)
3. IPC-DD-135, Qualification Testing for Deposited Organic Interlayer Dielectric Materials for Multichip Modules, *IPC* (Aug. 1995)
4. IPC-SM-840C, Qualification and Performance of Permanent Solder Mask, *IPC* (Jun. 2000)
5. IPC-CC-830A, Qualification and Performance of Electrical Insulating Compound for Printed Board Assemblies, *IPC* (Jul. 1999)
6. MIL-C-28809, Circuit Card Assemblies, Rigid, Flex, and Rigid-Flex, (inactivated for new designs).
7. IPC-A-610C, Acceptability of Electronic Assemblies, *IPC* (Jan. 2000)
8. Sinnadurai, N., The Use and Abuse of HAST, *IEEE Advanced Stress Technology (AST) Workshop*, Boston (Oct. 1999)
9. Sinnadurai, N., Plastic Packaging Solutions for High Reliability Applications, Albuquerque, NM (Aug. 1998)
10. Pecht, M., Dasgupta, A., Barker, D., and Leonard, C., The Reliability Physics Approach to Failure Prediction Modeling, *Quality and Reliability Engineering Int.*, 6:267–273 (1990)

11. Dasgupta, A., Barker, D., and Pecht, M., Reliability Prediction of Electronic Packages, *J. Institute of Environmental Sciences*, 33(3):36–45 (1990)
12. Pecht, M., and Dasgupta, A., Physics-of-Failure: An Approach to Reliable Product Development, *J. Institute of Environmental Sciences*, 38:30–34 (1995)
13. Dasgupta, A., and Pecht, M., Material Failure Mechanisms and Damage Models, *IEEE Transactions on Reliability*, 40(5):531–536 (Dec. 1991)
14. Osterman, M., and Stadterman, T., Failure-Assessment Software For Circuit-Card Assemblies, *Proc. Annual Reliability and Maintainability Symp.*, pp. 269–276 (Jan. 1999)
15. Osterman, M., Dasgupta, A., and Tonnelier, L., Simulation Improved Testing of Electronic Hardware, 2002 *Proc. 48th ATM*, ISBN: 1-877862-81-9, Document No. 2011 (Apr. 1, 2002)
16. Martin, P. L., *Electronic Failure Analysis Handbook*, McGraw-Hill (1999)
17. Akanni, K. A., Electrically Induced Failures In Electronic Products and Assemblies, 3rd *Int. SAMPE Electronics Conf.*, Los Angeles, CA (Jun. 1989)
18. Lee, S. M., Licari, J. J., and Valles, A. G., Properties of Plastic Materials and How They Relate to Device Failure Mechanisms, (M. E. Goldberg and J. Vaccaro, eds.), *Physics of Failure in Electronics*, Vol. 4, RADC Series on Reliability, Defense Documentation Center (1966)
19. Katsev, G. A., et al., Effect of Absorption of Certain Amines on Semiconductor Surface on the Principal Parameters of Germanium Transistor Triodes (A. N. Frumkin, ed.), *Surface Properties of Semiconductors*, Consultant Bureau (1964)
20. Brandewie, J. V., Eisenberg, P. H., and Meyer, R. A., Investigation of Surface Failure Mechanisms in Semiconductor Devices by Envelope Ambient Studies, (M.E. Goldberg and J. Vaccaro, eds.), *Physics of Failure in Electronics*, Vol. 4, RADC Series on Reliability, Defense Documentation Center (1966)
21. Etchason, P. T., and Licari, J. J., High Reliability Polyurethane Insulation Coating for Circuit Board Protection, *Insulation* (Jun. 1962)
22. Doctor and Franklin, Corrosion of Copper Wire by Resins, *Electronic Equipment* (Jul. 1956)
23. Licari, J. J., Selection and Control of Plastics for Semiconductor Packaging, Inform. Microelectronics, Navy Equipment μ -Notes, 25, U. S. Naval Ammunition Depot, Crane, IN (Aug. 1968)
24. Kohman, G. T., Hermance, H. W., and Downes, G. H., Silver Migration in Electrical Insulation, *Bell Systems Technical Journal*, 34(6) (Nov. 1955)

25. Chaikin, S. W., Janney, J., Church, F. M., and McClelland, C. W., Silver Migration and Printed Wiring, *Industrial and Engineering Chem.*, 51(3) (Mar. 1959)
26. Shumka, A., and Piety, R., Migrated-Gold Resistive Shorts in Microcircuits, *13th Annual Proc. Reliability Physics Symp.* (1975)
27. Licari, J. J., and Enlow, L. R., *Hybrid Microcircuit Technology Handbook*, 2nd Ed., Noyes Publ., Westwood, NJ (1998)
28. Riemer, D. E., Material Selection and Design Guidelines For Migration-Resistant Thick-Film Circuits With Silver-Bearing Conductors, *Proc. 31st Electronic Components Conf.* (1981)
29. Augis, J. A., et al., *3rd Int. SAMPE Electronics Conf.* (1989)
30. Bent, W. R., and Turbini, L. J., Evaluating the Effect of Conformal Coatings in Reducing the Rate of Conductive Anodic Filament Formation, *Proc. APEX*, San Diego, CA (Jan. 2002)
31. Hunsicher, H. Y., and Kenspf, L. W., Growth of Whiskers on Tin-Aluminum Bearings, *Quarterly Transactions, SAE*, 1 (1947)
32. Stupian, G. W., Tin Whiskers in Electronic Circuits, *Aerospace Report TR-92* (Dec. 20, 1992)
33. Lee, B. Z., and Lee, D. N., Spontaneous Growth Mechanism of Tin Whiskers, *Acta Mater.*, 46(10) (1998)
34. Zhang, Y., et al., Understanding Whisker Phenomenon, *Proc. IPC APEX Conf.*, San Diego, CA (Jan. 2002)
35. <http://nepp.nasa.gov/whisker>
36. Kadesch, J., and Leidecker, H., Effect of Conformal Coating on Tin Whisker Growth, *Proc. 37th IMAPS Nordic Annual Conf.* (Sep. 2000)
37. Brusse, J., Tin Whiskers, Revisiting an Old Problem, *NASA EEE Links Newsletter* (Dec. 1998)
38. Kim, Y. H., et al., *J. Adhesion Sci. Tech.*, Vol. 2 (1988)
39. Ho, P. S., *Principles of Electronic Packaging*, (D. P. Seraphim, R. Lasky, and C. Y. Li, eds.), McGraw-Hill (1989)
40. Adema, G. M., Turlik, I., Smith, P., and Berry, M., *Proc. EIA/IEEE, Electron. Components Tech. Conf.*, Las Vegas, NV (1990)
41. Messner, G., Turlik, I., Balde, J. W., and Garrou, P. E., Thin Film Multichip Modules, *ISHM Monograph* (1992)
42. Paik, K. W., and Ruoff, A. L., *Proc. MRS Meeting*, (154), 227 (1989)
43. Reche, J. J., Implications of Properties of Thin Films in Wafer-scale Multilevel Interconnect, *Proc. 2nd SAMPE Int. Electronics Conf.*, Vol. 2 (Jun. 14–16, 1988)
44. Heistand, R. H., et al., *Proc. ISHM Int. Symp.*, Orlando, FL (1991)

45. Alimarin, I. P., and Petrikova, M. N., *Inorganic Ultramicroanalysis*, MacMillan, New York (1964)
46. Hagge, J., Commercialization of Military and Space Electronics, *5th Annual Conf.*, Los Angeles, CA (Feb. 2001)
47. IPC-TM-650, Test Methods Manual, *IPC*.
48. MIL-PRF-55110F, Printed Wiring Board.
49. Day, R. A., Underwood, A. L., and Underwood, A. L., Jr., *Quantitative Analysis*, 6th Ed., Prentice Hall (1991)
50. Cheremisinoff, N. P., *Polymer Characterization: Lab Techniques and Analysis*, William Andrew Publ., Norwich, NY (1996)
51. IPC-A-25A, Multipurpose 1 Sided Test Pattern, *IPC* (2002–2003)
52. IPC-A-25, Multipurpose 1 & 2 Sided Test Pattern, *IPC* (2002–2003)
53. www.ipc.org/html/CFCtestboards.htm
54. IPC-9201, Surface Insulation Resistance Handbook, *IPC* (Jul. 1990)
55. IPC-TR-468 Factors Affecting Insulation Resistance Performance of Printed Boards, *IPC* (Mar. 1979)
56. Ganesan, G. S., Lewis, R., and Berg, H. M., Characterizing Organic Contamination in IC Package Assembly, *Int. J. Microcircuits and Electronic Packages*, 17(2) (1994)
57. Uner, J., et al., The Application of Atmosphere Pressure Plasma to Various Steps in IC Packaging, *Proc. 3rd Annual Semiconductor Packaging Symp.*, Semicon West (2000)
58. Ahn, S., Yoon, H., and Oh, S., Reliability Improvement of Plastic Ball Grid Array Package by UV/Ozone Cleaning, *Proc. 1st Int. Symp. on Ball Grid Array Technol.*, *ISHM*, Los Angeles, CA (Oct. 1995)
59. JEDEC Standard No. 22B, Method A101-A, Steady-State Temperature Humidity Bias Life Test, *Electronic Industries Alliance* (Jul. 1988)
60. JEDEC Standard No. 22, Method A110, Highly Accelerated Temperature and Humidity Stress Test (HAST), *Electronic Industries Alliance* (Jul. 1988)
61. JEDEC Standard 22, Method JESD22-A102-B, Accelerated Moisture Resistance-Unbiased Autoclave, *Electronic Industries Alliance* (Mar. 1991)
62. Murphy, C. F., Kodnani, R., and Peterson, D. W., Evaluation of Non-Hermetic Coatings for MCM Applications Through HAST, 85/85, and PCT, *Proc. Int. Conf. Multichip Modules*, Denver, CO (1994)
63. *CRC Handbook of Chemistry and Physics*, 81st Ed., (D. R. Lide, ed.), CRC Press (2000)
64. Licari, J. J., NASA Final Report NAS-7-1368 (Jun. 1997)

65. Licari, J. J., Evaluating the Moisture Barrier, *Advanced Packaging* (Jul./Aug. 1997)
66. Licari, J. J., and Tanielian, A., U. S. Patent 5606264 (Feb. 25, 1997)
67. Licari, J. J., and Jones, E., A Non-Hermetic Packaging Technology For Low-Cost, Low-Weight Multichip Modules, AFRL-VS-TR-1999-1107, Final Report (Aug. 1999)
68. Licari, J. J., and Jones, E., Reliable Low-Cost, Low-Weight, Non-Hermetic Coatings for MCM Applications, *IMAPS/JPL Conf.* (Jun. 1999)
69. Sweet, J. N., et al., Short and Long Loop Manufacturing Feedback Using a Multisensor Assembly Test Chip, *Proc. 9th Int. Electronic Mfg. Technol. Symp.*, IEEE (1990)
70. Sweet, J. N., Peterson, D. W., Tuck, M. R., Kelly, M. J., and Guillinger, T. R., Evaluation of Chip Passivation and Coatings Using Special Purpose Assembled Test Chips and Porous Silicon Moisture Detectors, *Proc. 41st Electronic Components and Technol. Conf.* (1991)
71. Dallimore, G. R., Stukki, F., and Kasper, D., Measurement of Internal Stresses in Electronic Encapsulating Resins with a Small Solid State Transducer, *SPE J.*, 20(6) (1964)
72. Johnson, S. I., and Ryan, R. J., Encapsulated Component Stress Testing, *Proc. 6th Electrical Insulation Conf.* (Sep. 1965)
73. Schwartz, S., (ed.), *Integrated Circuit Technology*, McGraw-Hill, New York (1967)
74. Sweet, J. N., Peterson, D. W., Tuck, M. R., and Green, J. M., Assembly Test Chip Ver. 04 (ATC04) Description and User's Guide, Sandia National Laboratories (Aug. 20, 1993)
75. Lee, S. M., Licari, J. J., and Litant, I., Reliability of Parylene Films, *Technical Conf. on Defects in Electronic Materials for Devices*, The Metallurgical Society, Boston, MA (1969)
76. Beake, B. D., Goodes, S. R., and Smith, J. F., Micro-impact Testing: A New Technique For Investigating Thin Film Toughness, Adhesion, Erosive Wear Resistance, and Dynamic Hardness, *Surface Engineering*, 17(3) (Feb. 2001)

6

Test Methods

Many test methods, as they relate to assuring reliability, were discussed in Ch. 5. In this chapter, specific details of some of the more widely used methods for testing coatings are given.

Test methods for organic coatings may be characterized at various levels, for example, those used for initial selection and design, qualification, receiving inspection, in-process control, final inspection, and, if necessary, for failure analysis. Test methods may also be broadly classified as: Physical, Electrical, Environmental, Thermal, and Chemical/Analytical (Table 6.1). Only a few of the hundreds of methods used to test the quality and properties of organic coatings and only those most applicable to electronics will be discussed in this chapter. Properties more applicable to commercial and industrial paints and finishes, such as gloss, color, and transparency are omitted. Information on these procedures may be obtained from other sources such as ASTM, IPC, and ISO documents; from paint, varnish, and coatings associations such as the National Paint and Coatings Association, the Paint Research Association, or the Coatings Division of the American Chemical Society; or from companies that supply test instruments such as BYK-Gardner of Columbia, MD and Paul N. Gardner Co., Pompano Beach, FL.

Table 6.1. Tests for Polymer Coatings

Physical/Mechanical	Electrical	Environmental	Thermal	Chemical/Analytical
Viscosity	Insulation Resistance	Humidity Resistance	Thermal Conductivity	Composition and Chemical Changes (IR spectra, mass spectroscopy, gas chromatography, XPS)
Density	Volume Resistivity	Salt Spray Resistance	Thermal Stability (TGA, RGA)	Ionic Content (water extract resistivity, titration)
Surface Tension/ Wettability	Dielectric Constant	Corrosion Resistance	Phase Changes (DTA, T_g)	Elemental Analysis (flame photometry, atomic absorption spectroscopy)
Adhesion	Dissipation Factor	Oxidation Resistance	Coefficient of Thermal Expansion	Voids/Delamination (acoustic microscopy)
Thickness	Dielectric Breakdown Voltage	Solvent and Chemical Resistance	Flammability	
Hardness	Arc Resistance	Radiation Resistance	Temperature Cycling	
Film Integrity/Coverage		Fungus Resistance	Thermal Shock	
Abrasion Resistance				
Flexibility				
Water Absorption and MVTR				
Tensile Strength and Elongation				
Tear Strength				
Stresses (cure shrinkage, CTE mismatches)				

6.1 PHYSICAL/MECHANICAL TEST METHODS

Numerous physical and mechanical tests are available to measure coatings in the liquid state prior to curing and in the solid state after curing or drying. Physical tests such as viscosity, density, and surface tension are useful at the liquid prepolymer stage for quality incoming testing and in-process testing. The integrity of cured films, before and after various stress conditions, may be determined by visual inspection under magnification (to examine for flaws, cracks, pinholes, blisters, or loss of adhesion) and by test methods such as abrasion resistance, adhesion pull testing, and flex testing. If necessary, more detailed and expensive analytical methods such as scanning electron microscopy (SEM), atomic force microscopy, and colorimetric pinhole detection techniques can be employed while SEM of surfaces, cross-sectioning, and other destructive physical analyses (DPA) provide valuable information on failure modes and mechanisms.

