Corrosion Prevention by Protective Coatings

Third Edition

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Acknowledgments

It is amazing how much a person can learn from colleagues in the wonderful world of protective coatings. Such has been the case as I set out once more to update and expand the NACE International book, *Corrosion Prevention by Protective Coatings*. I would be remiss in my duties if I did not mention several people who have been a tremendous influence on my career and in particular in providing valuable information and technology for this Third Edition of what is commonly known as *The Munger Book*.

First of all is **Charles G. Munger**, "Chuck" as he is fondly remembered. He was my mentor when I first started out in the protective coatings industry, as well as a true friend.

Carl Angelof and **Todd Williams** of Bayer Material Sciences for some much needed new information on polyurethanes, polyureas, and polyaspartics.

Pete Englebert of Job Safety Associates, Inc. for his excellent revision and update of Chapter 16, "Safety."

Hasan Sabri of Kuwait Oil Company for almost single handedly guiding me through the creation of the new Chapter 23, "Pipeline Coatings and Linings."

Terry Greenfield of Corrometric Services, Inc. for his excellent Chapter 21, "Computer-Assisted Coatings Project Management Programs."

John Kelly of Akzo Nobel for all his expertise in anti-fouling and foul release coatings contained in Chapter 22, "Coatings for Marine Vessels."

Alex Szokolic and **R.A. Francis**, Australian colleagues, for their broad knowledge of the history and development of inorganic zinc coatings.

All of the students in NACE Coating Inspector Program (CIP) and Protective Coatings Specialist courses that I have taught over the years. I learned so much from their real-world practical experience.

Last, but certainly foremost in my thoughts, is **Mary Ann Vincent**, my lovely wife since 1952 for her love and patience when I was cranky and short-tempered while grinding away at the computer on this, my last update and revision of *Corrosion Prevention by Protective Coatings*.

It is my fervent hope that someone will take up the gauntlet at some point in the future to make new updates and revisions as new coatings technology becomes a reality.



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Author's Preface for the Third Edition of *Corrosion Prevention by Protective Coatings*

There has been a tremendous increase in the introduction of new technology in the coatings industry since the publication of the second edition of *Corrosion Prevention by Protective Coatings* in 1999. That has been the driving force behind my desire to update Charles G. Munger's original work once again in order to keep his pioneering work alive as a valuable reference work for anyone involved in the prevention of corrosion by the proper use of protective coatings.

For the guidance of the reader of this third edition of the book, I have included references to new or improved technologies in the following chapters:

- Chapter 1: Protective Coating Specialist certifications, waterjetting, smart coatings
- Chapter 2: Updates of NACE standards SP0198-2010, "Corrosion Control Under Thermal Insulation and Fireproofing Materials," and SP0178-2007, "Design, Fabrication and Surface Finish Practices for Tanks and Vessels to be Lined for Immersion Service"
- Chapter 4: IMO Performance Standard for Protective Coatings (PSPC) regulations, polyaspartic resins, nano-sized pigments, the International Convention on the Control of Harmful Anti-fouling Systems on Ships (AFS) banned the use of tin-containing anti-fouling coatings in 2001
- Chapter 5: Polyaspartic resins; nano-sized pigments; latest technology in polyurethanes, polysiloxane, and polyureas.
- Chapter 6: High ratio waterborne inorganic zinc, updated ASTM standards
- Chapter 7: A new (2011) two-component, high-build, high-temperature resistant "cold spray" applied coating based on titanium modified inorganic copolymer technology pigmented with aluminum flake that is capable of providing corrosion protection under thermal insulation operating in thermal cycling conditions between –321 °F (–196 °C) and 752 °F (400 °C) without the need of heat curing
- Chapter 9: Waterjetting, updated NACE/SSPC surface preparation standards
- Chapter 11: International Concrete Repair Institute (ICRI) Guideline No. 310.2 (1997; reapproved 2002)
- Chapter 12: The International Convention on the Control of Harmful Anti-fouling Systems on Ships (AFS) banned the use of tin-containing anti-fouling coatings in 2001; updated ASTM and ISO standards
- Chapter 16: An update on Occupational Safety & Health Administration (OSHA) safety regulations
- Chapter 19: Coatings under thermal insulation
- Chapter 21: A total update of computer-assisted coatings project management
- Chapter 22: A completely new chapter on marine coatings including new anti-fouling and foul release coatings introduced in 2013
- Chapter 23: A completely new chapter on pipeline coatings focusing on modern fusion bonded epoxies, polyethylenes, and polypropylenes

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1 Introduction to Corrosion

Introduction

Corrosion and corrosion engineering constitute a science that has only developed within the lifetime of many people working in the field today. This does not mean that corrosion is strictly a modern phenomenon, for it has, on the contrary, existed since humans first discovered ways to make metal from ores. It does, however, mean that prior to 1950, the existence of corrosion was passively accepted, along with death and taxes, as inevitable. In fact, many plant managers in this early period insisted that there was no corrosion in their plants; a little rust, which eventually called for the replacement of the plant's structures maybe, but never any corrosion. Such evasive attitudes, however, have changed over the years due to a better understanding of the subject and increased awareness of replacement economics. More recently, the impact of ever more stringent government regulations regarding worker safety and environmental protection have increased the cost of protective coatings maintenance, which in turn has heightened the awareness of the economic impact of improperly designed and applied coating systems even further. This, in turn, has created an increasing demand for corrosion prevention specialists, now known as *corrosion engineers*. In the protective coatings industry, the growing awareness of the critical function that coatings play in the prevention of corrosion has led to continuing education courses with the certification of the successful participants as *Protective Coatings Specialists*.

In the past, there was no formal training for corrosion engineers. They developed into specialists from their various roles as chemists; metallurgists; physicists; and chemical, civil, mechanical, maintenance, industrial, and piping engineers; as well as from their roles as experts in petroleum refining; petrochemicals; paper, water, sewage, and ship operation; and other industrial operations that are adversely affected by corrosion. While today there are some graduates with corrosion engineering courses as part of their degree programs, the majority were still initially trained in other engineering sciences and have come to specialize in this field because of their experiences with corrosion and their developing interest in its prevention. Despite their interest and expertise in the field of corrosion, and as a consequence of their training in other disciplines, the science and technology of coatings is generally foreign to them. This, however, is understandable given that high performance coatings represent a relatively recent (i.e., prior to 1950) and specialized branch of a much broader, established field.

NACE International has lead the way in providing continuing education courses for corrosion engineers and personnel of all disciplines with the courses listed in Table 1.1.

TABLE 1.1: NACE International Education and Training Courses as of 2014

Basic Corrosion
Basic Internal Corrosion for Pipelines
Chemical Treatment Specialist
Coating Inspector Program (CIP) Level 1
CIP Level 2
CIP Level 2—Maritime
CIP One-Day Bridge
CIP Level 3 Peer Review
Coatings in Conjunction with Cathodic Protection (CP)
Corrosion Control in the Refining Industry
Corrosion Specialist
Corrosion in the Water and Wastewater Industry (online training)
CP Interference
CP 1—Cathodic Protection Tester
CP 2—Cathodic Protection Technician
CP 2—Cathodic Protection Technician-Maritime
CP 3—Cathodic Protection Technologist
CP 4—Cathodic Protection Specialist
Designing for Corrosion Control
Direct Assessment—Pipelines
In Line Inspection—Pipelines
Internal Corrosion for Pipelines—Basic
Internal Corrosion for Pipelines—Advanced
Introduction to Coating Inspection (online training)
Marine Coating Technology
Materials Selection/Design Specialist
Nuclear Power Plant Training for Coating Inspectors
Offshore Corrosion Assessment Training (O-CAT)
Pipeline Coating Applicator Training
Pipeline Corrosion Assessment Field Techniques (P-CAFT)
Pipeline Corrosion Integrity Management
Protective Coating Specialist (PCS) 1—Basic Principles
PCS 2—Advanced
PCS 3—Management
Pipeline Corrosion Assessment Field Techniques
Pipeline Corrosion Integrity Management (PCIM)
Shipboard Corrosion Assessment Training (S-CAT)



FIGURE 1.1: A painting found in an Egyptian tomb reveals their use of synthetic blue pigment along with natural earth tones.



FIGURE 1.2: An Egyptian painting illustrating that most paints and pigments of this era were used for decorative purposes.

While the general area of coatings (or paint) has only come into its own as an industry during the Modern Age (post-World War II era), the discovery and development of materials used by that industry have it roots in more primitive times. A general survey, therefore, of the emergence of such materials may serve as a practical prelude to the development of today's more specialized protective coatings, especially since some of the early materials and even attitudes have carried over into the present industry. The following historical analysis can thus provide a valuable background from which to evaluate many of the materials, procedures, and processes common in today's protective coating field.

Historical Background

Thousands of years before their protective qualities were discovered, coatings were used for decorative and identification purposes. The earliest known paintings, which were found in caves in France and Spain, were made from naturally occurring iron oxides.[1] These were apparently applied without a binder by merely rubbing the iron oxide into the surface of a cave's interior. This, then, was the primitive basis for the subsequent development in paints, which took place primarily in two separate areas of the world.

Early Materials

Egypt developed the first synthetic pigment, which was known as Egyptian Blue, and was made from lime, sand, soda ash, and copper oxide heated together and ground to a relatively fine powder. This was developed in addition to a number of natural pigments that were already in use[2-4] (Figures 1.1 and 1.2).

At a somewhat later date, the Egyptians (as well as the Chinese who earlier developed calcined or fired pigments and some organic pigments[(1)]) began the use of additional paint vehicles. These included gum Arabic, egg white, gelatin, beeswax, and glue. This led to the Egyptian development of the first actual protective coating, which involved the use of various pitches and balsams to coat their ships.[1,4] The Chinese, as well as the Koreans and Japanese, used a lacquer for the decoration of buildings, instruments, and weapons.[1] Not much is known as to whether this early lacquer was of one type of material or several. It is known, however, that at some point, the Japanese developed a coating made from the sap of a "varnish tree."[4] This was used in much of their early decorative painting and in the lacquer ware that we know most about today (e.g., antique trays, vases, boxes, and small bottles and containers). The original sap required cleaning and filtering and was quite poisonous (similar to poison sumac and poison ivy or oak in its effects). When applied in relatively thin layers and kept in a damp, humid atmosphere, it cured or polymerized into a dense, high-gloss coating, which had excellent resistance to aging and no poisonous effects.

The Romans, during this same era, learned the techniques of making paint from the Egyptians, many examples of which can still be seen in the ruins of Pompeii. While the Romans used essentially the same materials as the Egyptians, they also developed several artificial colors. These materials were primarily lead based since the Romans had extensively developed the technology of mining and extracting lead from ores. The Romans also copied the Egyptians in the use of a protective coating for their vessels, adding wax to the Egyptian pitch combination.[4] The American Indians of the Canadian West Coast used a variety of organic materials for their pigments. These included charcoal, lampblack, graphite, and powdered lignite for black; diatomite mined from the bottom of shallow lakes, or calcined deer bones or antlers for white; calcined yellow ocher or roasted hemlock fungus for reds; yellow ocher or ground hemlock fungus for yellow; and copper carbonates and Peziza (the mycelium of a fungus) to prepare blues and greens.[4] Salmon eggs, both fresh and dried, were used for vehicles, which were prepared by chewing the eggs with the bark of red cedar. Fish oil from eulachon (Thaleichthys pacificus) or from perch was also used. Boiling the singed skins of mountain goats made sizes or mixing saliva with Peziza fungus, and mountain goat fat was used as the vehicle for their cosmetics.[4] The early American Indians also made rock paintings, or pictographs, which have lasted for centuries (Figure 1.3). These were all done in earth colors and made mostly from iron oxide, which was probably rubbed into the rock with fingers and twigs.[4]

Burma and Thailand were the original producers of shellac, which is possibly the oldest known clear finish. The shellac resin, which is still imported from there today, is made by the lac bug, an insect that during its life cycle attaches to small branches of a variety of the fig tree. This insect converts the tree's sap into a brittle reddish-brown resin with which it covers itself. The resin is gathered, crushed, washed, and bleached for use by the present paint industry. In its pure state, it is colorless, odorless, and edible.



FIGURE 1.3: In this centuries-old Algonquian pictograph, red pigment (finely ground iron oxide) is mixed with vegetable oil, blood, and egg white. Source: *America's Fascinating Indian Heritage* (Pleasantville, NY: Reader's Digest Association, Inc., 1978), p. 140.

Emerging Technology

The late eighteenth century saw the slow emergence of the paint and varnish industry. Although an actual varnish factory was reportedly established in England at this time,[4] paint was still made by individuals in small volumes for their own use and according to their own method. Much of what was made adhered primarily because of the affinity of the pigment for the surface, and much of it could be rubbed from the surface with a wet finger.

By the early 19th century, some power-driven equipment was used to manufacture paint. These manufacturers, however, only used the equipment to manufacture paint ingredients from which the individual painter combined these ingredients into a usable medium of his or her own formulation. It was not until the latter part of the century that paint manufacturers put their first prepared paints on the market. This early manufacturing process involved grinding with oils or varnishes on simple stone mills, which became the universal machines for dispersing pigments. Some of these mills remained in use until World War II, which indicates that the technology and business of making paint was extremely primitive and still in its infancy well into the twentieth century. Table 1.2 provides a more detailed summary of the development of coatings up to this point of an emerging industry.

A Coating System

The railroad made a significant contribution to the development of protective coatings in the early 1900s. Bridges were a vital part of the rail system and many of the major ones were constructed with riveted steel; thus, it was necessary that they be given maximum corrosion protection. One of the most effective systems consisted of a red lead-linseed oil primer applied in one or more coats, followed by a linseed oil-graphite topcoat applied in two or more coats. The ability of the linseed oil to penetrate and wet the mill scale on the surface of steel beams, plates, and structures played a significant part in the ability of the coating system to resist corrosion. This marked the first of the truly protective coatings and created the dark gray color characteristic of these steel bridges. This first system provided good long-life corrosion protection, except in extremely corrosive marine or industrial conditions. The coating was brush-applied and thoroughly wet the steel surface. The system's heavy red lead primer offered some corrosion inhibition and the graphite topcoat increased water resistance, with its flake structure protecting the vehicle from weathering. This type of coating became a standard of the day for exposed steel structures such as the one shown in Figure 1.4.