6.1.1 Viscosity

Viscosity, a measure of the flow behavior of a liquid, plays a key role in initial receiving inspection of a coating and in its subsequent application. *Viscosity* is a measure of the internal friction of the liquid resulting from intermolecular forces of attraction and other interactions among constituents. For most liquids, known as Newtonian liquids, viscosity, a constant at constant temperature and pressure, decreases with an increase in temperature, and increases with pressure.

Measuring the viscosity of a liquid or paste coating and comparing it with a specified value is an inexpensive method and the results are a good criterion for accepting or rejecting an incoming lot of material. The viscosity of a coating should also be tested periodically during processing since variations occur during spraying or dip immersion of a part and adversely affect the quality, uniformity, and thickness of the coating. Increases in viscosity occur from evaporation of solvent (for solvent-based coatings) and from premature polymerization. Viscosity can be controlled by adjusting the solvent, controlling the temperature, or discarding the coating if its pot life has expired.

Numerous methods and instruments are available for measuring the viscosities of liquid coatings. Among the most widely used are the Brookfield viscometers. They come in several models such as LV for low viscosities,

RV for medium viscosities, and HA or HB for high viscosities. Regardless of model, multiple speeds and interchangeable spindles accommodate different viscosity ranges. Coating viscosities generally range from low 30–1,000 cps for most solvent-based coatings to medium 1000–5000 cps for 100% solids coatings and high, up to 100,000 cps for solder maskants and polymer thick-film pastes. Typical test conditions are Brookfield RV, 5 rpm, # 5 spindle at 25°C for a medium viscosity coating, Brookfield HB, 5 rpm, #14 spindle at 25°C for a high viscosity paste, and a Brookfield LV viscometer for a low viscosity coating.

In addition to the Brookfield viscometers, other instruments that are based on comparing the flow of the coating with standards can be used. Among these are bubble viscometers, cone and plate viscometers, and flow cups. A list of specifications governing viscosity measurements is given in the Table 5 in Ch. 7.

6.1.2 Density

The density of a liquid is the weight per unit volume at a specified temperature, usually 25°C. The density of coatings is often used as a quality control test to verify that changes have not been introduced in the coating formulation by the supplier. Weight-per-gallon cups, also called *pycnometers*, meeting ISO^[1] or ASTM^[2] standards are used. Stainless-steel cylindrical cups holding exact volumes are filled with the coating and weighed. Cups are available having volumes of 8.32 ml, 83.2 ml, and 100 ml. A multiplying factor is used to convert the weight in grams to pounds/gal or to specific gravity. Besides these cup methods, other methods for measuring density are described in ISO-2811-2 to -4.^[3]

6.1.3 Surface Tension and Contact Angle

A knowledge of the surface tensions of both the coating and the substrate to which it will be applied is important in predicting the wettability and subsequent adhesion of the cured or dried coating. As a general rule, the surface tension of the coating should be less than the surface tension of the substrate. Additives are often added to coating formulations to reduce their surface tensions and surfaces such as polyethylene and Teflon are chemically or mechanically treated to increase their surface tensions. Various

instruments for measuring surface tension known as *dynameters* or *tensiometers* are available. Of these, the *DuNouy tensiometer* has been used for decades to measure surface tension. It is based on measuring the force in dynes/cm required to pull a horizontally suspended platinum ring from a liquid. The test method is described in ASTM D971 and ASTM D1331.^[4]

Measuring the contact angle that a liquid makes with a solid surface is a measure of the wettability of the liquid to that surface as well as the cleanliness of the surface. The height of a water droplet on a surface relative to the base area it covers is indicative of the surface's affinity to wetting. Contact angles going from 90 degrees to 0 degrees indicate progressive improvement in wettability with 0 degrees being completely wettable. Contact angles increasing from 90 degrees to 180 degrees indicate progressively poorer wettability with 180 degrees being completely non-wetting.

Contact angle meters, known as *goniometers*, are useful quality control tools to assure that a cleaning process has removed hydrophobic residues or that a liquid coating will wet and adhere to a surface. Instruments to measure surface tensions and contact angles are available from Paul N. Gardner Co. or BYK-Gardner.

6.1.4 Visual Inspection

Microscopic inspection is the simplest method to determine the existence of major flaws in a cured coating. Inspection at 30 times is often all that is necessary to ascertain anomalies such as voids, blemishes, discolorations, and delamination in the coating. Most coatings are now formulated with a small amount of ultraviolet (uv) indicator so that the extent of coverage can be determined by examining the coated part under a uv lamp. Automatic optical inspection equipment is also available.

6.1.5 Adhesion

In practice, three test methods are used to measure and compare *adhesion*, the resistance of coatings to separation from the substrates to which they are applied.

- Tape Adhesion Test (also called the Cross-cut or Cross-hatch Test)
- Scrape Adhesion Test
- Pull-off Test

Tape Adhesion Test. According to this rather simple, but semi-quantitative test, a pattern of lines is cut through the coating to the substrate, a pressure-sensitive adhesive tape is applied, and the tape is pulled rapidly at a 90° angle. Both the tape and the substrate are examined to determine how much coating, if any, was detached and they are rated on an ISO scale of 0 to 5. A simple pattern consists of an X cut, but a right-angle lattice pattern of either six or eleven cuts in each direction provides more quantitative data. Standard patterns are defined in ASTM D3359^[5] and ISO-2409.^[6] A recommended tape is Permacel 99 (Permacel, New Brunswick, NJ). Figure 6.1 pictorially shows the different adhesion classifications. The effects on adhesion of accelerated humidity and temperature or temperature cycling can be determined by first subjecting the coated specimens to the accelerated conditions, then performing the adhesion test.

Scrape Adhesion Test. There are a number of adhesion tests that are based on scraping or scratching the surface of a coating. According to one method, the coating is deposited and cured on a flat metal panel which is then pushed beneath a rounded stylus or loop that is loaded with increasing weights until the coating detaches from the panel. A variety of scratch testers^{[7][8]} is commercially available that meet the requirements of ASTM specifications such as ASTM D2197, D2454, and D5178.

Pull-off Test. According to this test, the minimum tensile stress to detach or rupture the coating in a perpendicular direction is measured. A loading fixture is adhesive bonded perpendicular to the surface of the coating. After the adhesive has been cured, a testing apparatus is attached to the loading fixture and aligned to apply tension perpendicular to the test surface. The force applied is gradually increased and measured until either a plug of coating material is detached or a specified value is reached. The adhesive used must be such that its strength to the coating is greater than the adhesive strength of the coating to the substrate.

6.1.6 Thickness Measurements

Numerous methods and instruments may be used to measure thicknesses of coatings both in the wet stage and the cured stage. The simple micrometer method, ASTM D1005,^[9] is useful more for test panels than for actual parts because sections of the parts must be masked off to obtain an initial thickness reading of the part itself and the base part is usually too thick or bulky to measure with a micrometer. More useful methods are based on magnetic flux and eddy current measurements. ASTM D1186,^[10] for

example, describes two methods for the nondestructive measurement of dry-film thicknesses of nonmagnetic coatings on ferromagnetic surfaces. Test method A utilizes a spring calibrated to measure the force required to pull a permanent magnet from the coated ferrous substrate. The instrument must make good contact with the coating. The magnetic force of attraction varies inversely with the thickness of the film. In method B, a probe in contact with the coating measures the magnetic flux, whose value was previously calibrated with known thicknesses of the film.

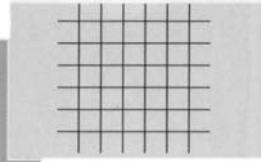
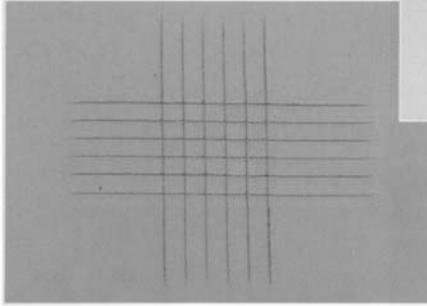
The eddy current method, ASTM D1400,^[11] is another widely used nondestructive method for measuring thickness of coatings—in this case of nonconductive coatings on a nonferrous base. According to this method, a probe in direct contact with the coating is energized by an alternating current that induces eddy currents in the metal substrate. The currents, in turn, create opposing alternating magnetic fields in the substrate that modify the electrical characteristics of the probe coil. The extent of change depends on the distance between the probe and the metal, namely the thickness of the coating.

Other thickness measurements may be made using a light-section microscope, an interferometer, or an ellipsometer. Ellipsometers are used to measure the thickness and monitor the quality of thin dielectric films and also to analyze surface roughness and defects. Ellipsometry is based on the fact that polarized light is altered when reflected from both plain and coated surfaces. From a coated surface, the analysis of the elliptically polarized reflection can be used to determine the thickness of the coating and its refractive index.

6.1.7 Hardness Testing

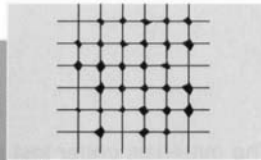
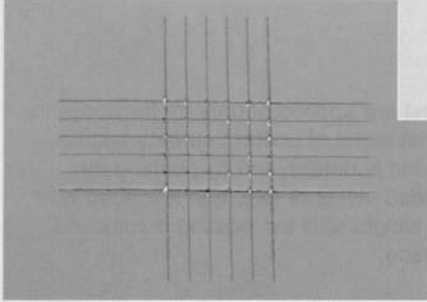
The *Sward hardness test* is a popular and widely used method for measuring hardness. This test is based on the principle that the amplitude of oscillation of a rocking device decreases more rapidly the softer the surface of a coating on which the test is performed. The tester (Fig. 6.2) automatically records the number of swings made by a standard rocker in contact with the test surface before it comes to a stop. The rocker is placed on the test sample and is rolled to the right until the bubble in the left-hand vial is visible. The rocker is then released and each total appearance of the bubble in the right-hand vial is counted. The counter is stopped when the bubble is no longer seen. The automatic counter is based on the photoelectric-eye principle; a shutter on the rocker interrupts the light beam once during each

ISO Class.: 0/ASTM Class.: 5B



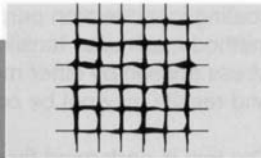
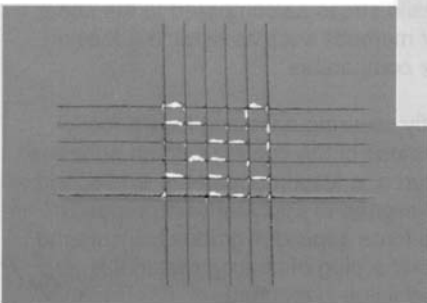
The edges of the cuts are completely smooth; none of the squares of lattice is detached.

ISO Class.: 1/ASTM Class.: 4B



Detachment of small flakes of the coating at the intersections of the cuts. A cross-cut area not significantly greater than 5% is affected.

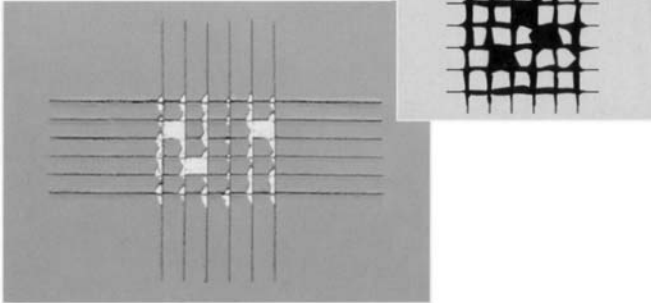
ISO Class.: 2/ASTM Class.: 3B



The coating has flaked along the edges and/or at the intersections of the cuts. A cross-cut area significantly greater than 5%, but not significantly greater than 15%, is affected.

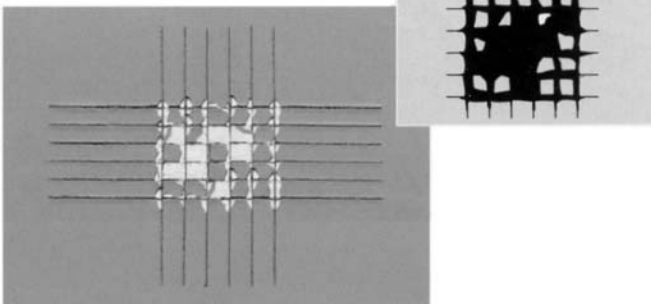
Figure 6.1. Pictorial representations of degrees of adhesion by the tape pull test.
(Courtesy BYK-Gardner.)

ISO Class.: 3/ASTM Class.: 2B



The coating has flaked along the edges of the cuts, partly or wholly in large ribbons, and/or it has flaked partly or wholly on different parts of the squares. A cross-cut area significantly greater than 15%, but not significantly greater than 35%, is affected.

ISO Class.: 4/ASTM Class.: 1B



The coating has flaked along the edges of the cuts in large ribbons, and/or some squares have detached partly or wholly. A cross-cut area significantly greater than 35%, but not significantly greater than 65%, is affected.

ISO Class.: 5/ASTM Class.: 0B

Any degree of flaking that cannot even be classified by classification 4.

Figure 6.1. (cont'd.)

complete oscillation. The coating is normally applied to a rigid, thin substrate, such as aluminum. The test is reported to be sensitive to ± 1 unit.^[12] Values are referenced to the value for polished glass, which is taken as 100.

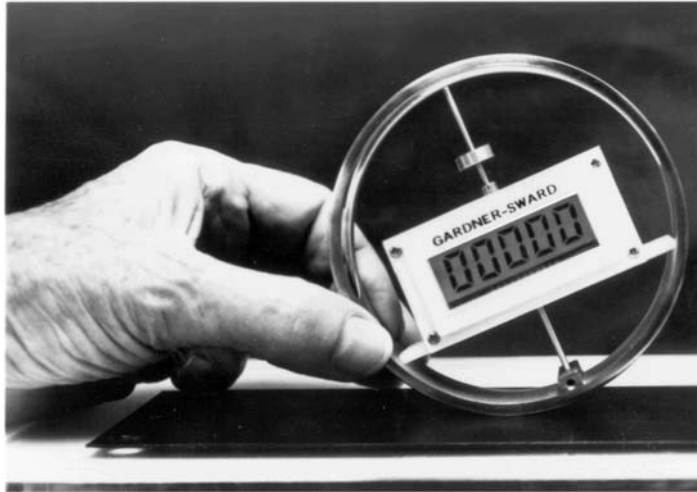


Figure 6.2. Sward Hardness Rocker. (Courtesy Paul N. Gardner Co.)

Other widely used hardness measurements involve indentation of the coating using various instruments. One of these, the durometer, is a small portable spring-loaded indenter that, pressed into the sample, gives a relative analog or digital reading on a 0 to 100 scale. The Shore A durometer is used for soft materials, Shore B for moderately hard, Shore C for medium hard, and Shore D for hard materials. Procedures for durometer hardness testing are given in ASTM D2240.^[13]

The Buchholz indentation tester^[14] and Barcol impressor^[15] are two more examples of easy-to-use portable hardness testers. Some commercial instruments have the capability of measuring Buchholz hardness, adhesion by cross-hatch, and thickness, and all with one portable instrument.^[16]

6.1.8 Pinhole Detection and Porosity Tests

Tests for the detection of pinholes have been covered in Ch. 5 “Reliability Testing and Assurance.” Porosity tests are especially important in determining the penetration of moisture through a coating, for example, moisture vapor transmission rates as described in Sec. 6.1.12. Besides moisture, porous coatings also permeate ambient gases such as sulfur dioxide or other sulfur and nitrogen-containing pollutants that, together with moisture, produce corrosive acids.

Scanning electron microscopy and acoustic microscopy of coated surfaces and cross-sections are two high-resolution methods used to study the morphology of coatings. A simpler test involves changes in reflectance of a coating surface after applying a penetrating colored dye. For a porous surface, the dye will have a high degree of penetration and will change the reflectance properties of the original coating. The dye is applied to the surface, the excess wiped off, and reflectance remeasured according to ASTM D3258.^[17]

6.1.9 Abrasion Resistance

The most widely used test for abrasion is the Taber Abrasion Test, as described in ASTM D4060.^[18] According to this test, two standardized abrading wheels are contacted against a rotating sample that consists of a coated 4-inch square metal panel having a center spindle hole. The panel, weighed to the nearest milligram, is placed on a turntable that rotates at a constant speed while the two abrading wheels are fixed on each side of the spindle in direct contact with the coating. A fixed load, generally 1,000 grams, is attached to the wheels (for example, Calibrase C-17 wheel) and the weight loss of the coating after a specified number of cycles, generally 1,000, is measured. The type of abrading wheel, number of cycles, and load should be specified. The abrasion test can be customized by varying the abrasiveness of the wheels, the weight on the wheels, and the rotations of the sample. In the equipment (Fig. 6.3), a built-in tachometer records the number of turntable revolutions while a vacuum attachment removes the abraded particles from the surface. Results are reported as either the number of cycles to failure per mil of coating thickness or the weight loss, in milligrams, for a specified number of cycles, ranging from 100 to 1,000, referred to as the Taber wear index.



Figure 6.3. Taber Abraser, dual sample Model 5150. (Courtesy BYK-Gardner.)

6.1.10 Flexibility

Although the modulus of elasticity, percent elongation, and tensile strength give quantitative data on the flexibility of a coating, an empirical, but practical and inexpensive test, consists of bending a coated panel around a mandrel and observing any failures due to cracking or loss of adhesion. Several variations of this test are defined by ISO and ASTM specifications. ISO-1519^[19] specifies the use only of cylindrical mandrels, while ASTM D522 and ISO-6860^[20] describe the use of conical mandrels, the latter providing much more information in a single test since the cone mandrel provides a large variety of bending radii in one test.

The impact test, also called the falling-weight test, is a second method to measure the durability of a cured coating. According to this test, a coated panel is subjected to deformation caused by dropping a weight from a specified height. An impact tester is used that consists of a solid base with a guide tube support. The tube has a slot to guide and direct the falling weight. A coated panel is placed under the punch, the weight lifted to a desired height and allowed to free fall onto the panel. Damage to the panel is viewed visually or under magnification. The force of impact is equal to the height times the weight and is recorded in in-lb or m-kg. In addition to indentation on the coated side, bulging can be determined if the uncoated side is also subjected to the falling weight.

6.1.11 Water Absorption

Water absorption for a cured sample of given formulation is reported as the percent of water absorbed at a given temperature in a given period of time. A precisely weighed amount of material is immersed in water at a given temperature or exposed to ambients of various relative humidities at given temperatures and periodically weighed until moisture saturation has been achieved at which point no further increase in weight occurs. Precise gravimetric measurements are generally made using a microbalance or electrobalance. In a rather new automatic method, Dynamic Vapor Sorption (DVS)*, the sample is placed on a Cahn electrobalance, then exposed to a continuous flow of air at a predetermined and constant relative humidity. By plotting the sample mass as a function of time and varying the relative humidity of the air flow, water sorption and desorption curves can be obtained. Figure 6.4 shows a schematic of the DVS analyzer and Fig. 6.5 shows the instrument. Figure 6.6 gives sample absorption curves for Dexter FP4450, an epoxy encapsulant, uncoated and overcoated with silicon oxynitride.^[21]

Suppliers generally measure and report water absorption data based on ASTM D570-98^[22] where a weighed sample is exposed for 24 hours in water at room temperature or at an elevated temperature and then re-weighed. This is a convenient and rapid method to compare coatings, but may not represent the full saturation amount which may take weeks to equilibrate.

6.1.12 Moisture Vapor Permeability

Two widely used methods for measuring the permeability of moisture through a coating (moisture vapor transmission rate) are described in ASTM E96-00^[23] and ASTM D1653-93.^[24] ASTM D1653-93 defines a permeability cup method in which a pinhole-free film of the coating is cast and applied over the mouth of a wide shallow cup or dish that contains a desiccant such as anhydrous calcium chloride or magnesium perchlorate. The cup consists of a shallow cylinder with a threaded flange, a flat retaining washer, and a threaded ring cover (Fig. 6.7). A rubber gasket is used to tightly seal the film between the cup and the ring cover. The sealed part is

*Dynamic Vapor Sorption (DVS)[®] is a trademark of Surface Measurement Systems Ltd-NA.

next accurately weighed on a microbalance and placed in a chamber of controlled humidity and temperature whereby the desiccant draws water vapor through the coating film into the cup. The cup is then reweighed after a specified time period, normally 24 hours. From the surface area of the film, its thickness, and the weight gain of the desiccant, the MVTR can be calculated and reported in standardized units so that various coating types and formulations can be compared. This is called *the Dry Cup* or *Desiccant method*. An alternate method is the *Wet Cup* or *Water method* in which the process is reversed: the cup contains the water and the desiccant is contained in the enclosed chamber. Different relative humidities can be produced in the enclosure by using saturated solutions of various inorganic salts maintained at constant temperature. Both methods require that the coating is free of pinholes or other imperfections and is tightly sealed to the cup.

6.2 ELECTRICAL TESTS

The main electrical properties related to organic coatings are: insulation resistance and volume resistivity, dielectric constant and dissipation factor (derived from capacitance measurements), dielectric breakdown voltage (dielectric strength), and arc resistance. These electrical parameters were discussed in Ch. 1, "Functions of Coatings." Test methods, defined in ASTM, IPC, Military and Federal specifications have been used reliably for many decades by both suppliers and users of coatings. For example, ASTM D150 for dielectric constant and dissipation factor and ASTM D149 for dielectric strength are universally used. These and other electrical test methods are listed in Table 7.4 of Ch. 7.

6.3 ENVIRONMENTAL EXPOSURE TESTS

Predicting the reliability and life expectancy of polymer coatings and coated electronic hardware requires exposure to various accelerated or simulated environments. Environmental chambers are available to test parts at different temperatures, humidities, radiation exposures, pressures, chemicals, and bioorganisms.

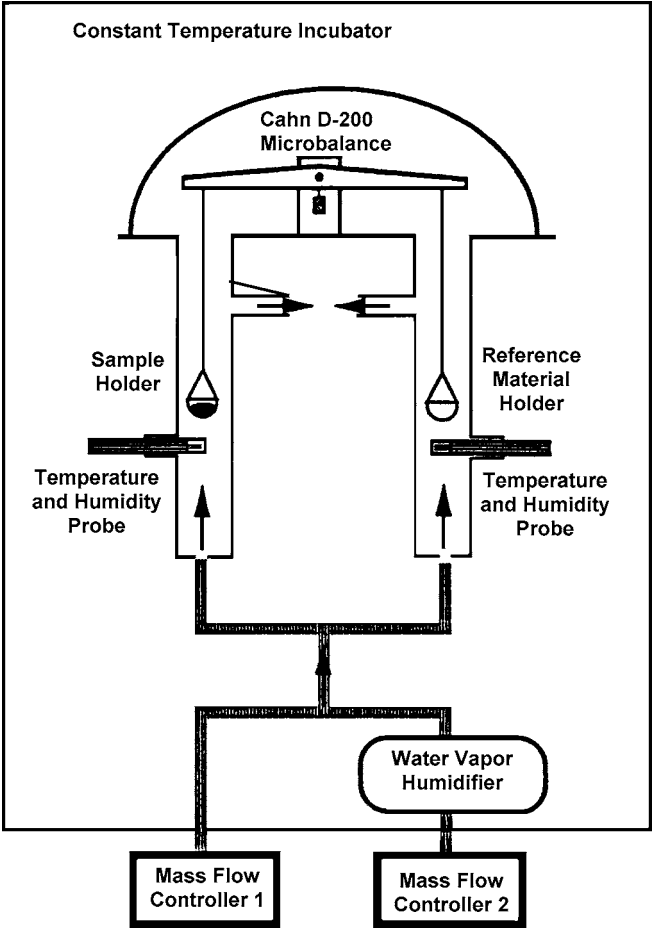


Figure 6.4. Schematic of dynamic vapor sorption analyzer. (Courtesy of Surface Measurement Systems Ltd.)



Figure 6.5. Dynamic vapor sorption analyzer. (Courtesy Surface Measurement Systems Ltd.)

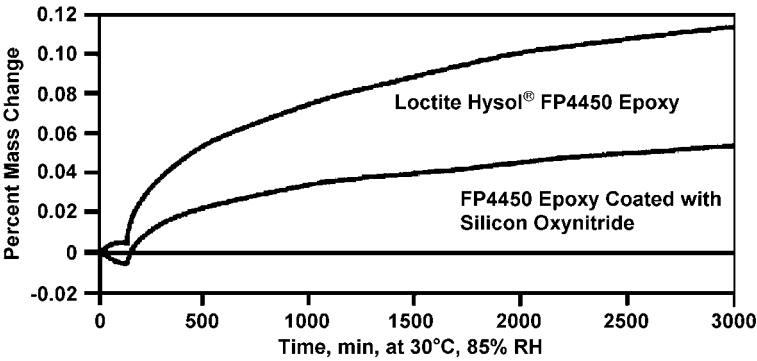


Figure 6.6. Water absorption curves using the DVS Analyzer.^[21]

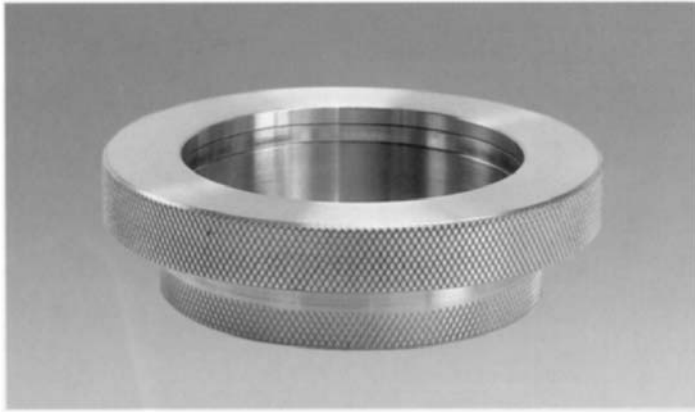


Figure 6.7. Moisture permeability cup. (Courtesy BYK-Gardner.)

6.3.1 Temperature and Humidity Testing

Ovens are available to test parts at elevated temperatures or low temperatures in air, nitrogen ambient, or vacuum at either a constant controlled temperature or with programmed temperature cycling. Other chambers combine temperature with humidity and both temperature and humidity can be kept constant or cycled. The 85/85 test (85°C/85% RH) for 1,000 hours with or without power or a bias is popular in qualifying plastic-coated or encapsulated devices.

In recent years, test chambers with highly accelerated conditions have been developed to obtain data in a matter of hundreds instead of thousands of hours. Among these tests are the HAST (highly accelerated stress test) and PCT (pressure cooker test). In HAST, in addition to temperature and humidity, the parts are subjected to at least 2 atmospheres of pressure as in an autoclave. Conditions can be varied, but are generally either 121°C and 85% RH at 2 atms or 130°C, 85% RH and 2 atm as defined in JEDEC Standard 22-A110.^[25] Although the JEDEC document also allows a 140°C temperature condition, this condition is not advisable since it is known that moisture reduces the effective T_g of a polymer and that stress temperatures above the T_g lead to failure mechanisms unrelated to the

normal degradation mechanism or to the standard 85/85 stress test. In HAST, the parts are biased or powered during the exposure.

The PCT test is essentially HAST without the electrical power or bias as defined in JEDEC Standard A102-A.^[26] Both HAST and PCT are destructive tests used primarily for qualification, life prediction, or initial material selection.

Other simpler environmental chambers can be used to produce relative humidity environments at constant temperatures. Constant humidity ambients may be generated by confining the parts in a desiccator over saturated aqueous solutions of various inorganic salts at some specified temperature. Some of these salt solutions, temperatures, and the respective humidities generated are given in Table 6.2. Other relative humidities ranging from 3.2% to 100% may be produced from aqueous solutions of sulfuric acid at various concentrations and temperatures.^[27]

6.3.2 Weatherability

Weatherability chambers such as the Atlas Weather-Ometer* are used to simulate and accelerate outdoor exposure conditions. They are used extensively by manufacturers of commercial products to determine deterioration from the combined effects of sunlight, temperature, humidity, and rain. Coatings and paints used for corrosion protection of electronic enclosures, connectors, and printed wiring boards can be evaluated to determine their performance under various terrestrial environments such as temperate, subtropical, or tropical.