As long as the making of paint was considered more of an art than a science, progress in the industry was slow. It was not until the early 20th century that an increased emphasis on science and chemistry in particular, brought a new era in the coating industry and was recognized.

Until the late 1920s, however, the number of chemists in paint factories was still limited and their sphere of activity restricted. Coating

TABLE 1.2: Historical Development of Paint	
15000 BC	First known painting: caves at Lascaux, France and Altamira, Spain.
8000–6000 BC	Egypt: First synthetic pigment, Egyptian Blue; natural pigments used were red and yellow ochers, cinnabar, hematite, orpiment (yellow), malachite, azurite, charcoal, lampblack, and gypsum; vehicles used were egg white, gelatins, and beeswax; developed crude brushes to apply paint.
6000 BC	Asia: Calcined (fired) pigments and organic pigments. Vehicles used were egg white, beeswax, and gelatins. Chinese lacquer is prehistoric.
1500 BC	Egypt: Imported indigo and madder to make blue and yellow, developed first protective coating, pitches and balsams to coat boats.
1000 BC	Egypt: Developed varnish from the gum of the acacia tree (gum acacia).
1122-221 BC	Chinese buildings decorated with lacquer inside and out, lacquer used on carriages, wagons, and harnesses, lacquer also used in Japan and Korea.
Roman Era	Same essential materials as Egypt. Also, several artificial colors (white lead, litharge, red lead, yellow oxide of lead, Verdigris, and bone black). Pitch used for tarring ships. Pitch was used on ship bottoms.
400 AD	Japan: Japanese lacquer-sap from "Varnish Tree," sap also used to waterproof drinking vessels.
600 AD	First suggestion for use of vegetable oil in varnish.
1100 AD	First written description for preparing an oil varnish. Dissolved molten rosin in hot oil.
Middle Ages	Considerable use of paint to protect wood.
American Colonists	Made paint using sage and skimmed milk with earth pigments.
1773	Watin first described the paint and varnish industry. Copals and amber used as resins and turpentine as thinner. One lb of resin used with ¼ to ½ lb of oil.
1790	First varnish factory established in England.
1804	First classes of varnish described by Tingrhy.
1883	J. Wilson Neil: first to give details of varnish manufacture.
1840	First reference to use of zinc as a protective coating.
1850	Zinc oxide introduced in white pigment in France; was one of first steps towards a change in the paint industry.
1867	First prepared paint on the market.
1736-1900	Watin book on varnish formulas: varnish makers standard up to 1900, reprinted 14 times.
1800-1900	Red lead-graphite linseed oil paint, first protective coating system.

Sources: *Encyclopedia Britannica, Macropedia*, Vol. 13, Paints, "Varnishes and Allied Products," pp. 886-889, 1974; *World Book Encyclopedia*, Vol. 15, "Paint," p. 24, 1978; Mattiello, Joseph J., *Protective and Decorative Coatings*, Vol. 1, "Introduction, Rise of the Industry," John Wiley & Sons, Inc., New York, NY, pp. 1-8, 1941; Neil, J. Wilson, *Manufacturers of Varnishes*, Vol. 49, Part 2, Trans. Roy. Soc. Arts, pp. 33-87, 1833; Mallet, R., *British Assn. for Advancement of Science*, Vol. 10, pp. 221-288 (1840).



FIGURE 1.4: Complicated bridge structure, all of riveted construction with openwork vertical supports and multiple angle braces, shows clean, rust-free trusses.

technology consisted largely of empirical data obtained through trial and error. White lead in oil remained standard for exterior house paint, although ready-mixed paint containing white lead and zinc oxide was making headway. Titanium dioxide pigments were still around the corner, and choices in pigments were extremely limited, or in some cases nonexistent. The principal varnish oils used at this time were linseed and tung. Although many varnish makers resented the intrusion of so-called upstart chemists, new "wonder" varnishes were nevertheless being produced. These varnishes, which dried faster and resisted turning white in water, were developed through a combination of tung oil and ester gum made by heat-reacting rosin and glycerol. The first completely synthetic resin introduced was made from phenol-formaldehyde,[5] but even this development was considered only a minor one. It was not until at least a decade later that significant improvements were made following the availability of 100% oil-soluble phenolic resins. These vastly upgraded the varnishes of the time by increasing flexibility, decreasing the drying time, and making them much more durable to both weather and water.

World War I produced nitrocellulose, which was also a completely synthetic resin. It was made by reacting cellulose with sulfuric and nitric acids, and was produced as an explosive in extremely large quantities during World War I. Thus, as the war

came to a close, there were large unwanted volumes of nitrocellulose still available. The material was a hazard to keep in inventory as well as a disposal hazard. DuPont chemists, however, soon determined that if the material were put into solution it would form a clear, continuous film. This discovery was the beginning of the lacquer industry, which had a major impact on the automotive industry. Prior to the early 1920s, all automotive finishes were of a varnish type, requiring multiple coats with long drying times. Nitrocellulose, however, dried as soon as the solvent evaporated, leaving a clear film that could be easily pigmented. In addition, nitrocellulose in solution form was no longer an explosion hazard.

The principal varnish oils used at this time were linseed and tung. Although many varnish makers resented the intrusion of so-called upstart chemists, new "wonder" varnishes were nevertheless being produced. These varnishes, which dried faster and resisted turning white in water, were developed through a combination of tung oil and ester gum made by heat-reacting rosin and glycerol. The first completely synthetic resin introduced was made from phenol-formaldehyde,[5] but even this development was considered only a minor one. It was not until at least a decade later that significant improvements were made following the availability of 100% oil-soluble phenolic resins. These vastly upgraded the varnishes of the time by increasing flexibility, decreasing the drying time, and making them much more durable to both weather and water.

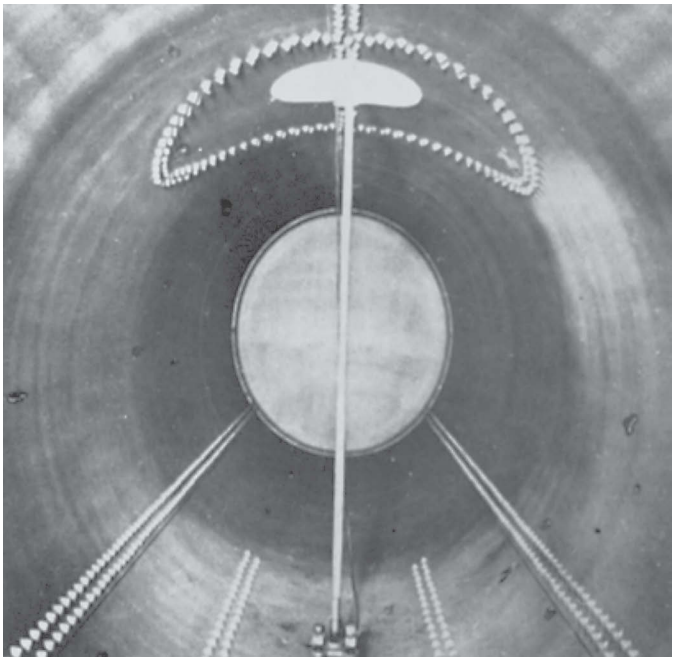


FIGURE 1.5: Riveted tank car coated with chlorinated rubber primer, two vinyl chloride acetate silica-filled intermediate coats, and two or more clear vinyl chloride acetate finish coats.

Binders

The synthetic resin developments, which came out of this field of organic chemistry, became the basis for protective coatings used from that time on. Alkyd resins, chlorinated rubber, vinyl copolymers, acrylics, and methyl-cellulose were all developed during this period. While these materials were extensively tested in coating formulations during this period, progress was still slow. A number of other developments were necessary before the new coating materials could be successful. One such development was that of proper solvents. The vinyl resins were soluble only in extremely strong solvents and, while acetone was available, its evaporation rate was so rapid that satisfactory films could not be formed from the acetone solution. Many of the new resins were brittle as well, and required the addition of some softening agent in order to provide a durable surface film.

It was actually the development of solvents and plasticizers, occurring at the same time as that of synthetic resins, that made coatings possible. Some early vinyl coatings, as well as some made from chlorinated rubber, were developed in the 1930s. Both had good chemical resistance. The original vinyl copolymers, however, would only adhere to a very porous surface and were therefore not satisfactory for application to steel surfaces.

When used alone, chlorinated rubber was likewise unsuitable because it was an extremely brittle, hard, and horny-textured substance. It was soon discovered, however, that its addition to oils and alkyd resins increased drying speed and resistance, and conversely plasticized the chlorinated rubbers. In later years, the modification with acrylic resins further increased the color and gloss retention properties of chlorinated rubber coatings. It is interesting to note that the first satisfactory primer for vinyl resin was actually one developed from chlorinated rubber. Not only did it adhere to steel, but the combination of a chlorinated rubber primer and vinyl copolymer body coats and topcoats formed the first of the really chemical-resistant protective coatings. There were, however, some application problems since both materials dried rapidly.

The material nevertheless provided the most resistant protective coating available at that time and was used as a chemical-resistant coating on into the early 1940s. This coating system found application in the chemical, sewer, and marine industries, and as a lining for wine tank cars (Figure 1.5) and for bait and fish storage tanks in the tuna industry. The new chlorinated rubber-vinyl copolymer combination thus represented the first major breakthrough in the development of a corrosion-resistant coating

Surface Preparation

A second breakthrough, which also occurred at this time, was the increased use of sandblasting. Although sandblasting was a well-known technique in the 1930s, it was considered a messy process in which very few plant managers wanted to be involved. It was soon recognized, however, that a sandblasted surface was necessary for proper performance of the new synthetic resin coatings.

This discovery came when the U.S. Navy realized that in order to prolong the life of their ships at sea, it would be necessary to improve ship coating effectiveness. They soon found that the chip-and-scrape procedures were not adequate in achieving the kind of surface preparation essential to improved coating life. Thus, the Navy's eventual acceptance of sandblasting as a standard method of surface preparation was the beginning of a more general use of proper surface preparation. This new practice of thoroughly cleaning a steel surface prior to coating application, in addition to the improved adhesion of vinyl coatings to steel, provided the foundation for the protective coating industry.

A significant breakthrough in surface preparation began in 1975 with the commercialization of the first waterjet pump by Flow Corp. In 1975 a method of adding garnet abrasives into the waterjetting stream increased its cutting efficiency. It should be recognized that waterjetting alone does not create profile on a surface, but it does a very efficient job of cleaning existing profile. As this technology continued to develop and the power of the waterjet pumps increased to 72,000 psi or more, waterjetting created a major advance in surface protection for maintenance operations in both industrial and marine structures. Many contractors and owners shifted away

from dry abrasive blasting to either pure waterjetting (only water) or water blasting (water and abrasive combinations) in order to meet increasingly stringent governmental regulations regarding health, safety, and hazardous waste disposal.

This new technology created a need for new surface preparation standards since a surface cleaned with waterjetting looks different than the same level of cleanliness developed with dry abrasive blasting. The development of pictorial standards by major coatings manufacturers such as Hempel and International Paint that were eventually transformed into industry-wide visual standards by SSPC and NACE, along with the development of surface-tolerant epoxy coatings by most global scale manufacturers, have made waterjetting the fastest growing surface preparation method since the year 2000.

Protective Coatings

This period produced two other breakthroughs, which added to the beginning revolution in corrosion control through protective coatings: the Australian development of the first inorganic zinc (IOZ) coating (stoving grade) followed by an American refinement involving the use of a post-curing solution rather than heat curing, and, at about the same time, the European development of organic zinc-rich coatings. Both events were significant in that they eventually led to the use of zinc primers for almost all high-performance protective coating systems. Their value, however, was not commonly recognized until a practical method of applying the coatings to existing structures was developed more than a decade later.

While World War I marked the beginning of what is now the paint industry, World War II provided the impetus behind the development of the protective coating industry. The need to conserve labor, to lengthen the time a ship could be at sea without returning to drydock, to protect structures against corrosion that developed from rapidly expanding chemical and fertilizer industries, and to conserve existing plants by preventing their deterioration by corrosion, all pushed the development of the protective coating industry away from paint and toward the more resistant polymers and film-forming materials.

Shortly after World War II, the development of another type of material, epoxy resins, had a major impact on the protective coating field. These materials reacted in place to form a protective coating that was easier to apply and had good adhesion and acceptable resistance to corrosion. The epoxies were originally amine cured. Later, however, polyamide epoxy coatings were developed, which provided increased adhesion, some flexibility, and increased water and chalk resistance as compared to earlier products. Today there are more than 75 categories of epoxy coatings with numerous different curing agents.

Polyurethane coatings were also developed during this period, but the early polyurethane resins were considered inferior to epoxy because of their poorer water resistance and tendency to yellow over a period of time. Development of newer, higher solids polyurethane resins beginning in the 1990s eliminated the yellowing tendency and increased their flexibility. Water resistance remains weaker than epoxies. Further refinements of the polyurethane technology resulted in the introduction of very high-build, direct-to-metal products classified as polyaspartics.

Polyisocyanate resins first became available in 1952. However, the polyisocyanate build coats and finish coats did not make a major impact on the coatings industry until the marketing of an epoxy modified polysiloxane coating with excellent film strength, color, and gloss retention capabilities in 1994. More recently, polyurethane-modified polysiloxane coatings have been introduced with the same level of color and gloss resistance but increased flexibility compared with the epoxy polyisiloxanes.

A major breakthrough in the IOZs field came with the development of self-curing IOZ coatings. These materials eliminated the difficulty of applying the curing agent to the post-cured products, and their rapid cure to insolubility eliminated much of the difficulty with weather during the application stage. While the first self-curing IOZ coatings were water-based, the later development of solvent borne IOZ coatings based on ethyl silicate had a major impact on the protective coating field.