In the Weather-Ometer, a high-intensity xenon-arc lamp is situated at the center of a stainless-steel chamber. Specimens to be exposed are mounted on a barrel-shaped rack that rotates about the center of the lamp. The shape and motion of the rack are designed to uniformly enhance the irradiation. Atomized water is introduced into a compressed stream of air to generate various relative humidity conditions. If desired, simulated rain can be produced from an array of water nozzles. The lamp output simulates sunlight.

All four exposure parameters can be increased to accelerate the testing. The percentage of time that the part is exposed to the simulated sunlight in a 24-hour period can be increased to 100% and light levels greater

*Weather-Ometer® is a trademark of Atlas Material Testing Technology LLC.

than “one sun” can be used. Superimposed on this added radiation, higher air temperatures and humidities can be used.^[28]

Table 6.2. Constant Humidities of Aqueous Solutions of Inorganic Salts

Saturated Aqueous Solution of:	Formula	Temp, °C	% Humidity
Sodium iodide	NaI	100	50.4
Sodium bromide dihydrate	NaBr · 2H ₂ O	20	58
Magnesium acetate tetrahydrate	Mg(C ₂ H ₃ O ₂) ₂ · 4H ₂ O	20	65
Ammonium chloride and potassium nitrate	NH ₄ Cl, KNO ₃	25	71.2
Sodium acetate trihydrate	NaC ₂ H ₃ O ₂ · 3H ₂ O	20	76
Ammonium chloride	NH ₄ Cl	20	79.5
Ammonium sulfate	NH ₄ SO ₄	20	81
Potassium bromide	KBr	20	84
Zinc sulfate septahydrate	ZnSO ₄ · 7H ₂ O	20	90
Sodium sulfite heptahydrate	Na ₂ SO ₃ · 7H ₂ O	20	95
Copper sulfate pentahydrate	CuSO ₄ · 5H ₂ O	20	98

6.3.3 Ionizing Radiation Exposure

A cobalt-60 source is the preferred source for total dose radiation testing because it penetrates all the electronics and packages and uniformly irradiates the part. Cobalt-60 produces a 1.1 and 1.3 MeV gamma pair. A testing procedure is defined in MIL-STD-1019.5, according to which parts are irradiated over a period of several days or weeks. Generally, for space missions, where the dose rates are low, the total doses are high due to the lengths of the missions.

6.3.4 Fungus Resistance

Fungus resistance tests are used to determine the resistance of materials to various species of fungi under favorable growth conditions of high humidity, warm ambient, and the presence of inorganic salts. One

method, widely used to test polymer coatings for fungus resistance, is described in IPC-TM-650, Method 2.6.1.1.^[29] Directions are given for the careful preparation of spore suspensions of five different fungi (Table 6.3). A mixed suspension of the five different spores is prepared and sprayed onto coated glass slides to inoculate them. At the same time, control samples coated with a material known to be fungus nutrient are also inoculated. The samples are stored in an incubator chamber at 30°C and a relative humidity of ≥85% and examined after 7 days. If both the nutrient controls and the test specimens show fungus growth, the test coating is considered fungus nutrient. If the control shows growth, but the test specimen does not, the incubation period is extended for a total of 28 days. The test coating is considered resistant to fungus if, at the end of this time, it does not show fungus growth. Some specimens may show corrosion that must be distinguished from fungal growth and reported as such.

Other test methods for fungus resistance are listed in Table 7.5, Ch. 7.

Table 6.3. Mixed Spore Suspension for Fungus Resistance Test^[29]

Description of Fungus	ATCC* Number
Aspergillus niger	9642
Chaetomium globosum	6205
Gliocladium virans	9645
Aureobasidium pullulans	9348
Penicillium funiculosum	9644
*American Type Culture Collection	

6.4 THERMAL TESTS

Thermal testing comprises tests to measure thermal conductivity, thermal stability and phase changes, and flammability.

6.4.1 Thermal Conductivity and Test Methods

Thermal conductance and conductivities are derived from the Fourier equation given below. The total amount of heat a material conducts

rectly proportional to the surface area, the time of contact, and the temperature gradient and is inversely proportional to the thickness of the sample, according to the equation

$$\text{Eq. (6.1)} \quad Q \propto (T_2 - T_1) \frac{At}{d}$$

where: Q = total heat flow in joules (J)

A = surface area, m^2

d = thickness of sample, m

T_2 = temperature of the hot surface, $^{\circ}\text{C}$ or K

T_1 = temperature of the cold surface, $^{\circ}\text{C}$ or K

t = time, sec

When a proportionality constant, k , is introduced, the thermal conductivity equation becomes

$$\text{Eq. (6.2)} \quad Q = k(T_2 - T_1) \frac{At}{d}$$

$$\text{and} \quad k = \frac{Qd}{(T_2 - T_1)At} = \frac{J}{m \text{ K sec}}$$

$$\text{since} \quad \text{watts} = \frac{J}{\text{sec}}; k = \frac{\text{watts}}{m \cdot K}$$

The constant k is a material constant called the *coefficient of thermal conductivity*. It is the time rate of heat flow under steady-state conditions through a unit area and unit thickness per unit temperature gradient. Thermal conductivities of electronic materials are generally expressed as watts per meter per degree Kelvin (watts/m·K).

Several methods for measuring thermal conductance are available, of which the *guarded-hot-plate* and *heat-flow meter* methods are the most widely used. The most accurate method for plastics having thermal conductivities of 3.4×10^{-3} cal/(sec)(cm)($^{\circ}\text{C}$) or less (most filled and unfilled polymers) is the guarded-hot-plate method as described in ASTM C177.^{[30][31]}

Guarded-hot-plate Method. Two types of guarded-hot-plate apparatus can be used. They are similar in principle, but differ somewhat in construction. One example, shown in Fig. 6.8, consists of three sections: a central heating plate, guard heating plates, and cooling plates. The guard portion insures unidirectional heat flow from the central heater and

eliminates any influences from the edge of the sample. Thermocouples are located at various positions in the guarded hot plate to measure the difference between the temperature of the guard ring and central heater and the temperature of the hot and cold surfaces. The central heating unit and cooling units are adjusted until the temperature drop through the two sides does not differ by more than 1% and the fluctuation over a one-hour period is no greater than 0.5% of the temperature difference between the hot and cold plates. When equilibrium is reached, measurements are taken of the temperature differences across specimens; the hot-plate temperature, T_2 ; the cold-plate temperature, T_1 ; and the electrical power input, Q , to the central heater. Knowing the thickness and area of the sample, the thermal conductivity can be calculated using the thermal conductivity equation given above. The sample thickness may vary with the maximum thickness based on calculations listed in ASTM C177.^[30]

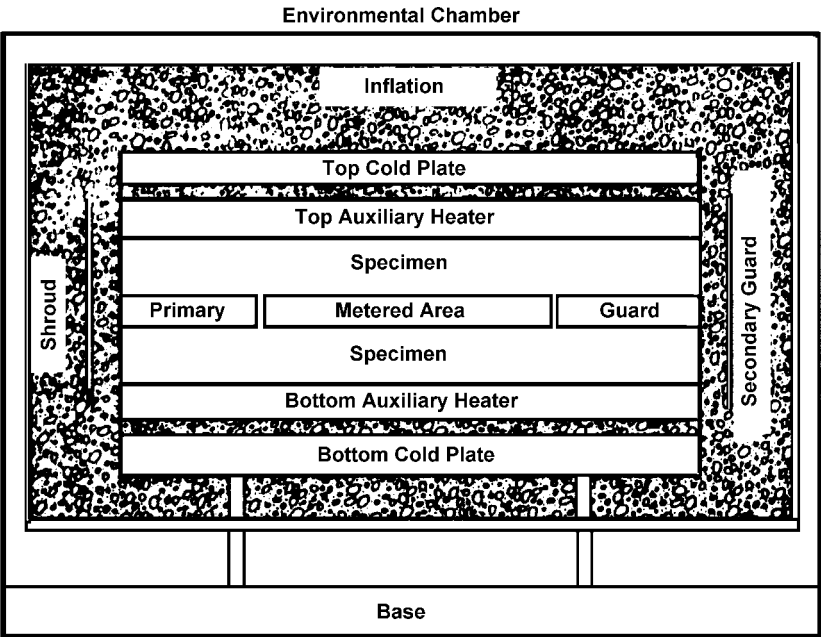


Figure 6.8. Schematic for guarded-hot-plate apparatus.

Heat-Flow-Meter Method. The steady-state thermal transmission properties of an insulator can be measured using a heat-flow meter. This

is a secondary or comparative method of measuring thermal conductivity since only the ratio of the thermal resistance of the specimen to that of a standard specimen is measured. According to this method, described in ASTM C518,^[32] a sample is placed between a warm and cold plate. The meter measures heat flow through the specimen by generating a temperature difference across a slab of material of known thermal resistance.

A calibration curve is generated using samples of known thermal conductivities. These samples should have thermal conductivities close to those expected of the samples tested. Sample thicknesses may range from 0.001 to 0.8 inches, but for accuracy, the sample should have a C value (thermal conductivity divided by sample thickness) of less than 400 W/m.K. In the heat-flow meter method, the spacing between the warm and cold plates is based on the theoretical maximum thickness of the specimens in the conventional guarded-hot-plate apparatus. Calculations of this spacing may be found in ASTM C518.

6.4.2 Thermal Stability

With increasing temperature, organic coatings and plastic materials, in general, undergo a variety of changes from simple changes of state (for example, melting, softening, subliming, or glass transition phase changes) to catastrophic decomposition due to fracture of the polymer structure, oxidation, and outgassing of decomposition products. The thermal limits of a coating should be known or measured to assure that the material will remain stable under the actual operating conditions or accelerated conditions, if those are used as screening or qualifying tests. Key methods used to assure thermal stability include TGA, DTA, TMA, Infrared (IR) spectrographic analysis, gas chromatographic and mass spectrometric analyses, and changes in mechanical properties such as tensile strength and elongation. These analytical methods may also be used to study chemical and physical changes that occur from exposure to various types and intensities of radiation. The degradation products of radiation often parallel those from thermal exposure.

Thermal Gravimetric Analysis. Thermal gravimetric analysis (TGA) has been used for many decades as a quantitative measure of the total weight loss of outgassed products from polymers as they are heated at a controlled rate. A TGA apparatus consists of a precision electrobalance contained within a controlled temperature oven such that the change in mass of a sample can be dynamically measured as a function of increasing

temperature. The temperature is increased at a programmed rate or the sample may be kept at constant temperature and weight changes recorded as a function of time (isothermal gravimetric analysis, IGA). Sample weights of several milligrams to several grams can be accommodated and weight losses or gains as little as 0.5 micrograms can be measured. The programmed rate of temperature increase is normally 10°C per minute. Weight-loss versus temperature curves (TGA curves, also known as pyrograms) are useful in determining the onset of outgassing, the weight loss at a specified temperature, and the temperature at which total decomposition occurs. TGAs may be conducted in nitrogen or, when thermal oxidative stability is being evaluated, in air.

Thermogravimetric analyzers may be connected to a variety of chemical analyzers to determine the exact composition of the outgassed materials as they are evolved. Among chemical analysis methods are gas chromatography, infrared spectroscopy, and mass spectroscopy; for example, a TGA apparatus may be coupled with a FTIR (Fourier Transform Infrared) spectrophotometer to measure the thermal oxidative stabilities of several fluorinated polyimides.^[33]

Differential Thermal Analysis. In differential thermal analysis (DTA), also known as differential scanning calorimetry (DSC), the heat input (endotherm) or heat generated (exotherm) of a material is continuously monitored while it is subjected to a controlled temperature increase. The heat changes measured correspond to phase changes that occur at the indicated temperature, for example, they may consist of glass transitions, softening or melting, oxidation, sublimation, or decomposition—all characteristics of a given material.^{[34]–[36]} Applications include determination of the degree of cure and thermal stability of polymeric materials. Like TGA, small sample sizes in the low milligrams are used. The heating rate may be 5 to 20°C/min, and the thermal exposure may be conducted in an inert or air ambient.

Thermomechanical Analysis. Thermomechanical analysis (TMA) is used to measure a material's expansion coefficient or deflection temperature under load. Thermomechanical analysis continuously monitors the expansion or contraction of a sample as a function of loading and temperature. Numerous references and books on thermal analysis are cited by Wunderlich.^[37]

6.4.3 Flammability

Flammability tests for coatings and other polymeric materials are governed by several documents including ASTM D635, UL-94, UL-1581, and NASA-STD-6001.^[38] Since the Apollo fire in 1966, considerable attention has been given to the materials used in all manned spacecraft. Flammability tests in air and in oxygen have been developed and thousands of materials tested and rated based on their degree of flammability. All flight hardware used in NASA manned space programs must now comply with the requirements of NASA-STD-6001. In this specification, a *nonflammable material* is defined as one that self extinguishes within six inches when ignited and does not propagate a flame by transferring burning debris. The standard chemical ignition source is energy of 750 ± 50 cal, $2000 \pm 160^\circ\text{F}$, for 25 ± 5 sec.

A variety of bench-scale equipment is available to produce precise analytical data used to predict full-scale fire performance. Samples are exposed to a controlled flame in horizontal, vertical, or combined horizontal-vertical flame chambers that meet UL requirements.^[39]

In general, polymer coatings do not constitute a major fire hazard since they are used in small amounts and in thin layers. Many, such as polyimides, silicones, and fluoropolymers, are inherently nonflammable. In fact, some fluoropolymer coatings such as Fluorel* are used as an overcoating to protect flammable plastics from burning.

6.5 CHEMICAL/ANALYTICAL TESTS

A wide variety of chemical and instrumental methods are available for analyzing chemical structures, composition, outgassing products, and products of decomposition of organic materials resulting from exposures to elevated temperatures, humidity, or radiation. Some of these methods are particularly useful in conducting failure analyses of electronic circuit boards and modules.^{[40][41]} Because of the expense of equipment and the expertise

*Fluorel® is a tradename of 3M Co.

involved, most companies procure the services of certified analytical laboratories. A few of the methods and instruments most widely used in electronics are discussed below.

6.5.1 Infrared Spectroscopy

Infrared spectroscopy (IR) is an excellent method for determining chemical changes that occur in organic materials through decomposition, oxidation, polymerization, reactions with other compounds, or changes in the formulation.

Infrared spectroscopy is also a valuable tool for detecting and identifying organic compounds, polymer types, impurities in compounds, and for quantitative analysis of mixtures of compounds. Infrared spectra result from different modes of vibration and rotation within a molecule. Pure rotational spectra occur at the long wavelengths (greater than 25 μm). At shorter wavelengths, the radiation has sufficient energy to cause changes in vibrational levels of the molecule. Thus, the frequencies of vibration are related to the masses and binding forces of the atoms which become the basis for infrared in determining the structure of a compound. The region of most interest for the analysis of organic materials lies between 2 μm and 15 μm where specific groups absorb at definite frequencies or wavelengths.

The percent absorption or transmission of infrared radiation by a material when scanned over wavelengths of approximately 2 μm to 15 μm provides a “fingerprint” of the material that is useful in determining the exact nature of the compound. Absorptions at specific wavelengths in the near infrared are indicative of various groups within a molecule such as amino, carboxyl, keto, or hydroxyl groups, while absorption in the far infrared is indicative of the nature of the molecule as a whole. The spectrum obtained may also be compared with spectra of known compounds as recorded in the literature.^{[42][43]}

6.5.2 Gas Chromatography

In gas chromatography, the components of a mixture are separated by volatilizing the sample and passing the gases through a column of solid porous material of 20 to 200 mesh or onto thin layers of finely divided solids. In one method, gas-liquid chromatography, the surface of the packing

is coated with a nonvolatile liquid (the stationary phase). If the liquid is not present, the process is called gas-solid chromatography. The principle of chromatography is based on the different rates at which the chemical components pass through the packing material and their detection as separate species as they exit the column. The components may be detected by thermal conductivity changes, density differences, or by ionization detectors.

6.5.3 Mass Spectrometry

Mass spectrometry is an excellent analytical method for the quantitative measurement of trace amounts of gases and low molecular weight organic species. In residual gas analysis (RGA), the outgassing from coatings and other organic materials such as moisture, carbon dioxide, carbon monoxide, and low molecular weight hydrocarbons can be measured in low parts per million.

By mass spectrometry, molecules are first activated and dissociated into ionic fragments that are then separated according to their charge-to-mass ratios. Mass spectrometers essentially consist of four parts: equipment to ionize the sample, an ion accelerator, an ion separation system, and a detection system. The sample may be ionized by bombardment with electrons from a heated filament or by several other means. The ions produced are then accelerated and focused electrostatically and separated according to their atomic masses while traveling through a magnetic field. A variation of magnetic separation equipment, widely used today, is the quadrupole mass spectrometer. This equipment consists of four cylindrical rods arranged in an orthogonal array. Opposite rods are electrically connected and opposite voltages applied. The positively charged pair acts as a low-mass pass filter while the negatively charged pair acts as a high-mass pass filter. By adjusting the voltages on the two pairs of rods, the quadrupole is made into a narrow bandpass mass filter. The separated ions are then detected electrically. The ion beams are scanned across a collector where they pick up electrons and generate an electric current that is amplified and analyzed by computer. As with infrared spectra, an extensive database of mass spectra of chemical compounds is available and can be used to compare with the mass spectrograph of an unknown to verify its nature.^[43]

6.5.4 Elemental Analysis

The total ionic content and the amounts of specific metal ions such as sodium and potassium greatly affect the electrical properties of a coating and of the electronic circuits they are intended to protect. A simple test to determine the total ionic content of a polymeric material is to digest a weighed powdered sample in deionized water and measure the resistivity of the water extracts. This test gives a rough idea of the extent of ionic contaminants in the sample. For example, a drop in resistivity from 10 megohm-cm to 10,000 ohm-cm indicates a considerable amount of ionic species. Exact elemental analysis can then be performed by evaporating off the water and analyzing the residue by atomic absorption spectroscopy or flame photometry. These are emission spectrographic methods whereby the atoms or molecules of the sample on being excited by energy input from an arc, spark, or flame, emit wavelengths of radiation as they return to the normal state. These wavelengths indicate qualitatively and quantitatively the atomic species present in the sample. The spectra of the elements consist of lines of distinctive color, for example, the yellow sodium D line for sodium. The spectra of molecules consist of groups of lines called bands. The number of lines present in an emission spectrum depends on the number and position of the outermost electrons and the degree of excitation of the atoms.

A simple qualitative test for chloride ions consists in immersing or swabbing the part in deionized water and adding a few drops of 0.1N silver nitrate solution to the water extracts. A white turbidity or precipitate indicates that an insoluble silver chloride has formed and that chloride ions may have been present. The test, however, is not entirely specific for chlorides since a few other anions such as sulfate also form an insoluble compound and must then be distinguished by other qualitative or quantitative methods.

6.5.5 X-ray Photoelectron Spectroscopy

X-ray photoelectron spectroscopy (XPS), also known as ESCA (Electron Spectroscopy for Chemical Analysis), is based on the ejection of electrons from a surface when photons impinge on it. Photon sources are usually Al K α (1486.6 eV) or Mg K α (1253.6 eV). XPS analysis is highly surface specific due to the short range of the photoelectrons that are excited from the solid. The analysis must be performed in ultrahigh vacuum. The energy of the photoelectrons leaving the sample are determined using a

concentric hemispherical analyzer that gives a spectrum consisting of a series of photoelectron peaks. The binding energy of the peaks is characteristic of each element. The peak areas can be used with appropriate sensitivity factors to determine the composition of the material surface. A compilation of XPS spectra is available for comparison and verification of results.^[44] XPS can detect all elements except hydrogen and helium.

6.5.6 Acoustic Microscopy

Surface acoustic microscopy (SAM) is an ideal nondestructive method for revealing internal flaws within and between materials. It is particularly useful in the analysis or evaluation of many types of electronic parts, including ceramic and plastic encapsulated ICs, plastic encapsulated microcircuits (PEMs), hybrid microcircuits, CSPs, PBGAs, and PWBs.

The acoustic microscope produces an image by mechanically scanning with an ultrasonic transducer in an *X,Y* pattern over the test specimens. This “scan” is performed in a vessel filled with deionized water or other liquid that couples the ultrasonic energy from the transducer to the part. Water is the most effective medium, but where the electronic part is sensitive to moisture, other liquids such as alcohols can be used. The transducer emits a short ultrasonic pulse and then detects the echo. If the part is free of defects, there will be two signals, from the near and far surface. If there is an internal defect, such as a void or delamination, the transducer will detect an additional return signal. This signal has a direct relationship to the depth of the defect. Moreover, acoustic images from several depths can be acquired simultaneously, revealing defects at each interface in an electronic device.

Images are typically displayed as either C-scans or B-scans. A C-scan is an overall *X,Y* view of the test specimen at a particular depth or interface. A color scale or black and white image displays signal amplitude. B-scans display an image of a cross-sectioned view at a chosen location with the scan indicating signal amplitude.

Acoustic microscopes have the flexibility to adapt different transducers for different applications from low-frequency transducers (1 through 15 MHz), used for finding large flaws in thick materials through which sound travels slowly, to 50 MHz transducers that can examine thin Kovar* of 30 mils or aluminum up to 200-mils thick. Higher frequency transducers

*Kovar® is a registered tradename of Carpenter Technology.

are needed for thin substrate materials such as alumina or gallium arsenide. The higher frequency transducers allow finer resolution and greater detail, but at the expense of lower penetrating power. The acoustic microscope has the software to analyze the image once the scan is completed. Analysis tools include: histogram (for percentage of voids), vertical and horizontal profile, zoom, manipulation of color scale, measurements, multiple scans format, and a variety of other analysis tools. The system also has the capability to print either in color or black and white, or to transmit images electronically over the network.

REFERENCES

1. ISO-2811-1, Determination of Density-Part 1: Pycnometer, *ISO Standards Handbook, Paints and Varnishes*, 1(1) (2002)
2. ASTM D1475, *Standard Test Method for Density of Liquid Coatings, Inks, and Related Products*, Am. Soc. for Testing and Mater.
3. ISO-2811: Determination of Density, Part 2: Immersed Body; Part 3: Oscillation Method; Part 4: Pressure Cup, *ISO Standards Handbook, Paints and Varnishes*, 1(1) (2002)
4. ASTM D971, *Surface Tension of Paints and Coatings by the DuNouy Ring Pull-off Method*, Am. Soc. for Testing and Mater.
5. ASTM D3359, *Standard Test Method For Measuring Adhesion by Tape Test*, Am. Soc. for Testing and Mater.
6. ISO-2409, Cross-cut Test, *ISO Standards Handbook, Paints and Varnishes*, Vol. 1 (2002)
7. Testing Instruments Catalog, Paul N. Gardner Co., Pompano Beach, FL (2001)
8. Instruments 2001 Catalog, BYK-Gardner, Columbia, MD (2001)
9. ASTM D1005, *Standard Test Method for Measuring Dry Film Thickness of Organic Coatings Using Micrometer*, Am. Soc. for Testing and Mater.
10. ASTM D1186, *Non-destructive Measurement of Dry Film Thickness of Non-magnetic Coatings Applied to a Ferrous Base*, Am. Soc. for Testing and Mater.
11. ASTM D 1400, *Non-destructive Measurement of Dry Film Thickness of Non-conductive Coatings Applied to a Non-ferrous Metal Base*, Am. Soc. for Testing and Mater.

12. Moore, D. T., Precision of the Sward Hardness Rocker, *Paint, Oil, Chem. Rev.*, 113(21):41 (1950)
13. ASTM D2240, *Standard Test Method for Hardness, Shore A or D*, Am. Soc. for Testing and Mater.
14. ISO-2815, Buchholz Indentation Test, *ISO Standards Handbook, Paints and Varnishes*, 1(1) (2002)
15. ASTM C581, *Standard Test Method for Hardness: Barcol Impressor*, Am. Soc. for Testing and Mater.
16. Elcometer 121/2, Technical Data Sheet, Elcometer Instruments, Ltd., Edge Lane, Manchester, England.
17. ASTM D3258, *Standard Test Method for Porosity of Paint Films*, Am. Soc. for Testing and Mater.
18. ASTM D4060, *Abrasion Resistance for Cured Paints by Taber Abrader*, Am. Soc. for Testing and Mater.
19. ISO-1519, Bend Test (cylindrical mandrel), *ISO Standards Handbook, Paints and Varnishes*, 1(1) (2002)
20. ASTM D522, *Standard Test Method for Mandrel Bend Test of Attached Organic Coatings*, Am. Soc. for Testing and Mater.
21. Licari, J. J., Congleton, H., and Stuhlbarg, S., A Novel Process For High Reliability Non-Hermetic Packaging, *Proc. IEPS Conference*, San Diego (1995)
22. ASTM D570-98, *Standard Test Method For Water Absorption of Plastics*, Am. Soc. for Testing and Mater.
23. ASTM E96-00, *Standard Test Methods for Water Vapor Transmission of Materials*, Am. Soc. for Testing and Mater.
24. ASTM D1653-93, *Standard Test Methods for Water Vapor Transmission of Organic Coatings*, Am. Soc. for Testing and Mater.
25. JEDEC Standard 22-A110, *Highly Accelerated Temperature and Humidity Stress Test (HAST)*, Electronic Industries Alliance (Jul. 1988)
26. JEDEC Standard 22, Method JESD22-A102-B, *Accelerated Moisture Resistance-Unbiased Autoclave*, Electronic Industries Alliance (Mar. 1991)
27. Lide, D. R., (ed.), *Handbook of Chemistry and Physics*, 81st Ed., CRC Press (2000)
28. Case, R., and Scott, K. P., *Coatings That Weather the Testing Storm*, Photonics Tech. Briefs (Jan. 2000)
29. IPC-TM-650, Method 2.6.1.1, *Fungus Resistance-Conformal Coating*, Institute for Interconnecting and Packaging Electronic Circuits, Northbrook, IL (Jul. 2000)

30. ASTM C177, *Standard Test Method for Steady State Heat Flux Measurements and Thermal Transmission Properties by Means of Guarded Hot Plate Apparatus*, Am. Soc. for Testing and Mater.
31. Anderson, D. R., Thermal Conductivity of Polymers, *Chem. Rev.*, Vol. 66 (1966)
32. ASTM C518, *Standard Test Method for Steady State Thermal Transmission Properties by Means of Heat Flow Meter Apparatus*, Am. Soc. for Testing and Mater.
33. Turk, M. J., et al., Evaluation of the Thermal Oxidative Stability of Polyimides via TGA Techniques, Part A, Polymer Chemistry, *J. Polymer Sci.*, Vol. 37 (1999)
34. Brennen, W. P., and Cassel, R. B., *Thermal Analysis Application Study 25*, Pittsburgh Conference Paper No. 569 (Apr. 1978)
35. Murphy, C. B., Differential Thermal Analysis, *Anal. Chem.* 32:168R–171R (1960)
36. Murphy, C. B., Differential Thermal Analysis, *Anal. Chem.*, 34:298R–330R (1962)
37. Wunderlich, B., *Thermal Analysis*, Academic Press (1990)
38. NASA-STD-6001, *Flammability, Odor, Offgassing and Compatibility Requirements and Test Procedures for Materials in Environments That Support Combustion*, NASA.
39. Technical brochures, Atlas Electric Devices Co., Chicago, IL.
40. Day, R. A., Underwood, A. L., and Underwood, A. L. Jr., *Quantitative Analysis*, 6th Ed., Prentice Hall, NJ (1991)
41. Mermet, J. M., Otto, M., Widmer, H. M., and Kellner, R. (eds.), *Analytical Chemistry*, John Wiley & Sons (1998)
42. Bellamy, L. J., *Infrared Spectra of Complex Molecules*, 3rd Ed., Chapman and Hall, London (1975)
43. NIST Standard Reference Database, No. 69, *NIST Chemistry WebBook*, <http://webbook.nist.gov/> (Jul. 2001)
44. Crist, B. V., *Handbook of Monochromatic XPS Spectra*, John Wiley & Sons (2000)

Specifications and Documents

Various types of specifications and documents are used to assure the quality of the incoming material, high process yields, and reliability during the life expectancy of the product. Specifications also serve as documents and agreements binding the customer, the contractor, and the contractor's suppliers. Hence, well-written, clearly defined requirements that are approved by all parties at the start of a program will avoid product failures, retrofitting costs, and legal disputes. Among documents recommended for coating electronic parts are: a top-level performance/requirements specification, material procurement specifications, process specifications, work instructions, test methods documents, and a failure analysis and corrective action document.