Most of the coating products developed during the World War II period remain in present use, with the exception of those that do not meet current standards for volatile organic compounds (VOC). VOC emissions control was an outgrowth of the Clean Air Act of 1978 and has led to major changes in volume solids of organic coatings. While improvements and developments in both organic and inorganic coatings continue to be made, there has been no breakthrough in coating technology since World War II that has had the impact of the IOZ and epoxy coatings, with the possible exception of aliphatic polyurethane topcoats. Significant improvements in epoxy technology has extended their use into both aggressive immersion situations and onto marginally prepared rusty surfaces.

Dr. Otto Bayer first created polyurethane polymers in 1937. Polyurethane foams were created in 1941. Coatings development since 1955 has made a significant impact on the use of protective coatings. Whereas the epoxy coatings had excellent durability and chemical resistance (dependent upon the formulation), all of them suffered from the poor resistance to ultraviolet attack on the epoxy resin. This created unacceptable aesthetics in the form of chalking and loss of gloss and color. The first attempts to rectify this shortcoming involved the use of vinyl/acrylic topcoats over the intermediate coat of epoxy. While this improved the retention of color and gloss, the period of retention was still not acceptable. With the advent of two-component aliphatic polyurethane topcoats in the late 1960s, a major improvement in color and gloss retention became available along with a corollary increase in chemical and solvent resistance of the topcoat compared to vinyl/acrylics. The result has been that current versions of aliphatic polyurethanes are the topcoats of choice in protective coating systems since the 1990s.

Another significant development in polyurethane technology that also occurred in the 1970s and 1980s was single-component, moisture-cured polyurethane systems. First developed in Europe by Bayer AG, these began to be tested on bridges in the United States in 1973. A trio of steel truss type bridges in Pittsburgh, Pennsylvania were painted beginning in 1978 and showed less than 5% corrosion in 1997. Aimed primarily at the maintenance market, systems commonly consist of an aromatic polyurethane primer, either an aromatic or an aliphatic polyurethane intermediate coat, and aliphatic polyurethane finish coat. Primers usually contain IOZ, aluminum, or inhibitive pigments such as various oxides and phosphates. Intermediate coats usually contain some type of barrier pigment such as micaceous iron oxide. Immersion resistant systems were originally based on coal tar pitch modifications Because of the concerns about the potential carcinogenic properties of coal tar pitch, more recent immersion-resistant epoxies are based on hydrocarbon resins. The major advantage of moisture cure polyurethane technology has been its ability to be applied over marginally prepared surfaces at relatively high humidity levels.

Two major technology improvements occurred in the 1990s: novolac-modified epoxies for tank linings and siloxane modifications for both linings and chemical/atmospheric environments. The novolac epoxies have had the greatest impact and are now available in

TABLE 1.3: Significant Developments in Paint and Coatings Since 1900	
1909	First completely synthetic resin introduced by Dr. Leo H. Bakeland. Made from phenol-formaldehyde. Was insoluble in oil and not useful until modified in 1920–24. Discovery was the beginning of the Bakelite Corp that became Union Carbide and is now Dow Chemical.
1918	First sale of titanium pigment.
1920–1925	Cellulose nitrate and acetate developed for the paint field. Alkyd resins developed.
1928	100% oil soluble phenolic resin developed.
1929	Urea formaldehyde resin developed.
1930	Chlorinated rubber developed.
1933	Vinyl copolymers developed from vinyl chloride, vinyl acetate, vinyl alcohol, and acrylic.
1935	Ethyl cellulose and cellulose acetobutyrate developed.
1938	First vinyl protective coating developed and used without baking. Five-coat systems: chlorinated rubber primer, two vinyl body coats, and two vinyl seal coats.
1939	First IOZ coating developed in Australia.
1940	Organic zinc-rich coatings started in England.
1941	Polyurethane foams created by Bayer in Germany.
1942–1945	Sandblasting specified as surface preparation on Naval ships. Vinyl wash primer developed. Vinyl tripolymer resin developed which provided good adhesion to steel. Silicone resins developed.
1945	First self-priming vinyl coating developed and used.
1948	Styrenated oils and alkyds developed.
1952–1955	First practical IOZ coating developed and used in U.S.A. Epoxy resins appeared as coating raw materials, amine cured. Polyurethane coatings in U.S.A., were known.
1955–1960	Epoxy polyamide coatings developed. First water-base self-curing IOZ coatings.
1960–1965	Self-curing, ethyl silicate base, IOZ coatings used in the U.S.A.
1965–1970	Single-package IOZ coating developed.
1972	First self-polishing copolymer antifouling paint.
1970–1975	Two-component aliphatic polyurethane coatings.
1975–1980	Moisture cured polyurethane coating systems used in the U.S.A.
1881	First anti-fouling paint.
1980	Waterborne acrylic maintenance coatings.
1980-1990	100% solids epoxies and polyurethanes.
1985-1990	Waterborne epoxy coating systems.
1990-1995	Epoxy-novolac tank linings. Polysiloxane coating systems. Polyaspartic coating systems.

Note: All of the above dates are approximate. Many materials shown were in the development stage for several years before entering the coating market.
Sources: Clark and Hawley, *The Encyclopedia of Chemistry,* "Protective Coatings," Reinhold Publishing Corp., New York, NY, pp. 785–789, 1957; Mattielo, Joseph J., *Protective and Decorative Coatings*, Vol. 1, "Introduction, Rise of Industry," John Wiley & Sons, Inc., New York, NY, pp. 1–8, 1941.

100% solids versions. The siloxanes have been married to various resin backbones for specialized purposes including heat resistance and color and gloss retention. Table 1.3 provides an outline of the significant developments in paint and coatings since their emergence as an industry at the beginning of the 20th century.

White Pigments

Without the development of several other ingredients in coatings, the binders themselves would have been of little consequence. The improvement of the white pigments, for instance, which paralleled the development of binders, was a major improvement in the industry. White lead was the primary white pigment available up until the mid-1800s when zinc oxide was developed as a white pigment. The combination of white lead and zinc oxide was soon used almost exclusively for good exterior white paints.

Titanium dioxide was introduced during World War I and also had a significant impact on the paint industry. As shown in Table 1.4, which lists the various white pigments in the order they were developed and used by the paint industry, titanium dioxide has 5 to 10 times the tinting strength and hiding power of the earlier white pigments. (Both pigment concentration and the type of binder influence hiding power. Various grades of the same pigment type also differ in hiding power.)

Significant improvements in the manufacturing process for titanium dioxide have yielded finer grades with greater resistance to degradation within the coating systems. Additionally, the advent of the pre-dispersion blends improved the manufacturing process of the finished paints and coatings at reductions in cost per gallon.

Titanium products were originally combined with other inert pigments. The original titanium dioxide was the anatase form of the pigment. This material, which had a number of drawbacks, particularly caused paint to chalk very readily and heavily. The rutile form of titanium dioxide was finally introduced in the early 1940s, and from that time on, served as a major white pigment for both the paint and the new protective coating industry. It was used in the protective coatings field primarily because of its very inert chemical characteristics. Titanium dioxide is inert to most acids and alkalis and is therefore incorporated into many chemical-resistant coatings.

TABLE 1.4: Tinting Strength and Hiding Power of White Pigments

	Tinting Strength	Hiding Power (ft^2/lb)	Hiding Units
Basic Lead Carbonate	100	15	1.00
Basic Lead Sulfate	85	13	0.87
Zinc Oxide	200	20	1.33
Zinc Oxide (35% Leaded)	170	20	1.80
Lithopone	260	20	1.33
Titanium Barium Pigment (a)	380	40	2.67
Titanium Barium Pigment (b)	430	46	3.07
High Strength Lithopone	400	44	2.93
Titanated Lithopone	400	44	2.93
Titanated Magnesium Pignment	440	47	3.13
Zinc Sulfide	540	58	3.87
Lead Tinanate	570	60	4.00
Titanium Dioxide	1,150	115	7.00

Source: J.J. Mattielo, *Protective and Decorative Coatings,* Vol. I, "Introduction, Development of Industry Today" (New York, NY: John Wiley & Sons, Inc., 1941) p. 13.

Solvent Development

The development of synthetic resins and white pigment was also paralleled by the development of other types of pigment, solvents, and plasticizers.

The large-scale use of nitrocellulose lacquers is attributed not only to the successful production of lower viscosity nitrocellulose (which was easier to use), but also to a large supply of n-butyl alcohol, which accumulated as a fermentation process byproduct in the production of acetone during World War I. This butyl alcohol was easily converted to butyl acetate, a very desirable nitrocellulose solvent.

With nitrocellulose available as a film-former, butyl alcohol and butyl acetate could be produced in quantity as solvents. The nitrocellulose lacquer industry was thus able to increase its volume from 1 to 70 million gallons in 25 years. This provided the impetus for the development of other solvents (ketones, esters, cellosolves, nitroparrafins, chlorinated hydrocarbons, and specialty solvents such as diacetone alcohol) that were eventually used in the protective coatings industry. They also allowed the use of very high molecular weight resins and combinations of resins, which otherwise would have been impossible.

Distinction in Terms

Up to this point, the words "paint" and "protective coatings" have been used rather loosely. Much discussion has revolved around the use of these two terms and there is little doubt that much of the terminology and many of the uses, basic materials, and even manufacturing processes are similar for both paint and protective coatings. On the other hand, there certainly is a case to be made supporting a distinction between the two materials, despite the opinion, particularly of many conventional paint suppliers, that paint and coatings are essentially one and the same. A majority of suppliers of protective coatings agree to the distinction, however, pointing to not only vast differences in composition, but also in use. This perspective is made even clearer by a statement from the *Encyclopedia of Chemistry*[5] that states:

> Films prepared from oils alone are totally inadequate for protective coatings and combinations of natural resins and derivatives of rosin do not meet the growing needs of industry for protective coatings with adequate resistance to acids, alkalies and weathering and with retention of high elasticity under stress and aging. To meet this need the chemical knowledge of polymerization has been utilized during the past 30 years to develop synthetic resins useful in the surface coating field.

Other references, however, make little distinction between the words "paint" and "coating." In fact, they are often used interchangeably (i.e., all paints are coatings and all coatings are paints). The definition of a coating taken from the "Glossary of Terms" in the *Manual for Coatings of Light Water Nuclear Plants,* for example, is "Coatings (paints) are polymeric materials that applied in fluid stage, cure to a continuous film.[6] This, of course, could serve as a general definition for either a paint or coating because it is a very broad and simple statement. When considering coatings in relation to corrosion, however, it becomes necessary to more specifically define the two terms.

Definitions

Paint may be defined as any liquid material containing drying oils alone or in combination with natural resins and pigments which, when applied to a suitable substrate, will combine with oxygen from the air to form a solid, continuous film over the substrate, thus providing a weather-resistant decorative surface. Paints continue to oxidize over their entire lifetime and gradually become porous to oxygen, water, and ions that may be deposited on the surface. Thus, they provide less permanent protection against corrosion than the more sophisticated protective coating.

Paint may also be defined as any liquid material containing aqueous dispersions of latex, polyvinyl acetate, or acrylic or modifications thereof, in combination with pigments, plasticizers, and additives, which when applied to a suitable substrate, will coalesce into a solid continuous film over the substrate, thus providing a weather-resistant decorative surface. These paints are semipermeable, thus allowing moisture vapor to penetrate and release from the dried film.

A protective coating is chemically a substantially different material. It outperforms paint in adhesion, toughness, and resistance

to chemicals, weather, humidity, and water. A protective coating is any material composed essentially of synthetic resins or inorganic silicate polymers which, when applied to a suitable substrate, will provide a continuous coating that will resist industrial or marine environments. A protective coating should prevent serious breakdown of the basic structure in spite of abrasion, holidays, or imperfections in the coating.

In order to provide corrosion protection, the protective coating must also:

(1) Resist the transfer or penetration through the coating of ions from salts that may contact the coating;
(2) Resist the action of osmosis;
(3) Expand and contract with the underlying surface;
(4) Have and maintain a good appearance, even under extreme weather conditions.

In addition, it must be able to fulfill these requirements over a period of time long enough to justify its price, surface preparation, and application costs.

In the context of this definition, the protective coating may be formed solely by the evaporation of solvents leaving a resinous film (lacquer), by condensation or internal chemical reaction (epoxy), by reaction with products in the air (alkyd, polyurethane, or IOZ coating), by coalescence (emulsions, plastisols, or dispersions), by heat as a hot-melt (coal tar or asphalt), as a powder that is melted on the surface (fusion-bonded epoxy), or by applying a preformed sheet of resinous coating material over the structure (e.g., vinyl or polyethylene sheet).

Naturally, there are exceptions to these definitions, including some alkyds, chlorinated rubbers, and epoxy esters, which are a combination of both oils and synthetic resins. These materials combine some of the properties of both paints and coatings and are very useful for some purposes. On the other hand, since they contain drying oils, their properties are limited because of the chemical nature of oils, and their use is limited to less severe exposures than those of most protective coatings.

For further clarification, the definition of a protective coating can be divided into two additional parts, according to the intended use of the material. *The Encyclopedia of Chemical Technology* makes the distinction as follows:

> A resistant coating is a film of material applied to the exterior of structural steel, tank surfaces, conveyor lines, piping, process equipment or other surfaces which is subject to weathering, condensation, fumes, dusts, splash or spray, but is not necessarily subject to immersion in any liquid or chemical. The coating must prevent corrosion or disintegration of the structure by the environment.
>
> A resistant lining is a film of material applied to the interior of pipe, tanks, containers or process equipment and is subject to direct contact and immersion in liquids, chemicals, or food products. As such, it must not only prevent disintegration of the structure by the contained product, but must also prevent contamination of the contained product. In the case of a lining, preventing product contamination may be its most important function.[7]

In the context of these definitions, paint would seldom, if ever, be used as a lining. On the other hand, a protective coating may well be used for decoration purposes only, and thus might qualify under the definition of paint.