7.1 TOP-LEVEL PERFORMANCE OR REQUIREMENTS SPECIFICATION

The responsibility for the top-level requirements specification rests with the customer or contracting agency. Generally, this is the manufacturer of the electronic product or system or the final user. In the performance specification, the requirements that the electronics must meet are specified. These include electrical and physical performance over a

defined period of time and under specified environmental conditions. The specification includes a variety of electrical, mechanical, and thermal tests that the product must meet. The contractor who builds the parts must select and demonstrate that components, materials, and processes will meet those specifications.

7.2 MATERIAL SPECIFICATIONS

The final choice of a coating, primer, or process is best implemented by means of material specifications written by the user and coordinated with the supplier. The material specification is a document used both for initial qualification of a material to specific engineering requirements and for receiving inspection of an already qualified source to assure continued consistency and quality. The material specification may also be used as a procurement document and, when called out on a purchase order, legally binds the supplier to meet the quality assurance provisions of the specification, especially if a certificate of compliance from the supplier is required. Material specifications may be general or specific. The general type defines the minimum engineering requirements and the maximum allowable tolerances that a product must meet. This type of specification is written without concern for what materials are on the market and thus may be satisfied by a number of different coating types and formulations. Conversely, its provisions may be such that only one material or no material will qualify.

The second type of material specification is specific and is written around the properties of a specific material, one that is known to qualify and whose reliability has been established. The actual formulation may be called out, or the physical, chemical, and electrical properties may be narrowly defined so that only one material will be able to qualify. To obtain extra assurance, a specific material specification may require that an infrared spectrograph be run and compared with the IR spectrum of the originally qualified material. The IR spectra of organic materials differ widely, depending on their chemical structure, formulation ingredients, and purity. Hence, to assure that the formulation has not been changed or the purity of the material altered, the IR spectrum of each lot of the material must match that of the original standard. The IR spectrum is fairly simple to run from a small sample and the test equipment, an infrared spectrophotometer, is available in many low-priced models or the sample may be sent out for analysis.

For electronic components or assemblies that are not coated in-house but purchased already coated, an acceptance specification will be useful to assure quality. In such cases, both nondestructive and destructive tests may be specified to assure that the product is adequately coated with the specified coating. In the case of low-cost electronic components such as capacitors or resistors, destructive analysis may be performed on a sampling basis from each lot. Examples of tests that may be performed include: adhesion, water soak, high-temperature exposure, salt spray, and humidity with and without power.

7.3 PROCESS SPECIFICATIONS

A process specification is written to provide a step-by-step procedure to produce a part in a manufacturing environment. It often calls out other process specifications, for example, the conformal coating portion of a printed wiring assembly specification may call out a separate specification that covers the processes for cleaning, applying, and curing the coating. A process specification should also contain quality assurance provisions such as in-process and end-of-process tests and inspection. The process specification should allow as much manufacturing freedom as possible within the constraints of the engineering requirements. For example, instead of specifying one cure schedule, whenever possible, a selection of equivalent schedules should be allowed. One approach that has proved convenient is to provide a time-temperature curve, however, the equivalence of the cure schedules should be proven by measuring the properties of the cured coating. If the method of application is not critical, the freedom to choose between spray or dip coating should also be allowed.

In summary, a rigid specification should be imposed only when absolutely essential; otherwise unnecessary cost will be imparted to the final product.

7.4 WORK INSTRUCTIONS

Work instructions are generated from the process specification. They consist of subtier documents that simplify, clarify, and provide details of the process for the factory operators. For example, from a coating

process specification separate WIs may be generated for the cleaning, application, and the curing steps.

7.5 FAILURE ANALYSIS DOCUMENTATION

The manufacturer should develop a document detailing the procedures for testing, analyzing, and taking corrective actions on parts that fail during all stages of manufacturing and from field returns. The document should include specific steps to be followed when a failure occurs including the sequence of tests starting with electrical probing, visual, and other nondestructive tests before destructive tests are instituted.

7.6 MILITARY, SPACE, GOVERNMENT, AND INDUSTRY SPECIFICATIONS

Thousands of military, space, government, and industry specifications relating to materials, processes, test methods, and test requirements already exist. Among test methods widely used for coatings are those described in MIL-STD-202, IPC-TM-650, and FED-STD-141.

Specifications should not be written where these government and industry association specifications already exist and are found to be applicable. It should be noted, however, that conformance of a material or process to a military, government, or industry specification does not assure that it will be suitable for the intended application. Too often military and industry documents are not specific enough to provide the required reliability. In those cases, a short internal company specification may be written that calls out the government or industry document, then adds the extra requirements.

In the last decade many military and government specifications have been canceled and replaced by industry documents, especially those relating to test methods. With the government's emphasis on using COTS (Commercial Off The Shelf) parts, specifications generated by industry associations such as ASTM, IPC, ANSI, ISO, EIA, and NEMA have become dominant. FED-STD-141, for example, that used to specify test

methods for paints, varnishes, lacquers, and other coatings is now simply a listing of methods that have been canceled and the ASTM methods that have replaced them.

7.7 SPECIFICATIONS RELATING TO ORGANIC COATINGS

Specifications and standards may be procured from the various organizations listed in Table 7.1. Tables 7.2–7.7 list some government and industry association specifications, test methods, and other documents pertinent to organic coatings, paints, and finishes for electronic applications.

Table 7.1. Sources of Specifications, Standards, and Other Documents

Organization	Address	Web Site
Military, Federal, and Government	DODSSP 700 Robbins Ave., Bldg 4D Philadelphia, PA 19111-5098	www.dodssp.daps.mil/oforms.htm
ASTM	American Society for Testing & Materials 100 Barr Harbor Dr. West Conshohocken, PA 19428	www.astm.org
EIA	Electronic Industries Alliance 2500 Wilson Blvd. Arlington, VA 22201	www.eia.org
EPA	Environmental Protection Agency Ariel Rios Bldg. 1200 Pennsylvania Ave, N.W. Washington, D.C. 20460 Superintendent of Documents P.O. Box 371954 Pittsburgh, PA 15250-7954	www.epa.gov
IPC	IPC Association Connecting Electronics Industries 2215 Sanders Road Northbrook, IL 60062-6135	www.ipc.org
ISO	International Organization for Standardization 1, rue de Varembe, Case Postale 56 CH-1211 Geneva 20, Switzerland	www.iso.org
JEDEC	Solid State Technology Association 2500 Wilson Blvd. Arlington, VA 22201-3834	www.jedec.org
NASA	National Aeronautics and Space Admin.	
NEMA	National Electrical Manufacturers Association 1300 N. 17th Street, Suite 1847 Rosslyn, VA 22209	www.nema.org
UL	Underwriters Laboratories, Inc. Corporate Standards 333 Pfingsten Rd. Northbrook, IL 60062-2096 comm 2000 1418 Brook Dr. Downers Grove, IL 60515	www.ul.com http://ulstandard.sinfonet.ul.com

Table 7.2. Materials: Paint, Varnish, and Coatings

Subject	Document	Title
Alkyd	AA-2962	Enamel, Alkyd Lusterless, Low VOC Content
Application of Dipped Films	ASTM D823	Application of Dipped Films
Colors	FED-STD-595	Colors Used in Government Procurement
Dielectric Coatings for Multichip Modules	IPC-DD-135	Qualification Testing For Deposited Organic Interlayer Dielectric Materials For Multichip Modules
Electronic Assemblies	MIL-STD-1861	Electrical and Electronic Assemblies, Boards, Cards, and Associated Hardware, Selection of
Epoxy	MIL-PRF-22750	Coating, Epoxy, High Solids
	MIL-I-16923	Insulating Compound, Electrical Embedding Epoxy
Epoxy Primer	MIL-P-23377	Primer Coatings: Epoxy, Chemicals, and Solvent Resistant
Finishes	MIL-F-18264	Finishes: Organic, Weapons System, Application, and Control of
Inspection and Testing	FED-STD-141D	Paint, Varnish, Lacquer, and Related Materials: Method of Inspection, Sampling, and Testing
Inspection	IPC-A-610	Acceptability of Electronic Assemblies. Section 9.1 “Inspection; Conformal Coatings and Solder Maskants”
Interlayer Dielectrics	see Dielectric Coatings	see Dielectric Coatings
Isocyanate	ASTM D2572	Available Isocyanate (NCO) in Urethanes
Plastics	MIL-HDBK-17	Plastics for Aerospace Vehicles
Polyurethane	MIL-C-46168	Coating, Aliphatic Polyurethane, Chemical Agent Resistant
Preparation of Films	ASTM D823	Practice for Producing Films of Uniform Thickness of Paint, Varnishes, and Related Products on Test Panels

(cont'd.)

Table 7.2. (cont'd.)

Subject	Document	Title
Printed Circuit Board Coatings	MIL-I-46058*	Printed Circuit Board Conformal Coatings (inactive for new designs)
	IPC-CC-830A	Qualification and Performance of Electrical Insulating Compound for PWAs
	IPC-HDBK-830	Guidelines for Design, Selection, and Application of Conformal Coatings
	NASA-STD-8739.1	Workmanship Standard for Staking and Conformal Coating of Printed Wiring Boards and Electronic Assemblies
Solder Maskants	IPC-SM-840C	Qualification and Performance of Permanent Solder Mask
Terminology	ASTM D16	Standard Terminology for Paint, Related Coatings, Materials, and Applications
	ASTM D6440	Standard Terminology Relating to Hydrocarbon Resins
	ASTM D883	Standard Terminology Relating to Plastics
	IPC-T-50F	Terms and Definitions for Interconnecting and Packaging Electronic Circuits
	ISO-4618	Terms/Definitions for Coating Materials
Varnishes	MIL-V-173	Varnish, Moisture, and Fungus Resistant (for Treatment of Communications, Electronics, and Associated Equipment)
	MIL-I-24092	Insulating Varnishes and Solventless Resins For Application by the Dip Process
	NEMA-STD Pub-RE2	Electrical Insulating Varnish
Wash primers	MIL-C-8514	Coating Compound, Metal Pretreatment, Resin-Acid
	DOD-P-15328	Primer (Wash) Pretreatment for Metals
Wire Insulation	NEMA-MW-1000	Magnet Wire (describes coatings and tests)
	MIL-W-81044	Wire, Electric, Crosslinked Polyalkene, Crosslinked Alkane-Imide Polymer, Poly-arylene Insulated Copper, or Copper Alloy
	MIL-W-81381	Wire, Electric, Polyimide-Insulated Copper or Copper Alloy
	MIL-W-22759	Wire, Electric, Fluoropolymer-Insulated, Copper or Copper Alloy
*Cancelled or inactivated for new designs		

Table 7.3. Corrosion and Corrosion Prevention

Subject	Document	Title
Cleanliness Levels	MIL-STD-1246	Cleanliness Levels
Contamination Control	MIL-HDBK-406	Contamination Control Technology
Copper Corrosion	ASTM D1616	Copper Corrosion (Aliphatic and Aromatic Hydrocarbons) Copper Strip Test
	ASTM D130	Standard Test Method for Detection of Copper Corrosion from Petroleum Products by Copper Strip Tarnish Test
Corrosion Control	TM-584C (revision C, Nov. 1994)	Corrosion Control and Treatment Manual (Kennedy Space Flight Center)
Corrosion, Filiform	ISO-4623-1	Determination of Resistance to Filiform Corrosion—Part 1: Steel Substrates
Dissimilar Metals	MIL-STD-889 B	Dissimilar Metals
Finishes	MSFC-SPEC-250	Corrosion Control, Finishes for Corrosion Protection
Fungus	MIL-STD-454, Req. 4	General Guidelines for Electronic Equipment (Lists Fungus Inert Materials)
Salt Spray	ASTM B117	Salt Spray (Fog Test)
Terminology	ASTM G15	Standard Terminology Relating to Corrosion and Corrosion Testing

Table 7.4. Electrical Tests

Subject	Document	Title
General Tests	MIL-STD-202	Test Method Standard, Electronic and Electrical Component Parts
Arc Resistance	ASTM D495	Standard Test Method For High-Voltage, Low-Current, Dry Arc Resistance of Solid Electrical Insulation
Dielectric Constant	ASTM D150	Standard Test Methods for AC Loss Characteristics and Permittivity (Dielectric Constant) of Solid Electrical Insulating Materials
Dielectric Strength and Breakdown Voltage	ASTM D149	Standard Test Method for Dielectric Breakdown Voltage and Dielectric Strength of Solid Electrical Insulation Materials
Dielectric Withstanding Voltage	MIL-STD-202 Method 301	Dielectric Withstanding Voltage
Dissipation Factor and Dielectric Constant	ASTM D150	Standard Test Methods for ac Loss Characteristics and Permittivity (Dielectric Constant) of Solid Electrical Insulation
Insulation Resistance	MIL-STD-202 Method 302	Insulation Resistance
Insulation Resistance	MIL-STD-202 Method 106	Insulation Resistance after Humidity
Resistivity	ASTM D257; ISO-3915, 1853	Standard Test Methods for dc Resistance or Conductance of Insulating Materials; Volume and Surface Resistivity

Table 7.5. Test Methods: Thermal, Mechanical, Physical, Chemical, and Biological

Subject	Document	Title
General Tests		
General Tests	IPC-TM-650	Test Methods Manual
	MIL-STD-202	Test Method Standard, Electronics and Electrical Component Parts
	FED-STD-141D	Paint, Varnish, Lacquer, and Related Materials: Methods of Inspection, Sampling, and Testing
	UL-746	Polymeric Materials, Use in Electrical Equipment Evaluations
	ASTM D115	Standard Test Method for Testing Solvent Containing Varnishes Used for Electrical Insulation
	ASTM D154	Standard Guide for Testing Varnishes
	ASTM D333	Standard Test Methods for Clear and Pigmented Lacquers
	ASTM D2305	Standard Test Methods For Polymeric Films Used for Electrical Insulation
	ASTM Manual 17	Paint and Coating Testing Manual
	ISO Standards Handbook, Vol.1	Paints and Varnishes: General Test Methods-Part 1
General Requirements	MIL-HDBK-2036	General Requirements For Electronic Equipment Specifications
	IPC-6012	Qualification and Performance Specification for Rigid Printed Boards
	IPC-A-610C	Acceptability of Electronic Assemblies
General Guidelines	MIL-HDBK-454A	General Guidelines for Electronic Equipment
	MIL-HDBK-1547	Electronic Parts, Materials, and Processes for Space and Launch Vehicles
Test Methods	MIL-STD-810	Environmental Test Methods and Engineering Guidelines
Specific Tests		
Abrasion	ASTM D4060	Abrasion Resistance for Cured Paints by Taber Abrader
Abrasion, Falling Sand	ASTM D968	Standard Test Methods for Abrasion Resistance of Organic Coatings by Falling Abrasive

(cont'd.)