Purposes

The range of reasons for using paint extends beyond the historically prevalent one of decoration, although appearance remains a primary consideration. A chapter in the *Facilities and Plant Engineering Handbook,* entitled "Painting," thoroughly summarizes its purposes as follows:

- **Protection**
  The major consideration in painting is preservation of the structure or equipment from the environment. Typical causes of failure are rainfall, water, vapor, sunlight, temperature variations overnight and between seasons, mildew, and rot. Other less prevalent causes include salt water and vapor, chemicals and chemical fumes, air pollution, and abrasive wear by traffic. Paint acts as a shield protecting the substrate from these elements. Proper paint choice and painting practices will definitely extend the life of the painted object and markedly reduce repair costs.
- **Appearance**
  The most important reason for painting (in mild environments) and second most important reason outdoors is the decorative value of paint in producing pleasant and attractive surroundings. The wide choice of colors, even in metallic finishes, the gloss and texture available, as well as its ease of application, make paint the ideal method of producing or changing the appearance of all surfaces on structures including floors as well as operating equipment and even furniture. Paints can be applied to almost all surfaces and substrates and to old painted surfaces as well, thus enabling the production of any aesthetic effect desired even when structural modifications are made (e.g., installation of new walls, partitions, and doorways). Furthermore, paint will readily cover these additions or changes so that they do not stand out.
- **Sanitation and cleanliness**
  Painted surfaces are generally relatively smooth and nonporous so that they are easily kept clean. The coating of rough and porous surfaces seals out dirt and other foreign matter that would otherwise be difficult to remove. Furthermore, light-colored painted surfaces, by contrast, will reveal the presence of dirt, grease, and other undesirable substances and thereby indicate that better housekeeping practices are in order. Therefore, painting for sanitation and cleanliness is especially important in food processing areas and hospitals.
- **Illumination**
  White and pastel-colored paints, when applied to ceilings, are highly efficient in natural and artificial light. Therefore, they can be used to advantage to brighten rooms and work areas and also to reduce lighting costs, when used to cover darker substrates or old paint. On the other hand, darker colors can be used to reduce and soften illumination, where so desired (e.g., in private offices). Furthermore, low-gloss (flat) finishes will soften and diffuse illumination, thus reducing glare.
- **Efficiency**
  Improved illumination and reduction of glare both aid markedly in improving efficiency of personnel in the area. The ability to use a variety of colors, as well as combinations, also will lead to more pleasant surroundings, another aid to improvement in morale and productivity. Paint can also be used to color-code areas, equipment, piping, and valves, and traffic paints can be used to guide traffic flow, all of which improve efficiency and reduce errors.
- **Visibility and Safety**
  Increased illumination improves general visibility in the area, thus also preventing potential accidents. However, colored paints can be used alone or in combination to designate dangerous areas and safety equipment such as fire extinguishers. Certain combinations, such as yellow stripes or letters on a black background or orange combined with white, are visible at much greater distances than single colors. The latter are used on TV, radio, and telephone relay towers to warn aircraft, for example.[8]

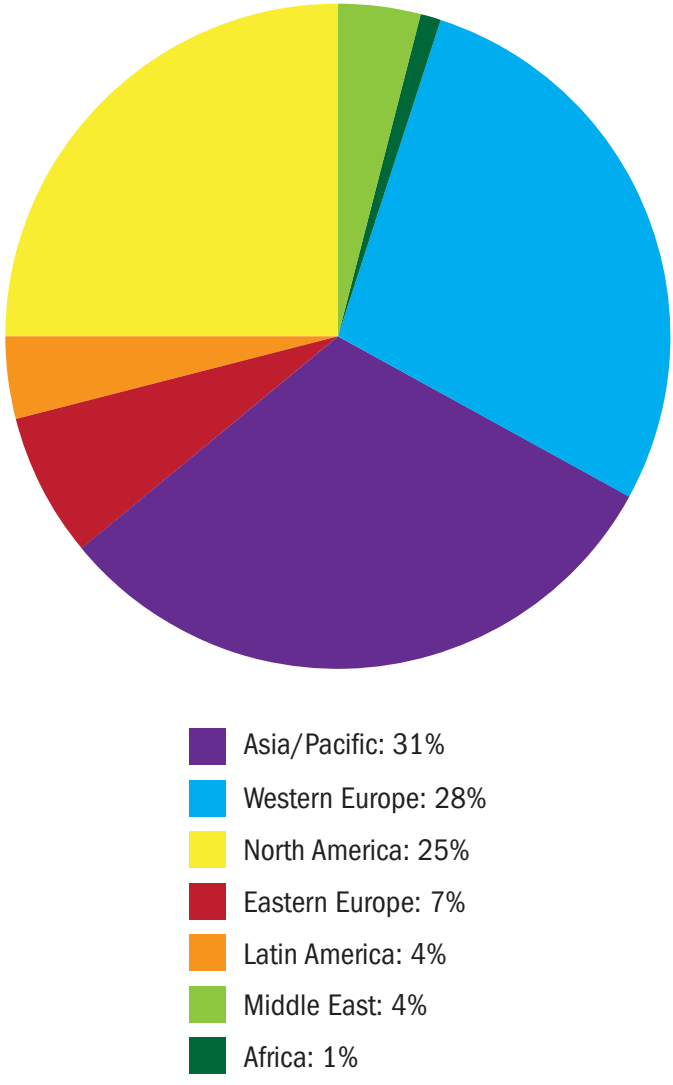


FIGURE 1.6: Global coating market share as of 2005. Source: Infinity Research.

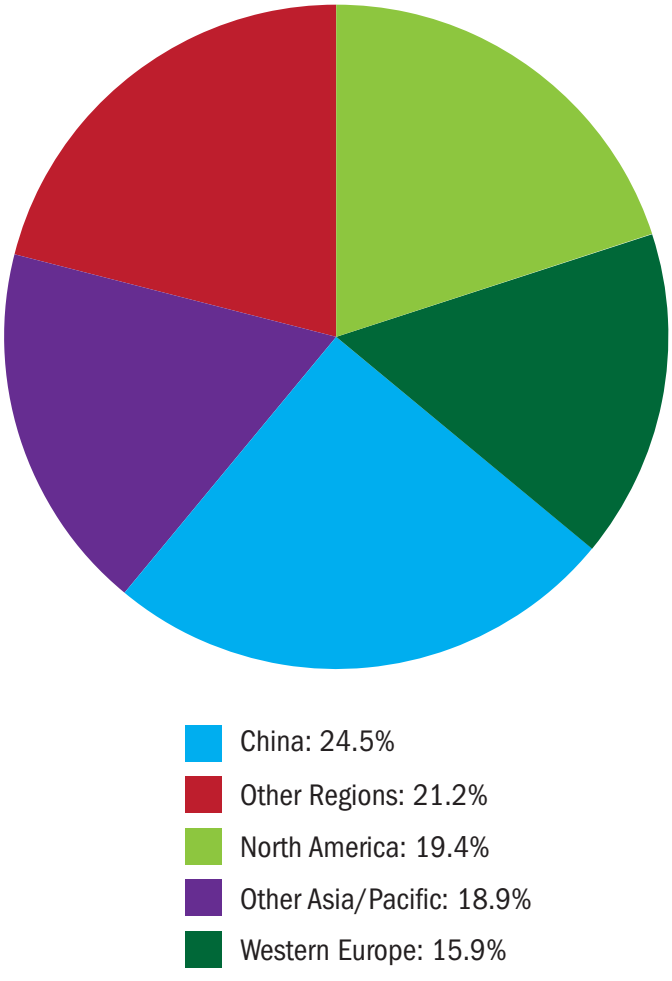


FIGURE 1.7: World paint and coatings demand by region, 2010 (35.1 million metric tons). Source: The Freedonia Group, Inc.

The above summary, however, does not cover all of the reasons for using points, as it does not address the more severe problems for which protective coatings are produced. Protective coatings also act as a barrier, prevent fouling attachment, reduce or increase friction, reduce abrasion, reflect or absorb heat, and, most importantly, prevent disintegration or failure of the substrate by various forms of corrosion (e.g., marine, atmospheric, chemical, or underground corrosion). Thus, the specific purpose of a protective coating is to provide a film that will separate noncompatible materials or conditions.

Protective coatings, or in this case linings, may also be used to prevent contamination, as in the case of atomic power plants where coatings are used to prevent radioactive contamination of the underlying surface. On the other hand, as a lining for a tank car containing caustic, wine, sugar, syrup, or petroleum products, the coating provides a film separating the steel surface from the contained material. Fire-retardant coatings also apply these principles in that they act as a barrier to heat as well as to oxidation. From a corrosion standpoint, the advertising slogan, which was popular a number of years ago, "Save the surface and you save all," aptly applies.

The paint industry is a technically complex one as well, which has grown in accordance with the 20th century's tremendously increasing production of objects and structures requiring paint or protective coatings. The corresponding increase in paint products has been achieved through intensive efforts of not only paint companies, but of major chemical companies and raw materials suppliers as well. The dye industry has contributed technology and information needed to upgrade and evaluate pigments. The plastics industry, which developed around organic chemical technology, has contributed their development of polymers and gigantic molecules containing hundreds of repeating basic molecules. Thermodynamics has proved a useful tool for understanding the chemical reaction of paint ingredients and the more subtle interactions involved in solution compatibility and pigment wetting. Rheology, the science of the deformation and flow of matter, has also had a great impact on the paint industry.

Hundreds of new types of coating materials have evolved as well. These include resins, solvents, diluents, plasticizers, pigments, dryers, foam control agents, adhesion promoters, and fire-retardant chemicals and pigments. These materials have helped to achieve corrosion resistance, heat stability, and new methods of application. Paint manufacture has thus progressed from the state-of-the-art to that of a science deeply rooted in the technically complex chemical industry.

Coating Market Projections

According to a report published by Infiniti Research,[9] the global coatings market is forecast to increase at a compound annual

growth rate of 5.46% through 2015, with the industry set to hit 8.7 billion gallons and $107 billion by the year 2017. Production within the global coatings market is witnessing a major shift away from the developed regions of Europe and the United States to the developing economies such as Asia. Sustained demand from the developed countries and the burgeoning demand from the developing economies are contributing to the overall expansion of the coatings market worldwide. Key factors contributing to growth within the coatings market include the recovery of global economies from the recent economic turmoil, rapid industrialization, increasing demand from end-use sectors such as automotive and construction, the increasing stringency in regulations, rising competition, growth in unique formulations, and technological and product developments.

The pie chart shown in Figure 1.6 depicts a major change in the global coatings market beginning about the year 2000.

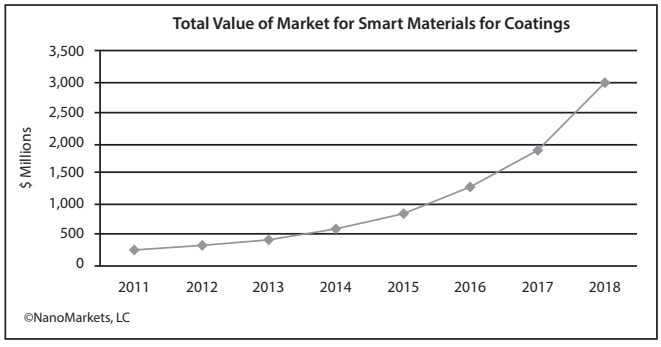


FIGURE 1.8: According to a study, the market for smart coatings will reach a size of U.S.$3 billion by 2018. Source: NanoMarkets, LC.

While the North American market remains significant, it is a relatively mature market. Overall, global coating sales were approximately $87 billion in 2005. The Asian markets are predicted to grow at an 8 to 10% rate between 2011 and 2015 whereas the overall global paint and coatings market is predicted grow at a rate of 5.46%. A significant impetus for the Asian market growth has been the heavy demand for shipping and offshore drilling structures such as tension leg platforms, drill ships, and floating production storage and offloading (FPSO) operations for deep-water areas of the world. New technologies such as foul release coatings and new regulations from the International Maritime Organization (IMO) have driven the marine industry growth. Global Industry Analysts, Inc. predicts that the global coatings market will reach U.S.$107 billion by 2017.[10]

Global demand for paint and coatings is forecast to rise 5.4% per year to 45.6 million metric tons in 2015. Advances will be driven by a strong acceleration in world building construction, which is expected to rebound in North America and Western Europe, according to "World Paint and Coatings,"[11] a study from The Freedonia Group, Inc., a Cleveland-based industry market research firm. Figure 1.7 shows global paint and coatings demand by region as of 2010.

Healthy growth in global manufacturing activity will also fuel increased demand for coatings used in the production of motor vehicles and other durable goods, as well as industrial maintenance applications. Solvent-based paint and coatings will continue to see their share of the market decline in both developed and developing markets. The Asia/Pacific region will remain the leading consumer of paint and coatings through 2015, and will also see the most rapid gains. Above-average advances are also forecast for North America, rebounding strongly from the declining demand of the 2005-2010 period. While painting and coatings demand in Western Europe will see a similar recovery from recent declines, the region will be the world's slowest-growing regional market.

The market for smart coatings is forecasted to reach a size of U.S.$3 billion by 2018[12] (Figure 1.8). Although many of the most interesting smart coatings are only just beginning to emerge from industrial laboratories, research company NanoMarkets believes that these coatings have a huge future revenue potential.

With this in mind, the experts published the first market analysis of the smart coatings business, titled "Smart Coatings Markets 2011,"[12] including an eight-year quantitative forecast by application and material type. The report provides forecasts on various market sectors for smart coatings; for instance, medical, naval, and military applications. The experts expect the sectors considered in this report will be generating hundreds of millions of dollars in revenue and will therefore be well worth a look by a variety of firms looking for new opportunities in the materials space. At the present time, applications fall primarily into the medical and construction/architecture sector.