Table 7.5. (cont'd.)

Subject	Document	Title
Abrasion, Pencil Test	ASTM D3363	Method of Test for Film Hardness by Pencil Test
Adhesion	ASTM D2197	Standard Test Method for Adhesion of Organic Coatings by Scrape Adhesion
	FED-STD-141, Method 6301.3	Adhesion (Wet) Tape Test
	ASTM D3359	Standard Test Methods for Measuring Adhesion by Tape Test
	ASTM D1654	Adhesion Retention After Salt Spray
	IPC-D-320	Adhesion by Crosshatch test
	ISO-2409	Paints and Varnishes- Cross-cut Test
Bacteria Resistance	ASTM G22	Standard Practice for Determining Resistance of Polymeric Materials to Bacteria
Bend test	see Flexibility	see Flexibility
Blistering	ASTM D714	Standard Test Method for Evaluating Degree of Blistering of Paints
Chemicals, Resistance	ASTM D543	Standard Practice for Evaluating the Resistance of Plastics to Chemical Reagents
Cleanliness	see Water Extract Resistivity	see Water Extract Resistivity
Coefficient of Friction	ASTM D1894	Coefficient of Friction
Color	ASTM D1209	Standard Test Method for Color of Clear Liquids (Platinum-Cobalt Scale)
	ASTM D6605	Standard Practices for Determining the Color Stability of Hydrocarbon Resins After Heating
Cracking	ASTM D661	Degree of Resistance to Cracking of Exterior Paints
Curing Schedule	FED-STD-141 Method 4061	Curing Time and Temperature
Cure, degree of	IPC-TM-650, Method 2.3.31	Relative Degree of Cure in uv Curable Materials
Deflection Temperature	ASTM D648	Standard Test Method for Deflection Temperature of Plastics Under Flexural Load

(cont'd.)

Table 7.5. (cont'd.)

Subject	Document	Title
Density	see Specific Gravity	
Destructive Physical Analysis (DPA)	MIL-STD-1580	Destructive Physical Analysis for Space Quality Parts
Drying/Curing	ASTM D1640	Standard Test Method for Drying, Curing, or Film Formation of Organic Coatings at Room Temperature
Dye Penetrant	MIL-STD-883 Method1034	Dye Penetrant Test
Electrochemical Migration	IPC-TM-650, Method 2.6.7.1	Electrochemical Migration Resistance Test
Elongation	ASTM-D2370 ASTM D638	Elongation of Tensile Strength of Free Films or Cast Films
Environmental Tests	MIL-STD-810	Environmental Engineering Considerations and Laboratory Tests
Epoxy Equivalent	ASTM D1652	Epoxy Content of Epoxy Resins
Erosion	ASTM D662	Standard Test Method for Evaluating Degree of Erosion of Exterior Paints
Filiform Corrosion	ISO-4623-1	Determination of Resistance to Filiform Corrosion- Part 1: Steel Substrates
Flaking	ASTM D772	Standard Test Method for Flaking of Exterior Paints
Flammability	ASTM D635	Standard Test Method for Rate of Burning and/or Extent and Time of Burning of Self-supporting Plastics in a Horizontal Position
	NASA-STD-6001	Flammability, Odor, Offgassing, and Compatibility Requirements and Test Procedures for Materials in Environments That Support Combustion
	UL-94	Tests for Flammability of Plastic Materials

(cont'd.)

Table 7.5. (cont'd.)

Subject	Document	Title
Flash Point	ASTM D56	Standard Test Method for Flash Point by Tag Closed Tester
	ASTM D92	Standard Test Method for Flash and Fire Points by Cleveland Open Cup
	ASTM D93	Standard Test Method for Flash Point by Pensky-Martens Closed Cup Tester
	ISO-3679	Paints, Varnishes, Petroleum and Related Products—Determination of Flashpoint—Rapid Equilibrium Method
Flexibility	ASTM D522	Standard Test Method for Mandrel Bend Test of Attached Organic Coatings
	ISO-1519	Bend Test (Cylindrical Mandrel)
Flexural Modulus	ASTM D790	Flexural Modulus
Friction	ASTM D1894	Standard Test Method for Coefficient of Friction
	ASTM D3702	Standard Test Method for Coefficient of Friction
Fungus	ASTM G21	Standard Practice For Determining Resistance of Synthetic Polymeric Materials to Fungi
	ASTM D3274	Evaluating Degree of Surface Disfigurement of Paint Films by Microbial (Fungal or Algal) Growth or Soil and Dirt Accumulation
	ASTM D4610	Determining the Presence of and Removing Microbial (Fungal or Algal) Growth on Paint and Related Coatings
	ASTM D5588	Determination of the Microbial Condition of Paint, Paint Raw Materials, and Paint Areas
	ASTM D5590	Determining the Resistance of Paint Film and Related Coatings to Fungal Defacement by Accelerated Four-week Agar Plate Assay
	MIL-T-152	Treatment, Moisture and Fungus Resistant, of Communications, Electronic, and Associated Electrical Equipment

(cont'd.)

Table 7.5. (cont'd.)

Subject	Document	Title
Fungus Test	MIL-STD-810, Method 508	Environmental Test Methods and Engineering Guidelines
	IPC-TM-650, Method 2.6.1.1	Fungus Resistance—Conformal Coating
Fungus Inert Materials	MIL-HDBK-454, Guideline 4	Fungus Inert Materials
Gas Permeability	ASTM D1434	Standard Test Method For Determining Gas Permeability Characteristics of Plastic Film and Sheeting
Gel Time	ASTM D1955	Heating Test (Gel Time)
Glass Transition Temperature	ASTM D6604	Standard Practice for Glass Transition Temperatures of Hydrocarbon Resins by Differential Scanning Calorimetry
Hardness	ASTM D2240 ISO-868	Hardness, Shore A or D
	ASTM D1474	Indentation Hardness of Organic Coatings
	ASTM D3363	Method of Test for Film Hardness by Pencil Test
	ISO-2815	Buchholz Indentation Hardness
HAST	JEDEC Std. 22-A110	Highly Accelerated Temperature and Humidity Stress Test (HAST)
Heat Deflection	ASTM D648 ASTM D1525	Vicat Softening Method
Humidity (see also Moisture Resistance)	JEDEC Std. 22-A110	Highly Accelerated Temperature and Humidity Stress Test (HAST)
Hydrolytic Stability	MIL-I-46058, 4.8.12	Hydrolytic Stability
	IPC-TM-650, Method 2.6.11	Hydrolytic Stability Solder Mask and Conformal Coatings
Impact Resistance	ASTM D2794	Test Methods for Resistance of Organic Coatings on the Effects of Rapid Deformation (Impact)
	ASTM D5420	Gardner Impact Test
	ASTM D256	Izod, Gardner Impact Test

(cont'd.)

Table 7.5. (cont'd.)

Subject	Document	Title
Inspection	IPC-A-610	Acceptability of Electronic Assemblies. Section 9.1 “Inspection; Conformal Coatings and Solder Maskants”
	MIL-C-28809*	Circuit Card Assemblies, Rigid, Flex, and Rigid-Flex
Mar Resistance	ASTM D5178	Standard Test Method for Mar Resistance of Organic Coatings
Melting point	ASTM D3418	Standard Test Method for Melting Point
Microbial Resistance	See Fungus	See Fungus
Moisture Resistance	ASTM D2247	Method For Testing Coated Metal Panels at 100% RH
	JEDEC Std. 22-A100	Cycled Temperature Humidity Bias Life
	JEDEC Std. 22 – A102A	Accelerated Moisture Resistance Unbiased Autoclave
Moisture Vapor Transmission	see Water Vapor Transmission	
Odors	ASTM D1296	Standard Test Method for Odors of Volatile Solvents and Diluents
Ozone Resistance	ASTM D518; D1149; D1171	
Permeability to Gases	see Gas Permeability	
Pinholes	ASTM D1848	Standard Classification for Reporting Paint Film Failures Characteristic of Exterior Latex Paints
Porosity	ASTM D3258	Standard Test Method for Porosity of Paint Films
Radiation	MIL-STD-883E, Method 1019.5	Ionizing Radiation (Total Dose) Test Procedure
Refraction Index	ASTM D542	Standard Test Method for Index of Refraction of Transparent Organic Plastics
Rosin Flux	IPC-TM-650, Method 2.3.27	Rosin Flux Residue Analysis HPLC Method

(cont'd.)

Table 7.5. (cont'd.)

Subject	Document	Title
Rubber	ASTM D572	Standard Test Method for Rubber—Deterioration by Heat and Oxygen
	ASTM D6601	Standard Test Method for Rubber Properties- Measurement of Cure and After Cure Dynamic Properties Using a Rotorless Shear Rheometer
	ASTM C518	Standard Test Method for Rubber Deterioration- Surface Cracking
Salt spray	ASTM B117 ASTM D117-90	Standard Practice for Operating Salt Spray (Fog) Apparatus
	ASTM D1654	Adhesion Retention After Salt Spray
Shellac	ASTM D411	Standard Test Method for Shellac Used in Electrical Insulation
Softening point	ASTM E28	Softening Point by Ring and Ball Apparatus
Solvents	ASTM D268	Standard Guide for Sampling and Testing Volatile Solvents and Chemical Intermediates for Use in Paint and Related Coatings and Material
Solvent Resistance	ASTM D543	Chemical and Solvent Resistance of Coatings
Specific Gravity	ASTM D792	Standard Test Method for Density and Specific Gravity of Plastics by Displacement
	ASTM D1475	Standard Test Method for Density of Liquid Coatings, Inks, and Related Products
	ISO-2811	Determination of Density— Part 1: Pyknometer Part 2: Immersed body Part 3: Oscillation method Part 4: Pressure cup
Surface Tension	ASTM D971 ASTM D1331	Surface tension of paints and coatings by the DuNouy Ring-pull-off Method
Tear Strength	ASTM D624	Standard Test Method for Tear Strength of Conventional Vulcanized Rubber and Thermoplastic Elastomers

(cont'd.)

Table 7.5. (cont'd.)

Subject	Document	Title
Temperature Stability	JEDEC Std. 22-A101-A	Steady State High Temperature
	JEDEC Std. 22-103-A	High Temperature Storage Life
Tensile Strength, Elongation	ASTM D638	Standard Test Method for Tensile Properties of Plastics
Thermal Conductivity	ASTM D2214	Standard Test Method for Estimating Thermal Conductivity of Leather by Cenco-Fitch Apparatus
	ASTM C177	Standard Test Method for Steady State Heat Flux Measurements and Thermal Transmission Properties by Means of the Guarded Hot Plate Apparatus
	ASTM C518	Standard Test Method for Steady State Thermal Transmission Properties by Means of the Heat Flow Meter Apparatus
	ASTM C1044	Practice for Using the Guarded-Hot-Plate Apparatus in the One-Sided Mode to Measure Steady-State Heat Flux and Thermal Transmission Properties
	ASTM C1045	Practice for Calculating Thermal Transmission Properties from Steady-State Heat Flux Measurements
	ASTM F433	Standard Practice for Evaluating Thermal Conductivity of Gasket Materials
Thermal Expansion	ASTM D696	Standard Test Method for Coefficient of Thermal Expansion of Plastics between -30° and $+30^{\circ}\text{C}$ with Vitreous Silica Dilatometer
Thermal Shock	IPC-TM-650, Method 2.6.7.1	Thermal Shock—Conformal Coating
Thermal Stability	ASTM D2307	Thermal Stability of Wire Insulation by Twisted Pair
Thickness, Magnetic Gage	ASTM D1186	Nondestructive Measurement of Dry Film Thickness of Non-magnetic Coatings Applied to a Ferrous Base

(cont'd.)

Table 7.5. (cont'd.)

Subject	Document	Title
Thickness	ASTM D1400	Nondestructive Measurement of Dry Film Thickness of Non-conductive Coatings Applied to a Non-ferrous Metal Base
Thickness, Mechanical Gage	ASTM D1005	Standard Test Method for Measuring Dry Film Thickness of Organic Coatings Using Micrometer
Varnishes	ASTM D154	Standard Guide for Testing Varnishes
	ASTM D115-55	Standard Test Methods for Testing Solvent Containing Varnishes Used for Electrical Insulation
Viscosity	ASTM D445	Standard Test Method for Kinematic Viscosity of Transparent and Opaque Liquids
	ASTM D6606	Standard Test Method for Viscosity and Yield of Vehicles and Varnishes by Duke Viscometer
	ASTM D88	Standard Test Method for Saybolt Viscosity
	ASTM D789	Standard Test Method for Determining Relative Viscosity and Moisture Content of Polyamide
	ASTM D1200	Standard Test Method for Viscosity of Paints, Varnishes, and Lacquers by Ford Viscosity Cup
	ASTM D2196	Viscosity (Brookfield)
Volatiles	ASTM D2832 ASTM D2369	Standard Guide for Determining Volatile and Non-volatile Content of Paint and Related Coatings
Water Absorption	ASTM D570-98	Standard Test Method For Water Absorption of Plastics
Water Content	ASTM E203	Standard Test Method for Water Using Volumetric Karl Fisher Titration
Water Content in Coatings	ASTM D4017 ASTM D1364	Test Method for Water in Paints and Paint Materials by Karl Fisher Method
Water Content in Solvents	ASTM D1364	Standard Test Method for Water in Volatile Solvents (Karl Fisher Method)
	ASTM D1476	Water in Solvents and Thinners by Turbidity Method

(cont'd.)

Table 7.5. (cont'd.)