Coatings Technologies

The technology of coatings is based on organic and, more recently, inorganic chemistry, which has expanded tremendously within the last century. A plant manufacturing a broad line of trade sales, maintenance, and industrial paints now requires at least 500 to 600 different raw materials. The companies concentrating in high-performance coatings such as the epoxies, vinyls, polyurethanes, inorganics, and so forth, also require several hundred raw materials (e.g., organic monomers, polymers, resins, pigments, dryers, extenders or non-hiding pigments, plasticizers, and solvents). A single formulation may require as many as 15 to 20 individual ingredients to create the chemical forces that are responsible for the finished product's surface adherence.

So many raw materials are needed due to the great diversity of finished products necessary to best serve the innumerable specific purposes for which coatings are applied. Most people think of paint in its relation to houses and buildings since a great deal of so-called ordinary paint is purchased only for appearance purposes. On the other hand, most objects we come in daily contact with are coated with materials that were developed for a specific purpose. Residential aluminum siding, for example, is factory coated through a coil coating process. The finish is applied and hard baked in less than a minute, and is expected to last 15 years once the siding is applied to the house.

Some of the most sophisticated coating systems are applied to automobiles. In the 1920s, as many as 10 or 15 coats of lacquer were applied to automobiles. While the finely rubbed finish was beautiful when new, it lasted only a relatively short time before it started to dull, chalk, and, in many cases, change color. Today, only two or three coats of paint are applied, an outstanding gloss is obtained, color possibilities are almost innumerable, most colors will maintain their gloss and shade for a number of years, and little, if any, hand rubbing is necessary. Zinc-rich primers are applied to car frame structures by a dipping process that effectively coats all interior and exterior surfaces simultaneously. Robotic spray equipment applies colored body coats of polyurethane followed by clear coats of ultraviolet-resistant polyurethane.

Coatings Economics

It is easy to see the importance of protective coatings to the corrosion engineer. To put it in perspective, high-performance coatings

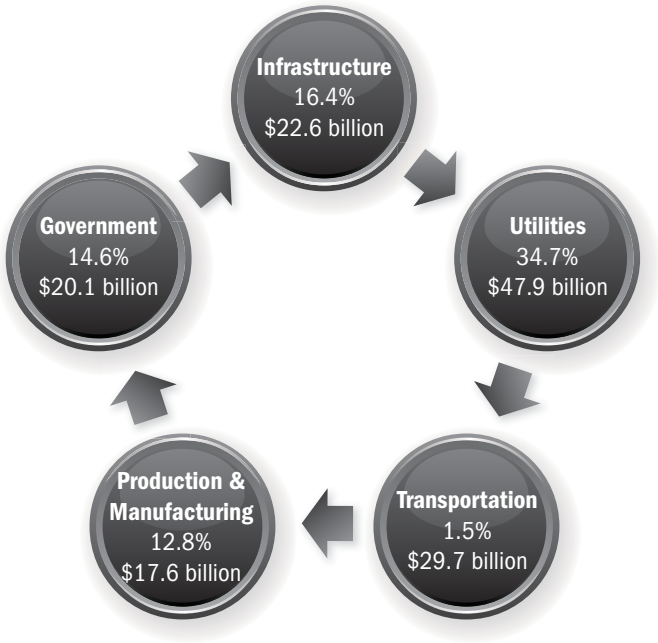


FIGURE 1.9: Breakdown of direct corrosion costs by industry. When extrapolated to the total U.S. economy, the annual costs of corrosion totaled $276 billion. Source: FHWA, 2002.

are used to protect structures that serve as the production facilities of the world. The value of both the old and new structures is escalating at a rapid rate, making it essential to have them protected against corrosion with high-performance coatings, which provide a barrier to keep these essential structures intact and free from failure.

In 2002, a study entitled "Corrosion Costs and Preventive Strategies in the United States,"[13] was conducted from 1999 to 2001 by CC Technologies Laboratories, Inc., with support from the FHWA and NACE (Figure 1.9). It revealed that corrosion costs amount to approximately $276 billion in the United States, which represents 3.1% of the Gross Domestic Product (GDP). As of February 2013, corrosion costs have been updated to $476 billion, 30% of which can be saved by implementing known corrosion mitigation technology. Studies in other countries such as the United Kingdom, Australia, Japan, etc., have placed the cost of corrosion at between 3 and 6% GDP in the individual countries.

However, the true cost of corrosion cannot be reckoned in any money sum representing replacements and maintenance. We have to visualize cases where some plant or machine that had been working perfectly is suddenly brought to a standstill by corrosion breakdown.[14]

A good example of the use of coatings to reduce corrosion cost is in refined oil tankers. In the 1930s and 1940s, tankers were built with an expected life of approximately 15 to 20 years. The first part of this life (approximately seven years) was in refined oil service. By the end of this service, the bulkheads in the tanker were corroded to one-half of the original steel's thickness. Any additional corrosion would have reduced the bulkhead below the point of minimum safety. Thus, the ships were usually transferred for the remainder of their existence to black oil service, which for the most part is much less corrosive than the refined products.

Today, however, the life of the tanker is considered 28 to 30 years with no allowance for interior corrosion. This has been accomplished through the use of high-performance IOZ coatings that have proven that with proper application they can maintain bulkheads of a refined oil tanker without loss of metal for 20 years. The entire 30-year life of the refined oil service vessel is thus used in hauling the refined products for which it was designed. The coating, in this case, not only allows the continued transportation of the higher-value cargo, but it also reduces the tank's interior maintenance costs to a minimal amount.

In an article in the *Marine Engineering Log* of August 1974,[15] an example is cited of three 71,000-ton vessels that were treated in 1964 with interior and exterior coatings.

> As of 1974, the coating was almost perfect, 95% to 97% intact; the value of the internal coating has been proved years ago—when coating eliminated the extensive steel renewals previously required.

Today, the bulkhead replacement costs mentioned in the article would amount to approximately $200 to $250 per ft^2, compared to $8 to $10 per ft^2 for a protective coating with a 20-year life span. In the case of chemical tankers, the increase in purity of chemical products has made them more aggressive, thus requiring ever more sophisticated coatings and linings. The life of a chemical tank lining rarely exceeds 10 years without extensive repairs and the cost per ft^2 commonly exceeds $12.

Thus, in a sense, coatings serve as an insurance policy on the life of the structure. The coating cost amounts to a very small percentage of any structure's total cost, and this small incremental cost protects the structure against disintegration for many years.

Coating Manufacture

Coating manufacture started when the first prepared paint was put on the market in 1867. This first product was primarily a mixture of white lead and linseed oil ground together on a burr stone mill. These mills usually consisted of two slabs of granite or similar hard natural stone cut so that the two flat surfaces rubbed together, with the grooves carrying the undispersed paint material in between them. Several runs through the mill were made before the required fine texture or proper pigment dispersion was obtained. Much of the paint manufacturing process involves the dispersion of pigments. The following is a review of the manufacturing process extracted from Unit 1 of the *Federation Series on Coating Technology*.[16]

In the manufacture of pigmented products, the most critical operation is the incorporation of the pigment in the binder or vehicle, as the case may be. If the ultimate pigment particles are too coarse, it is necessary to reduce them in size by a true grinding process. Most of the pigments used today are sufficiently fine that no grinding is required. However, they contain clusters or agglomerates that must be broken down to the separate particles, which must then be wetted by the binder. This process is correctly designated as dispersion. Some kinds of milling equipment perform both grinding and dispersion, while other types disperse only. In the former category were the stone mills, which were the most common milling equipment 60 years ago. A few plants bore with them until about 30 years ago. They were doomed to the scrap pile by slow production, high maintenance, variable results, and need for close attention.

Three roll steel mills appeared about 60 years ago. They operate with a small clearance between rolls and a speed differential between successive rolls. If used for grinding, they are inefficient and the rolls are etched. Their only proper use is for dispersion. Since dispersion depends on the shearing action produced by the differential in roll speed, a high viscosity vehicle is essential to good results.

Although largely displaced by newer, more efficient equipment, roller mills with three to five rolls continue in limited use. Next



Figure 1.10: Modern paint manufacturing plant showing large scale-supported mixing vessels and pipelines for raw materials and semi-processed liquids. Photo courtesy of Ameron, Inc., EFD Facilities, Wichita, KS.

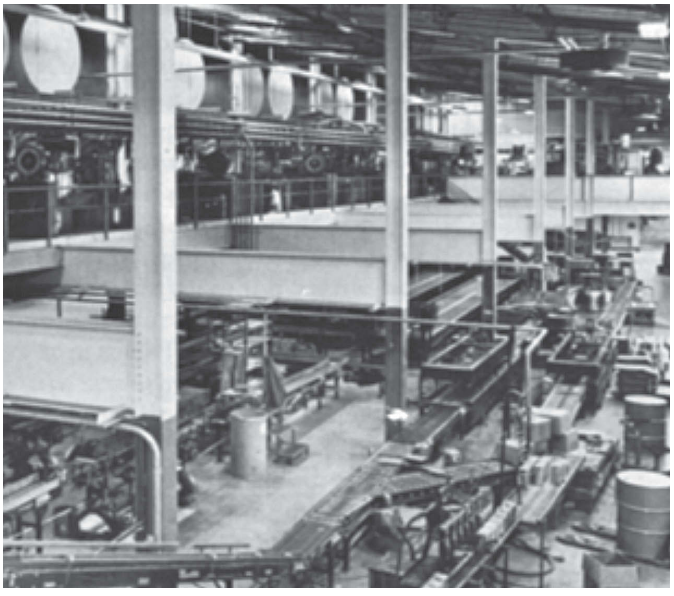


Figure 1.11: Manufacturing and packaging area of a large paint plant showing overhead storage of liquid materials, pipelines, automatic canning equipment, and end product conveyors. Photo courtesy of Ameron, Inc., EFD Facilities, Wichita, KS.

came pebble mills and, a little later, steel ball mills, the latter for dark colors only. Collision between the pebbles or balls and with the shell provides sufficient impact to reduce particle size as well as dispersion. Frequently, they have been used when dispersion only is required. Pebble and ball mills require little attention and are more economical than earlier mills. In general, they do not develop as high a gloss as roller mills.

Although pebble and steel ball mills are still used extensively, there is a strong trend toward newer types of equipment for products that do not require actual grinding. There was a period during which certain types of formulas required extreme, costly methods of pigment dispersion in order to develop the high gloss demanded. This was true of some nitrocellulose automobile lacquers and, more recently, it applied to some baking appliance enamels. The extra gloss was achieved by mixing in heavy-duty mixers a high content of pigment with a viscous liquid at very high consistency, which creates much greater shearing effect than roller mills. The Banbury Mill, designed for rubber compounding, was employed for this purpose. Two roll rubber mills were also used to disperse pigments in thermoplastic resins such as vinyls. Excellent pigment dispersions and a very high gloss were obtained by this method. Later, dough mixers of the Baker-Perkins type were found more suitable for some products. This high-cost process holds small and declining interest for the paint manufacturers. However, it is widely used by companies that specialize in difficult-to-make dispersions for sale to paint companies.

Both roller mills and dough mixers depend on a viscous liquid for shearing action at relatively slow speed. Good shearing action can also be obtained with a thin liquid, provided the mixing is done at an extremely high speed. This is the principle of dispersion on which much of today's paint is made. The principle is utilized in numerous designs of equipment, such as the Morehouse Mill, the Kady Mill, and the Cowles Dissolver. The economy of high-speed mixing makes it first choice whenever it produces satisfactory dispersion without undesirable side effects.

Milling methods that are based on dispersion without grinding owe much of their success to two contributing circumstances. The first is the development of fine particle grades of the common extenders, earth colors, and flatting agents. The second is the widespread use of wetting agents, which may be applied on the dry pigment by the supplier or incorporated in the paint formula.

One of the latest types of equipment for pigment dispersion is the first to offer the advantage of a continuous process. A stationary shell holds sand or pea-size porcelain balls. While the mass is being stirred by moving arms, the paint is forced upward through the chamber and out the top. The process is efficient in output and effective in the completeness of dispersion and the degree of gloss development. Its main limitation is unsuitability for short runs because of the problem of cleaning the sand or balls. Since there is no appreciable impact between the grains of sand or the balls, only a shearing and rubbing action, there is dispersion only and no reduction in particle size.

Figures 1.10 and 1.11 are examples of a modern plant capable of manufacturing millions of gallons of paint or protective coatings per year. Of necessity, it is highly automated with all liquid handled in pipelines and mixers, which drain the finished product through filters into automatic canning and packaging equipment. This paints a far different picture from the earlier plants of the 19th century with their oil-fired varnish cookers, stone mills, and belt-driven mixers.

While this discussion of manufacturing has primarily referred to paint, high-performance protective coatings are manufactured with the same types of equipment and essentially the same procedures and techniques. Most coatings are made in high-speed mixing tanks using a high-speed impeller for dissolving resins as well as dispersing pigments. Those requiring further processing to achieve a particular fineness of grind or development of color or gloss are normally processed through a bead mill. Although each manufacturing company has its own procedures that depend on the desired product and available equipment, most protective coatings (as well as most paints) are manufactured according to the batch process. (The average batch size is a thousand gallons or less.) This is particularly true with high-performance coatings, since numerous different materials are often added to satisfy the product and color specifications of individual purchasers. On the other hand, many companies in the protective coating field have endeavored to standardize coating colors and constituents.

Beginning in the 1980s and accelerating in popularity in the 1990s has been the practice of producing the largest economical size batches of pastel, intermediate, and deep tint bases, from which small batches could be color matched with high-strength color dispersions of solvent or waterborne acrylic tinting colors. This has been a common approach to solving the critical color needs without the cost of small batches.

Paint and coating factories vary enormously in size. At the outset of the 1970s, there were approximately 1,600 paint factories in the United States. Today there are less than 650. On the other hand, the methods used and equipment needed is approximately the same for even the largest manufacturers. The difference exists mostly in scale, since a small manufacturer with the required background and technology can produce an end product equivalent in quality to that produced in much larger plants. The real difference is that most of the smaller companies manufacture paint for distribution in a very restricted area and, for the most part, supply trade sales or small volume specialty products. Many of the large companies, however, make only trade sale products or industrial finishes, although some of them are active in all areas.

Since 1990, there has been a dramatic decrease in the number of small and medium-sized paint/coatings manufacturers as the industry has consolidated in the face of increasing costs to meet more and more stringent government regulations covering worker and health protection, hazardous waste disposal, and volatile emissions into the atmosphere. Today there are still a significant number of small, niche manufacturers who produce a specialty line of products for a very well defined market and there are the same large, multinational manufacturers who increasingly make inroads into the protective coatings market from their historically strong architectural and maintenance painting markets. The number of medium-sized manufacturers trying to serve a broad range of markets has dwindled considerably.

Protective coating manufacturers, in particular, have attempted to standardize products for use in various corrosive environments. These products are not limited to local situations, but for the most part are intended for national or international markets. This is due not only to the pervasiveness of corrosion problems, but also to the nature of the industries they serve. Marine installations, bridges, chemical plants, refineries, atomic energy plants, and paper plants, for instance, generally enjoy a worldwide demand for their products.

Due to this international scope, consistency has become a critical factor in the high-performance coating industry. That is, manufacturers must be sure a given product performs the same regardless of whether it was purchased from a plant in the United States, Europe, or Japan. This is often more difficult than it may sound. While most raw materials are standardized in the United States, there can still be differences in pigments or resins that are manufactured in different plants within the same country.

A plant in California, for example, developed a coating using a particular grade of red lead pigment. The coating was well received by industry, so the formula was eventually transferred to a second plant on the East Coast. The same number and grade of red lead was purchased from the same supplier for both the western plant and the one in the East. There was sufficient difference, however, in the red lead pigment of different origins, that the coating plant on the East Coast could not duplicate the original product, even though it utilized the same formulation. Thus, it was necessary to ship pigment from the West Coast in order to obtain consistent results.

More recently, the use of micaceous iron oxide lamellar pigments has grown in popularity because of the extra strength it imparts to the coatings film and the additional resistance to both permeation of moisture and penetration of ultraviolet rays into the resin structure of the coating. Originally mined in Europe and now sourced in other parts of the world, the specifications and performance of a given coating can be significantly affected by the source of the micaceous iron oxide pigment.

These are only two examples of the type of difficulty that often arises when trying to standardize a product manufactured in different places throughout the world. Raw materials that meet a United States standard are even more difficult to obtain in foreign countries. Nevertheless, most of the protective coating manufacturers who sell in the international market make every attempt to standardize their product so that when using it for prevention or control of a corrosion problem, the end results will be consistent worldwide. This is something to keep in mind when specifying products both in the United States and overseas where they may come from different manufacturing plants.

Other Coating Terms

Comparisons of various coatings are often made according to composition. The composition of paint is often expressed by dividing the total weight between the pigment and the vehicle as percentages. In this case, the pigment includes both the hiding and the reinforcing or extender pigments, and also any material used to regulate the gloss of the coating. The vehicle is the complete liquid portion of the paint. Normally, it consists of both nonvolatile matter and volatile materials.

In specifications, the nonvolatile portion of the vehicle is indicated as the vehicle nonvolatile, or more commonly as vehicle solids, binder, or film-former. The volatile portion of the vehicle is the solvent and is usually designated by that name. The sum of the pigments and the vehicle solids is the total nonvolatile or total solids of the coating. This is the part of the coating that remains on the surface after the coating is applied and after the solvent evaporates. It is the part that makes up the thickness of the coating as indicated by the term mil square feet per gallon/liter (i.e., the amount of total solids in one gallon/liter of coating spread one mil thick over a certain number of ft^2/m). A gallon/liter of coating would cover 1,604 ft^2 one mil (25 µm) thick if the coating were 100% solids. If the coating contained 50% solids, it would then cover 800 mil ft^2 per gallon. An understanding of these terms is important in comparing coatings received from the same manufacturer, from different plants, or from different manufacturers.

Coatings Complexities and Variables

A coating is a complex material made of a whole series of interacting ingredients such as resins, plasticizers, pigments, extenders, catalysts, fungicides, and solvents. All of these materials are then applied as a thin film of only a few microns or thousandths of an inch. The solvents must evaporate and the nonvolatile portion must deposit a continuous film over the surface. In some cases, this film will react with the surface, with internal curing agents, and with oxygen in the air to become insoluble, or with water in the air to hydrolyze and become insoluble. It must also adhere to the surface and provide an attractive finish that will withstand wind, rain, sun, humidity, cold, heat, oxygen, physical damage, chemicals, biodegradation, and many other physical, chemical, and natural forces.

The variety of materials within a coating and the innumerable conditions under which it must perform thus give rise to hundreds of

different types of coatings. Each variation is developed to address differences in material, application, or use. Today's coating process makes the old "anyone-can-grab-a-bucket-of-paint-and-a-brush" concept obsolete. Coatings are vital to the protection of all types of structures used by society which are, in themselves, becoming more complex and subject to increasingly more corrosive environments. Thus, coatings are becoming so vital to their protection that they should be considered an actual part of the structure and not simply a last-minute detail.

The drying process introduces even more variables. Industrial product finishes have been developed to limit many of the drying variables by controlling the type of application and the speed and temperature at which the coating is cured. Unfortunately, most industrial coatings are applied to structures where the curing of the coating cannot be accurately controlled. This is usually due to variables such as weather, humidity, surface conditions (rough, smooth, or filled with pinholes), the type of substrate (steel, concrete, wood, plaster, or one of the several nonferrous metals), surface cleanliness, and application techniques (brushing, rolling, spraying, or the application of a hot-melt). It may also be necessary to deal with a rather wide variety of coatings, which often dry in radically different ways, affecting the final dry film.

Types of Coatings

Thermoplastic Coatings

Thermoplastic coatings or lacquers dry solely by the evaporation of the solvent (the resin is already in its final form), and there is no chemical or physical change in the nonvolatile portion of the coating that forms the film. In this case, the film-forming process is merely the evaporation of the solvents from the liquid leaving the thermoplastic resins on the surface as a continuous film. This process is not as simple as it sounds, since most coatings are made up of a number of different solvents with different evaporation rates in order to ensure that the final film is continuous. If the solvent evaporates too quickly, it may cool the surface of the coating to such an extent that water is condensed on and in the film. This is not an uncommon phenomenon where coatings are applied under high humidity conditions. "Blushing" is the term that refers to water condensation, which makes the coating turn white. (Note: This is not the same as amine blush, which is discussed in Chapter 5, "Corrosion-Resistant Organic Coatings"). The film that is blushed is generally porous and does not have the same resistant characteristics as the smooth resin film that has properly formed over a surface. Examples of the thermoplastic-type coating are vinyls, acrylics, and chlorinated rubbers.

Conversion Coatings

Conversion coatings, on the other hand, dry or react in a whole series of steps. All such coatings undergo a chemical and physical change in the process of film formation. There are several different types of conversion coatings; the oldest and most familiar are paints that have a drying oil and a resinous varnish or resin as the binder. These usually dry more slowly than the thermoplastic coatings and the various drying stages are considerably more complex. These stages are solvent evaporation, oxidation, thickening or polymerization, and gelation.

Gelation occurs when the polymers reach a size and concentration that forms a continuous network. At this point, although the film is considered dry, it still contains a considerable amount of liquid material and may be somewhat soft. The remaining film continues to cure or dry until the paint becomes hard and ultimately brittle. A sunlight and heat mixture accelerates these latter changes. When the films reach their ultimate hardness, they generally tend to increase in porosity and lose resistance to moisture and chemicals.

Epoxy

A much more important conversion reaction, from a corrosion standpoint, is catalyst conversion or cross-linking at ambient temperatures. The epoxy coating forms by this process in which the epoxy resin is mixed with an amine just prior to application. The epoxy coating's drying process consists of solvent evaporation followed by a chemical reaction of the amine and the epoxy resin in such a way that cross-linkage (the joining of two or more molecules of the epoxy resin through a chemical bond with the amine) takes place. In this case, the amine actually becomes part of the chemical reaction and is an integral part of the new polymer. It is therefore not a true catalyst. This process is temperature-sensitive and can take place in the absence of air. Where cross-linkage takes place, the coating is called thermoset. Thus, it is no longer soluble in its original solvents, nor is it as sensitive to softening by heat.

Another conversion reaction takes place when an epoxy resin reacts with a second resin (e.g., a polyamide resin). Here, the same mechanism as with the amine takes place, only in this case the two resins, the epoxy and the polyamide, react and cross-link to form a solid resin film. The film is therefore somewhat more resilient and elastic than the films formed using the amine epoxy reaction.

Polyurethane

While these two-component products also form films through a conversion reaction and cross-link into a somewhat chemically resistant film, the main purpose is to improve the finished appearance to which the coating is applied. Polyurethanes form a film through the chemical reaction of either acrylic or polyester modified urethane base components with isocyanate reactive converter components. The process, however, is similar to that of epoxy in that nothing of any consequence happens in the way of a chemical reaction until the solvent evaporates from the applied film. At that point, cross-linking proceeds to ultimate hardness according to the resin choice and the ratio of base to converter. This process is not as temperature sensitive as epoxy but is more humidity sensitive during the curing process. Excess humidity at this point can lead to loss of gloss and to cheesy, nonuniform film formation, or wrinkling.

Moisture (Hydrolysis)

A third familiar process of film conversion takes place when water from the atmosphere converts the film from a liquid to a solid. This is one of the processes by which the moisture cure polyurethane coatings are formed. In this case, moisture from the air and/or substrate reacts with the polyurethane resins during the initial evaporation stage, cross-linking it and increasing the molecular size of the resin until it becomes solid. The solvent-borne IOZ coatings also require moisture from the air, whereas the waterborne IOZ coatings require carbon dioxide (CO_2) to change the silicate molecule (i.e., ethyl silicate) into a continuous coating by reaction with the zinc pigment and the steel substrate.

Some of the other conversion processes require baking or heating, which are not practical where coatings are to be applied to large

existing structures or equipment.

The Finished Product

In the painting or coating process, it is important to distinguish between the liquid coating prior to its application and the finished product. The final step in the coating formation process occurs only after the coating has been applied and is reacting in place. Thus, the completion of a coating is beyond the control of the original manufacturer so that the quality of the coating depends largely on the care taken during this final step of coating formation. Those with responsibilities for proper coating application and curing must not overlook this point.

Coatings are different from almost all other purchases, in that the buyer or the user can tell very little about the quality of the product from its appearance when purchased. The purchaser can only see the can, label, color card, and perhaps a set of application instructions. While the label may show the composition of the coating and may outline various safety procedures to be taken during its application, it offers very little information with regard to the ultimate effectiveness of the product. Two products with essentially the same label analysis can differ greatly in price and in performance. The liquid paint, then, is only of temporary concern to the paint user. The user's real interest and long-term concern is in the finished surface film after the drying or curing process has been completed.

The Development of Protective Coatings

Paint, coatings, and eventually high-performance coatings were developed as a need for them arose and as the materials became available that allowed their production. Of prime importance in the development of protective coatings was the petroleum industry, which produced most of the basic ingredients from which all or most of the synthetic resins were developed. The cracking of petroleum produced all types of workable compounds with unsaturated molecules (capable of cross-linkage and polymerization) that were important in the building of large resin polymers such as vinyls and acrylics. The solvents that were necessary for the solution of the resins also were derived from petroleum or natural gas. At a somewhat later date, the building blocks for the epoxies and polyurethanes were derived from petroleum refining. Through natural gas, the petroleum industry was responsible for the rapid growth of the fertilizer industry and of the very broad petrochemical industry. The growth of both of these increased corrosion problems, thus increasing the need to protect buildings, structures, and equipment. In moving to offshore sites, the petroleum industry created additional, massive corrosion problems that could only be solved with high-performance protective coatings.

The basic heavy chemical industries were also operating during this development period. These plants produced basic acids such as hydrochloric, sulfuric, and nitric acid (HCl, H_2SO_4, and HNO_3), as well as chlorine and caustic. The steel, paper, and marine industries all had massive corrosion problems, but prior to this time had been dealing with them through replacement rather than protection. Steel was inexpensive, so when a member corroded to the point where it was no longer structurally sound, it was replaced. When pipes and ducts in the paper industry rusted through, they were replaced. When tanker tank bulkheads in the marine industry were reduced to a dangerous level by corrosion, they also were replaced.

There was some thought being given to the protection rather than continual replacement of steel surfaces prior to World War II. The war itself, however, provided the impetus in actually developing a means of corrosion prevention. Not only was steel more costly during this period, but it was also in very short supply, making it necessary to take measures to protect the ships and structures that were already available. It was during this time that the first test application of a coating on the interior of a tanker tank was applied. The test utilized a very small area of only several hundred square feet, yet it did demonstrate that the new synthetic resins had the ability to withstand corrosive attack from salt water and refined petroleum products, and thus provide the protection needed for steel surfaces.

It is interesting to note that the intensified corrosion problems, the increased need for protection, the proper materials (i.e., new synthetic resins), and the tighter economic situation all developed during the same period to create the driving force in the production of new high-performance coatings. Since that time, not only has the economic need for the protection of steel and concrete surfaces increased, but the extremely rapid expansion of the world's various industries has increased corrosion problems as well. Thus, corrosion research and protective coating development has continued at an ever-increasing rate.

The need for these specialized coating products will continue to rise as new industries develop, new chemicals are made, new processes are used to protect the environment, and the cost of basic building materials increases. Their use will also increase as they become more widely recognized as a major source of energy savings, providing structural protection and thus added years of useful life.