Subject	Document	Title
Water Extract Resistivity	IPC-TM-650 ANSI-J-STD-001B MIL-STD-2000A	Resistivity of Deionized Water to Establish Purity or Amount of Ions Extracted from a Surface
Water Resistance	ASTM D870	Standard Test Method for Testing Water Resistance of Coatings Using Water Immersion
Water Vapor Transmission	ASTM D1653	Standard Test Method For Water Vapor Transmission of Organic Coating Films
	ASTM E96	Standard Test Method for Water Vapor Transmission of Materials
	ASTM F1249-95	Standard Test Method for Water Vapor Transmission Rate Through Plastic Film and Sheeting Using Modulated Infrared Sensor
Weathering	ASTM D1014	Standard Test Method for Conducting Exterior Exposure Tests of Paints on Steel
	ASTM D2565	Standard Practice for Xenon-Arc Exposure of Plastics Intended for Outdoor Applications
	ASTM D4364	Standard Practice for Performing Outdoor Accelerated Weathering Tests of Plastics Using Concentrated Sunlight
	ASTM G26	Standard Practice of Operating Light-Exposure Apparatus (Xenon-Arc Type) with and without Water for Exposure of Non-metallic Materials
Weathering, Accelerated	ASTM G23 ASTM D822	Accelerated Weathering, Open Arc Apparatus and Enclosed Arc Apparatus
*Cancelled or inactivated for new programs		

Table 7.6. Contaminants, Cleaning, and Solvents

Subject	Document	Title
Clean Rooms	FED-STD-209*	Clean Rooms and Work Station Requirements, Controlled Environment
Cleanliness of Printed Wiring Boards	IPC-TM-650, 2.3.5	Test Method for Cleanliness of Printed Wiring Boards
Cleaning Methods	MIL-HDBK-407	Precision Cleaning Methods and Procedures
	TT-C-490	Cleaning Methods For Ferrous Surface and Pretreatments for Organic Coatings
Cleanliness Levels	MIL-STD-1246C	Product Cleanliness Levels and Contamination Control
Cleanliness Test	IPC-TM-650, Method 2.3.27	Cleanliness Test, Residual Rosin
Contamination Control	MIL-HDBK-406	Contamination Control Technology
Halide Content	IPC-TM-650, Method 2.3.35	Halide Contents, Quantitative (Chloride and Bromide)
Ion Analysis	IPC-TM-650, Method 2.3.28	Ionic Analysis of Circuit Boards, Ion Chromatography Method
Ion Content	IPC-TM-650, Method 2.3.26	Mobile Ion Content of Polymer Films
Ionic Surface Contaminants	IPC-TM-650, Method 2.3.25	Detection and Measurement of Ionizable Surface Contaminants
Ionic Contaminants	MIL-PRF-55110F	Printed Wiring Board (Appendix A specifies requirements for ionic contaminants on electronic assemblies)
Particulate Contaminant	ASTM E1216	Standard Practice for Sampling for Surface Particulate Contaminants by Tape Lift
*Fed-Std-209 has been cancelled and superceded by ISO-14644-1 (Classification of Air Cleanliness) and ISO-14644-2 (Cleanroom Testing and Compliance).		

(cont'd.)

Table 7.6. (cont'd.)

Subject	Document	Title
Solvents	TT-I-735 ASTM D770	Isopropyl Alcohol
	TT-T-548	Toluene
	ASTM D1007	Sec. Butyl Alcohol
	ASTM D304	n-Butyl Alcohol (Butanol)
	ASTM D329	Acetone
	MIL-C-81302	Trichlorotrifluoroethane, Cleaning
Volatile Org. Compounds (VOC)	ASTM D3960	Standard Practice for Determining VOC Content of Paints and Related Coatings
	ASTM D2369	Test Method for Volatile Content of Coatings
Volatile Matter	EPA Fed. Ref. 24	Determination of Volatile Matter Content, Density, Volume Solids, and Weight Solids of Surface Coatings
	EPA 450/3-84-019	U.S. EPA Procedures for Certifying Quantity of Organic Compound Emitted by Paint, Ink, and Other Coatings
Volatile and Non-Volatile	ASTM D2832	Standard Guide for Determining Volatile and Non-volatile Content of Paint and Related Coatings

Table 7.7. Space Environment Effects

Subject	Document	Title
Atomic Oxygen	NASA-TP-1999-209260	Material Selection Guidelines to Limit Atomic Oxygen Effects on Spacecraft Surfaces
Destructive Physical Analysis	MIL-STD-1580	Destructive Physical Analysis for Space Quality Parts
Finishes	MSFC-SPEC-250	Protective Finishes for Space Vehicle Structures and Associated Flight Equipment
General	DOD-E-8983	Electronic Equipment, Aerospace, Extended Space Environment, General Specification
Materials Selection	MSFC-HDBK-527	Material Selection List for Space Hardware
Outgassing	ASTM E1559	Standard Test Method for Contaminant Outgassing Characteristics of Spacecraft Materials
	ASTM E595	Total Mass Loss (TML) and Collected Volatile Condensable Materials (CVCMD) from Outgassing in a Vacuum Environment
	NASA-RP-1124	Outgassing Data for Selecting Spacecraft Materials
	NASA-JSC-08962C	Compilation of VCM Data for Non-metallic Materials
Radiation	MIL-STD-883E, Method 1019.5	Ionizing Radiation (Total Dose) Test Procedure
Radiation Effects	NASA-CR-1871	Radiation Effects Design Handbook, Section 5: Radiation in Space and Their Interactions with Matter
	ASTM F1892-98	Standard Guide for Ionizing Radiation (Total Dose) Effects Testing of Semiconductor Devices
Test Requirements	MIL-STD-1540C	Test Requirements for Launch, Upper Stage, and Space Vehicles
Vacuum Stability	NASA-SP-R-0022A	Vacuum Stability Requirements of Polymeric Materials for Spacecraft Applications
	NASA-JSC-07572	List of Materials Meeting JSC Vacuum Stability Requirements

Appendix

Conversion Factors

Table A.01. Thermal Conductivity Units and Equivalents

Cal/ (sec · cm · °C)	BTU/ (hr · ft · °F)	W/ (m.K)	W/ (cm · °C)	W/ (in · °C)
1	241.9	418.6	4.186	10.63
4.13×10^{-3}	1	1.73	0.0173	0.044
2.39×10^{-3}	0.578	1	0.01	0.0254
0.239	57.8	100	1	2.54
0.094	22.74	39.4	0.394	1

Table A.02. Dimension Units and Equivalents

Mil	Inch	Centimeter	Millimeter	Angstrom	Micrometer	Microinch
1	0.001	0.00254	0.0254	254,000	25.4	1000
1000	1	2.54	25.4	2.54×10^8	25,400	1×10^6
394	0.394	1	10	1×10^8	1×10^4	3.94×10^5
39.4	0.0394	0.1	1	1×10^7	1×10^3	3.94×10^4
3.94×10^{-6}	3.94×10^{-9}	1×10^{-8}	1×10^{-7}	1	1×10^{-4}	3.94×10^{-3}
0.0394	3.94×10^{-5}	1×10^{-4}	0.001	10,000	1	39.4
0.001	1×10^{-6}	2.54×10^{-6}	2.54×10^{-5}	254	0.025	1

Table A.03. Pressure and Force Conversion Factors

To Convert From:	To:	Multiply By:
Pascals (Pa)	pounds per in ² (psi)	1.45×10^{-4}
Pounds	Newtons	4.44
Dynes/cm ²	pounds per in ² (psi)	1.45×10^{-5}
Newtons/mm ²	GigaPascals (GPa)	1×10^{-3}
MPa	Newtons/mm ²	1
Pascals [Pa]	Dynes/cm ²	10

Table A.04. Viscosity Conversion Factors

To Covert From:	To:	Multiply by:
Poise	Centipoises	100
Centipoises	Poise	0.01
Poise	lb/(sec · ft)	0.0672
Poise	lb/(hr · ft)	242
Poise	Pa sec	10
Pa sec	Poise	0.1
MPa sec	Centipoises	10,000
Poise = gm/(sec)(cm)		

Abbreviations, Acronyms, and Symbols

Table A.05. Abbreviations, Acronyms, and Symbols

ABS	Acrylonitrile Butadiene Styrene (a molded plastic)
ACS	American Chemical Society
ANSI	American National Standards Institute
ASIC	Application Specific Integrated Circuit
ASTM	American Society for Testing and Materials
ATC	Assembly Test Chip
ATCC	American Type Culture Collection
AWG	American Wire Gauge
BCB	Benzocyclobutene
BGA	Ball Grid Array
BT	Bismaleimide triazene; a high T_g epoxy resin formed from BT
BV	Breakdown Voltage
CAF	Conductive Anodic Filament
CALCE	Computer-aided Lifecycle Engineering
CFC	Chlorofluorocarbons
CMOS	Complementary Metal Oxide Semiconductor
COB	Chip on Board
COF	Coefficient of Friction
COSPAR	Committee on Space Research of the International Council of Scientific Unions
COTS	Commercial off the Shelf
cp	Centipoise
CPC	Ceramic Printed Circuit
CSP	Chip Scale Package
CTE	Coefficient of Thermal Expansion
CTFE	Chlorotrifluoroethylene
CVCM	Collected volatile condensable material
DBT	Dibutyl tin dilaurate
DEAPA	Diethylaminopropylamine
DETA	Diethylenetriamine

(cont'd.)

Table A.05. (cont'd.)

DF	Dissipation Factor
DGEBA	Diglycidylether of Bisphenol-A
DMP-30	Tris(dimethylaminomethyl)-phenol
DOD	Department of Defense
DOP	Degree of Planarization
DPA	Destructive Physical Analysis
DRAM	Dynamic Random Access Memory
DSC	Differential Scanning Calorimetry
DTA	Differential Thermal Analysis
DVS	Divinyl Siloxane
ϵ	Dielectric Constant
EIA	Electronic Industries Alliance
EMI	Electromagnetic Interference
EPA	Environmental Protection Agency
ESCA	Electron Spectroscopy for Chemical Analysis
ESD	Electrostatic Discharge
EV	Electron Volt
FEP	Fluorinated Ethylene Propylene
FET	Field Effect Transistor
FTIR	Fourier Transform Infrared
GHz	Gigahertz
GWP	Global Warming Potential
HAP	Hazardous Air Pollutants
HAST	Highly Accelerated Stress Test
HBFT	Hard Baked Film Thickness
HDBK	Handbook
HDI	High Density Interconnect
HDMI	High Density Multichip Interconnect
HMDS	Hexamethyldisilazane
HEPA	High-efficiency particulate (filter)
Hg	Chemical symbol for mercury
Hz	Hertz (cycle per second frequency)

(cont'd.)

Table A.05. (cont'd.)

IC	Integrated Circuit
IEC	International Electrotechnical Commission
IEPS	International Electronics Packaging Society (now merged with IMAPS)
IGA	Isothermal Gravimetric Analysis
IMAPS	International Microelectronics and Packaging Society
IPC	Institute for Interconnecting and Packaging Electronic Circuits
IR	Infrared (also insulation resistance)
ISHM	International Society of Hybrid Microelectronics (now IMAPS)
ISO	International Organization for Standardization
JEDEC	Joint Electronic Device Engineering Council (now Solid State Technology Association)
JPL	Jet Propulsion Laboratory
JSC	Johnson Space Center
k	Coefficient of Thermal Conductivity (CTE)
K	Degrees Kelvin
keV	Thousand Electron Volts
LEO	Low Earth Orbit
MAPTIS	Materials and Processes Technical Information Service
MCM	Multichip Module
MEMS	Micro-electromechanical System
MER	Mars Exploratory Rover
mg	Milligrams
MHz	Megahertz
ml	Milliliter
MMI	Multimode Interference
MMIC	Monolithic Microwave Integrated Circuit
MNA	Methyl Nadic Anhydride (a solvent)
MSC	Moisture Sensor Chip
MSDS	Material Safety Data Sheet
MSFC	Marshall Space Flight Center
MVTR	Moisture Vapor Transmission Rate

(cont'd.)

Table A.05. (cont'd.)

-NCO	Formula for isocyanate group
NEMA	National Electrical Manufacturers Association
NEPCON	National Electronics and Packaging Conference
NMP	n-methyl pyrrolidone (a solvent)
ODA	Oxydianiline
ODP	Ozone Depletion Potential
ODS	Oxygen Depleting Solvent
OSHA	Occupational Safety and Health Administration
ρ	Electrical Resistivity
Pa	Pascal
Pa·s	Pascal second
PAS	Polyarylsulfone
PBGA	Plastic Ball Grid Array
pbv	Parts by volume
pbw	Parts by weight
PCB	Printed Circuit Board
PCT	Pressure Cooker Test
PED	Plastic Encapsulated Device
PEEK	Polyaryletheretherketone
PEM	Plastic Encapsulated Microcircuit
PET	Polyethylene Terephthalate
phr	Parts per hundred parts of resin
PI	Polyimide
PIND	Particle Impact Noise Detection
PMDA	Pyromellitic dianhydride
PMMA	Polymethylmethacrylate
PoF	Physics of Failure
ppb	Parts per billion
ppm	Parts per million
PR	Propyl
PRF	Performance
psi	Pounds per square inch

(cont'd.)

Table A.05. (cont'd.)

PTF	Polymer Thick Film
PTFE	Polytetrafluoroethylene
PVF	Polyvinyl Fluoride
PWA	Printed Wiring Assembly
PWB	Printed Wiring Board
QPL	Qualified Products List
rad	Radiation Absorbed Dose (1 rad(Si) = 100 ergs/gm deposited in Si)
RF	Radio Frequency
RFI	Radio Frequency Interference
RGA	Residual Gas Analysis
RH	Relative Humidity
RIE	Reactive Ion Etching
RMA	Rosin Mildly Activated (flux)
rpm	Revolutions per minute
RT	Room Temperature
RTV	Room Temperature Vulcanizing
S	S within a hexagon indicates a saturated ring such as cyclohexane
SAE	Society of Automotive Engineers
SAM	Surface Acoustic Microscopy
SAMPE	Society for the Advancement of Material and Process Engineering
SBFT	Soft Bake Film Thickness
SEM	Scanning Electron Microscopy
SiP	System in a Package
SIR	Surface Insulation Resistance
SLA	Scanning Laser Ablation
SMT	Surface Mount Technology
SOG	Spun-on Glass
SPE	Society of Plastics Engineers
TAB	Tape Automated Bonding
TCR	Temperature Coefficient of Resistance
TDI	Tolyene Diisocyanate
TEM	Transmission Electron Microscopy
TFE	Tetrafluoroethylene

(cont'd.)

Table A.05. (cont'd.)

T_g	Glass Transition Temperature
TGA	Thermal Gravimetric Analysis
THB	Temperature Humidity Bias
TMA	Thermal Mechanical Analysis
TML	Total Mass Loss
torr	Millimeters of Mercury (pressure)
TT	Triple Track (resistor)
UL	Underwriters Laboratories
uv	Ultraviolet
VCM	Volatile Condensable Material
Vdc	Volts Direct Current
VFM	Variable Frequency Microwave
VLSIC	Very Large Scale Integrated Circuit
VOC	Volatile Organic Compounds
WI	Work Instruction
WVR	Water Vapor Regained
XPS	X-Ray Photoelectron Spectroscopy (also known as ESCA)
YAG	Yttrium Aluminum Garnet (laser material)

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