The Future of Protective Coatings

While the use of protective coatings is becoming more and more important, there have been changes in recent years that drastically affected both the paint and the protective coatings industries. Air pollution, hazardous waste disposal, and worker/health protection have become major areas of concern for several state and federal government agencies, and changes are being demanded that have made many presently available products unacceptable for use in the United States and continental Europe. To a lesser extent, the rest of the world has not yet incorporated all these restrictions, but the movement toward universal preservation of the environment is promoting these changes. Although the industry's corrosion problems are greater now than at any previous time in history, many presently effective solutions have given rise to new and different ones because of government requirements. The "advanced technology" coatings that resulted from these regulatory requirements have not always been as effective as the old "tried and true" systems.

It has become necessary to drastically reduce the emissions of VOCs or solvents, which have been a major ingredient in protective coatings. This is especially true for high molecular weight resins, which have the highest and broadest chemical resistance. Air pollution is a major area of concern for high-performance coating manufacturers, with all indications pointing to a major reduction of, if not complete restriction against, the use of solvents in any form. Present research by most high-performance coating production companies is in the area of high solids and 100% solids coatings, and toward waterborne or water-dispersed coating materials.

Whatever develops, whether it involves reformulation, higher solids coatings, water dispersed materials, or completely new approaches, the coatings will undoubtedly be even more complicated and demanding in manufacture, surface preparation, and application. More highly technical and highly trained individuals will be required to manufacture, sell, and apply them, and new raw materials and manufacturing techniques will undoubtedly be needed for their production.

This issue of changes within the industry is discussed in an article in *Maintenance and New Construction Coatings*[17] as follows:

> The era of change has arrived for the maintenance and new construction coatings industry. Starting from government regulations, vibrations of change are impacting the raw materials supplier on one end and the user engineering construction firm on the other. With change there are opportunities.
>
> It is obvious that coatings and raw materials producers are maintaining aggressive research and development efforts on low-solvent and/or no-solvent non-residential coating projects. It's imperative that all companies involved directly or indirectly with maintenance and new construction coatings be well aware of the changes taking place. Those companies that are taking steps to deal with these changes are the companies that will ultimately benefit.

This, of course, does not mean that the lessons that have been learned in the last half-century are to no avail. The knowledge gained from the study of corrosion and corrosion processes is as valid today as it ever was. The methods of testing coatings under corrosive conditions are equally as valid, the need for proper surface preparation may be even greater with the newer coatings, and while application procedures may change, the principles of application will remain the same.

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17 R.T. Ozumek, "Maintenance and New Construction Coatings," *Chem. Purchasing* (April 1979), p. 27.

2 Corrosion as Related to Coatings

Corrosion as defined in the NACE International book, *Corrosion Basics, An Introduction,* is "... the destruction of a substance (usually a metal) or its properties because of a reaction with its environment."[1] This definition does not make use of the terms chemical or electrochemical because such terms would define corrosion only as it relates to metals and would not allow its application to many other materials that disintegrate due to environmental exposure.

Corrosion of Materials Other Than Metal

As defined, then, corrosion may affect materials other than metals, such as concrete, wood, ceramics, and plastics. It must also be noted that the properties of a material, as well as the material itself, can and do deteriorate. Some forms of corrosion produce no weight change or visible deterioration, yet the material may fail unexpectedly because of certain property changes within the material that may defy ordinary visual examination or weight change determinations. Although these are not necessarily common changes, they are nevertheless important forms of corrosive action, which should at least be somewhat familiar to the corrosion engineer.[1]

A good example of such deterioration is the linear breakup of polyethylene sheet after its exposure to weather and sunlight for a period of time. The failure in this case, which is a breakup of the entire sheet structure, is usually sudden. On the other hand, a properly pigmented vinyl sheet may remain essentially unchanged for years with only minor chalking taking place.

Chalking is an example of the way in which coatings themselves may be said to corrode. It occurs when the binder disintegrates from the exposed surface through the depth of the coating until the substrate is exposed. Some coatings, such as the early epoxies, reacted rapidly to weathering; others, such as polyurethanes or vinyls, may chalk only marginally for years.

Early Corrosion Studies

While other materials are affected by corrosion, the area that has received the most intensive study is actually the corrosion of metals. Its attention is warranted by the fact that metals, and steels in particular, constitute the primary structural materials used around the world.

Corrosion studies were first launched at the beginning of the 19th century. In 1824, for instance, Sir Humphrey Davy initiated the use of zinc to control the corrosion of copper-sheathed ship hulls.[2] Today, this same procedure is used to protect steel hulls from corrosion initiated by bronze propellers. Almost a century later, Dr. Willis Rodney Whitney developed a principle that electrochemical reactions form the basis for corrosion. From his experiments involving the corrosion of steel pipe in water, he concluded:

> Practically the only factor that limits the life of iron is oxidation under which name are included all chemical processes whereby the iron is corroded, eaten away, or rusted. In undergoing this change, the iron always passes through or into a state of solution and we have no evidence of iron going into aqueous solution except in the form of ions. We have really to consider the effects of conditions upon the potential difference between iron and its surroundings. The whole subject of corrosion is therefore an electrochemical one and the rate of corrosion is simply a function of the electromotive force and resistance of the circuit.[3]

Fundamentals of Corrosion

Electrochemical Principles

The application of the electrochemical principles developed by early investigators provides the means for modern methods of corrosion control. The primary reason iron or steel corrodes is that elemental iron (i.e., the condition of iron as it exists after it has been reduced from its ores) is thermodynamically unstable. There does not seem to be any free iron available in nature. Rather, all of the iron that has been found exists in combination with other elements such as oxygen or sulfur. In order to change iron from an oxidized state to that of a metal, it is necessary to force a large amount of energy into the system. This energy is then stored in the metallic iron. The fundamental laws of nature governing the conservation of energy require that in time, the energy balance must be restored by returning the unstable metal to its oxidized state. The most common type of iron ore has a composition of ferric oxide (Fe_2O_3), and in its oxidized state usually appears as rust, with the red form being the Fe_2O_3. Iron is also found in ore as magnetite, or Fe_3O_4, which is also a common corrosion product. The same is true of other metals such as zinc, aluminum, and magnesium. In each case, it takes a massive amount of energy to change the ore into metal. The more energy that is absorbed by the metal, the easier it tends to corrode.

There are some metals, however, that exist in nature in a pure metallic form. These include tin, copper, silver, and gold. They may also exist in the form of ores in combination with other elements. In these cases, however, the extraction from the ore itself requires little input of energy (Table 2.1).

TABLE 2.1: Metals in Order of Energy Required for Conversion from Their Ores

Common Metals	Energy Required for Conversion
Potassium	Most
Magnesium	
Beryllium	
Aluminum	
Zinc	
Chromium	
Iron	
Nickel	
Tin	
Copper	
Silver	
Platinum	
Gold	Least

Source: F. L. LaQue, *Corrosion Basics—An Introduction*, Chapter 2, "Basics of Corrosion" (Houston, TX: NACE International, 1984) p. 23.

Table 2.2: Series of Metals by Decreasing Electromotive Force[A]

Potassium	
Calcium	
Sodium	
Magnesium	
Aluminum	
Manganese	
Zinc	
Chromium	
Iron	(–) active
Cadmium	= 0
Cobalt	inert (noble)
Nickel	(+)
Tin	
Lead	
Hydrogen	
Copper	
Silver	
Mercury	
Platinum	
Gold	

[A]Table 2.4 gives the complete Electromotive Force Series.

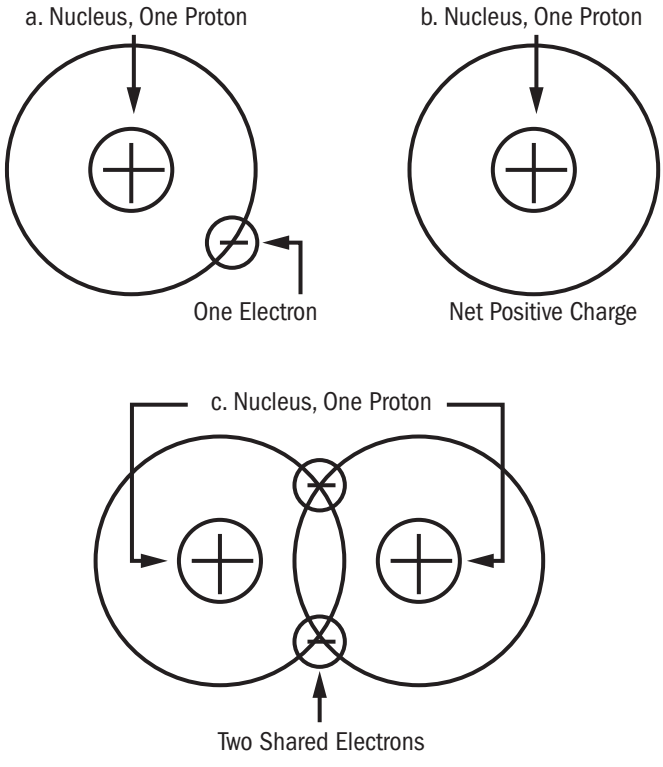


Figure 2.1: (a) Hydrogen atom; (b) hydrogen ion (H+); and (c) hydrogen molecule (H_2). Source: U.S. Dept. of Commerce, Civil Engineering Corrosion Control, Corrosion Control—General, Vol. 1, Dist. by NTIS, AD/A-004082, Jan. 1975, pp. 16, 33.

Electromotive Force

The same orientation of the metals exists in respect to electromotive force (Table 2.2). The ones that require the greatest amount of energy input in order to make the metal itself are also the ones with the highest electromotive force. They also have a greater tendency to go into solution and to form ions. Thus, the electromotive force is sometimes referred to as solution potential.

Hydrogen is used as a reference and is rated in the electromotive series as zero. Moving up the list from hydrogen, the metals become more active. Moving down the list from hydrogen, the metals become increasingly inert. This means the metals above hydrogen are increasingly able to corrode, and actually radiate energy as they go into solution. On the other hand, in order for the metals below hydrogen to ionize, or for them to form salts such as copper, mercuric chloride, or silver nitrate, it is generally necessary to add energy. For example, when a piece of metallic potassium is placed in water, the potassium almost explodes in its attempts to ionize. On the other hand, a piece of platinum may be placed in strong nitric acid (HNO_3) with no evidence of attack.

The electromotive series given in Table 2.2 also shows which metals can displace another metal in solution and suffer corrosion in the process. Any metal may displace the one below it from solution. Chemically, this is known as a double displacement reaction. If iron, for instance, is placed in a solution of copper, the iron will rapidly go into solution and the copper will plate out, thus becoming a metal. This reaction is used extensively in copper mining to obtain copper, which is leached out of copper ores.

As Dr. Whitney first indicated, most corrosion of metals is an electrochemical process that requires the presence of several elements in order to proceed: (1) an anode; (2) a cathode; (3) an electrolyte (i.e., a conductive solution in which the metal finds itself); and (4) an external contact or an external circuit between the anode and cathode (e.g., the metal itself or a wire between two different metals). These four elements constitute what is known as the corrosion cell or corrosion battery. Corrosion can only take place when these four elements are present. Oxygen, however, is a fifth element, which is also generally required in the corrosion process.

Ionization

The terms ion and ionization are important in an understanding of these corrosion cell elements. An explanation of their roles begins with the concept that all matter is made of atoms. Each atom, in turn, is made of a nucleus, which contains a given number of

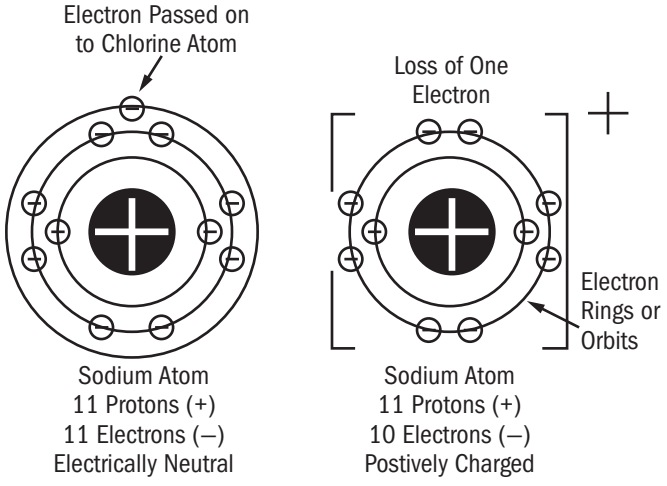


Figure 2.2: Change of sodium atom to a sodium ion.

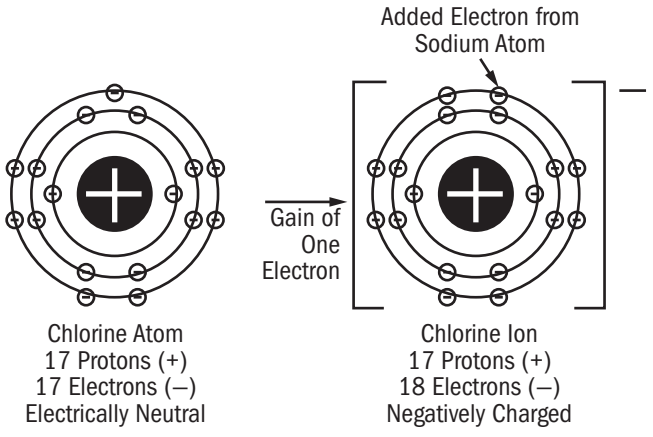


Figure 2.3: Change of chlorine atom to a chlorine ion.

particles of unit positive charge (protons), surrounded by particles of unit negative charge (electrons) of like number. Each positive charge balances a negative charge so that the atom itself is electrically neutral.

For example, hydrogen, an element that plays an important part in many corrosion reactions, has only one proton in the nucleus and is associated with a single electron. The hydrogen atom, therefore, represents the simplest form of element construction.

In more complex atoms, the charges are greater than one, but, in each case, the number of negatively charged electrons is equal to the number of positively charged protons in the nucleus. If one or more of these electrons are removed from any atom, the remaining electrons will not be sufficient to neutralize the positive charge in the nucleus, and the residual part of the atom, now called an ion, is positively charged. If one or more electrons are added to the neutral atom, a negatively charged ion results.[4] For example, if a hydrogen atom loses its electron, it becomes a hydrogen ion (H^+). If the hydrogen atom (H) shares electrons with another hydrogen atom, the two atoms form a hydrogen molecule (H_2) (Figure 2.1).

Ions can be defined as atoms or groups of atoms that have either taken up or surrendered one or more electrons from their outer electron rings. These ions bear positive or negative charges: positively charged ions are called cations while negatively charged ions are known as anions. (Positively charged ions are attracted toward the cathodes, therefore the term cation. Negatively charged ions are attracted toward the anode, therefore the term anion.) The charge carried by ions is largely responsible for their unique properties either in or out of solution, and the properties differ markedly from the neutral atoms or molecules.

Iron is a neutral atom when it is in its metallic form, but it becomes an ion when it loses two electrons and therefore becomes positively charged. Most of our common inorganic chemicals, such as acids (e.g., hydrochloric acid [HCl]), alkalies (e.g., sodium hydroxide [NaOH]), or salts (e.g., sodium chloride [NaCl]) are strongly ionized when in water solution. Water for example, contains about $10^{(-7)}$ molecules per liter of hydrogen or hydroxyl ions.[5] Although water is not considered highly ionized, if a hydrogen ion is removed from solution (i.e., during corrosion), another immediately takes its place so that the number of ions available from water remains about constant.

Ionization is the state of being ionized. A molecule of NaCl, for example, is only in molecular form when it is in the form of a solid. As the solid material dissolves in water, the sodium and chlorine separate to become a positive sodium ion and a negative chloride ion. In water solution, NaCl is always in a state of ionization. The same is true for ferric or iron chloride.

As previously shown, any atomic element can become an ion by either gaining or losing an electron. Atoms are made up of an equal number of positive and negative charges. If an electron or negative charge is lost, the atom becomes a positive ion. If an electron is gained, it becomes a negative ion. This principle is demonstrated in Figures 2.2 and 2.3

Ionization of a metal can be expressed in a chemical equation such as the following:

$$Fe \xrightarrow{H_2O} Fe^{++} + 2e^- \qquad (2.1)$$

In this case, the symbol "Fe" indicates atomic or metallic iron. The arrow with "H_2O" above it indicates iron in contact with water. The "Fe^{++}" represents an iron ion with a positive charge. The "e" stands for electrons that, as indicated, have a negative charge. Thus, for every iron ion with two positive charges, there are two negative electrons released. The ionization of zinc is indicated in the same way:

$$Zn \xrightarrow{H_2O} Zn^{++} + 2e^- \qquad (2.2)$$

The ionization of aluminum, magnesium, or any of the common metals for that matter can be indicated in a similar fashion, although there may be more or less electrons released, depending on the specific metal involved. Ions in solution form an electrolyte, and the electrical conductivity of the solution depends on the concentration and the mobility of the ions in the solution. The mobility of the ion depends on its size and upon the ion-solvent interaction. The electric current carried by the electrolyte results from the motion of oppositely charged ions in the solution. Each ion type; that is, positive or negative, carries a certain proportion of the current. The amount of current conveyed is generally in proportion to the concentration of the ions in the solution. In fact, electrical conduction in all aqueous and other nonmetallic systems is almost entirely carried on by the movement of ions. The energy released in ionic reactions may take the form of electrical energy, as in storage and dry cell batteries, as well as in the corrosion cell.

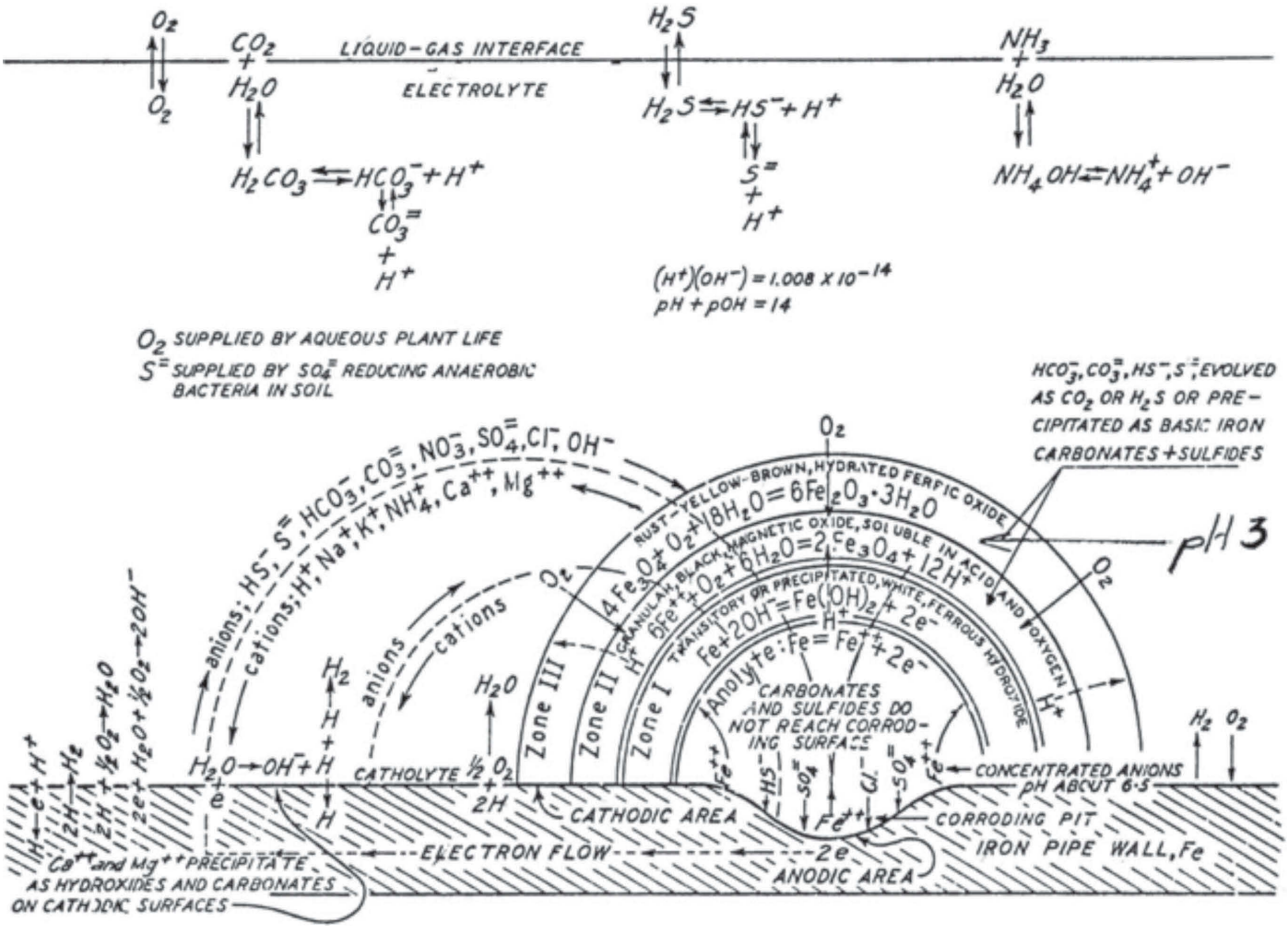


Figure 2.4: Schematic representation of the underground corrosion process. Courtesy Dr. Gordon N. Scott.

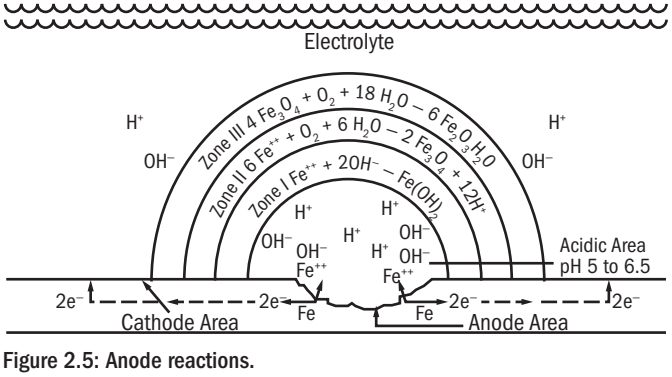


Figure 2.5: Anode reactions.

The Corrosion Cell

The Anode

The first of the four elements necessary to make a corrosion cell is the anode. The anode is the area where the metal goes into solution and where the actual metal loss takes place. Figure 2.4 shows the complex chemical reactions that take place at both the anode and the cathode, while Figure 2.5 illustrates the principal anode reactions. The first reaction in the anolyte zone occurs when metallic iron goes into solution as a ferrous ion with the release of two negative electrons. In Zone I, which is the area just beyond the anolyte area where the iron is going into solution, the iron ions react with hydroxyl ions in the area to form ferrous hydroxide. This reaction is important in that it removes the ferrous ion from solution and creates the reasonably insoluble ferrous hydroxide [$Fe(OH)_2$]. This changes the equilibrium in the corrosion cell and allows more iron to ionize and go into solution. $Fe(OH)_2$ is a transitory, whitish precipitate that forms at the interface of the corroding metal.

The reaction that takes place in Zone II to form Fe_3O_4, or magnetic iron oxide, is one of the more complex reactions. As shown in Figure 2.5, iron ions react with oxygen and water to form Fe_3O_4 with the release of hydrogen ions. (Other reactions probably take place as well.) The $Fe(OH)_2$ in Zone I can react with additional oxygen to form Fe_3O_4, or with any carbonate ion that may be in the area to form ferrous carbonate. The Fe_3O_4 is a jet-black material; where it exists in a deep pit, it is a black semisolid material, and where the corrosion product is dry, it is a black scale, often with yellowish cracks running through it.

Zone III is the top of the tubercle over the anode where a more straightforward reaction takes place. The uppermost Fe_3O_4 reacts with oxygen to form hydrated ferric oxide, or Fe_2O_3. This is the yellowish-reddish product commonly known as rust.

The negative ions in the electrolyte, such as carbonate, sulfate, and hydroxyl ions, are attracted toward the anode area because of the positive iron ions available at that point. As the hydroxyl ions react with the ferrous ions to form Fe(OH)2s, an excess of hydrogen ions remains in solution to create a slightly acidic condition. This was recognized by Speller, who explained in his book, *Corrosion Causes and Prevention,* that:

Table 2.3: Sign Conventions

Anode	Cathode
Metal loses an electron to become + ion (cation).	An atom gains an electron becomes a – ion (anion).
The electron that loses electrons is called the anode.	The electron that gains electrons is called the cathode.
Oxidation occurs at the anode.	Reduction occurs at the cathode.
Anions (–) move to the anode in the electrolyte.	Cations (+) move to the cathode in the electrolyte.
The anode is positive (+) in the chemical concept.[A]	The cathode is negative (–) in the chemical concept.[A]
The anode is negative (–) in the electrical or engineering concept.[B]	The cathode is positive (+) in the electrical engineering concept.[B]

[A]Chemically, electrons flow from the anode to the cathode in the metallic (internal) circuit.
[B]Electrically, conventional positive (+) current flows from the cathode to the anode in the metallic (external) circuit.

When a tubercle of rust forms with a dense envelope of ferric hydroxide, the inner anodic portion, which is undergoing corrosion, may become decidedly acid. Baylis has observed that the soluble portion of such rust tubercles has a pH of about 6 with a pH of 8 in the water outside. For these reasons it can be seen that as products of corrosion gather over the mouth of a pit, the metal at the bottom of the pit will become more anodic, so that the rate of penetration increases as the pit penetrates deeper into the metal.[6]

It should be noted that the anolyte area in Figure 2.5 is the acidic area with a pH ranging from 6.5 down to 5.0.

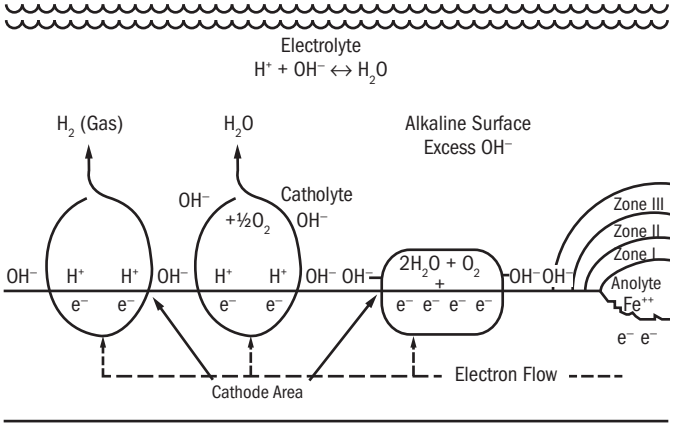


Figure 2.6: Cathode reactions.

The Cathode

The second element in the corrosion cell is the cathode. Cathode reactions, although in many ways less complex than anode reactions, are extremely important in controlling the rate that corrosion takes place at the anodes. The anodic reaction cannot occur at a higher rate than the corresponding electrons can be accommodated by the cathodic reaction. The reaction that takes place at the cathode is essentially the neutralization of the electrons that are created as the iron goes into solution. The electrons can be neutralized through one of these three reactions (Figure 2.6):

$$2H^+ + 2e^- \rightarrow H_2 \quad (2.3)$$

$$H^+ + e^- \rightarrow H_2 \quad (2.4)$$

$$2H + \tfrac{1}{2}O_2 \rightarrow H_2O$$

$$2H_2O + O_2 + 4e^- \rightarrow 4OH^- \quad (2.5)$$

The first neutralizing reaction is that of hydrogen ions with electrons to form gaseous hydrogen. Where a massive amount of hydrogen ion is available, as in an acid solution, the gas bubbles form rapidly and hydrogen gas can actually be obtained in volume from the solution of iron by HCl. The equilibrium electrode potential (referred to hydrogen) of iron at 25 °C in contact with a normal solution of ferrous ions is –0.44 V. Iron will therefore displace hydrogen from water.[5] This is the first step in the corrosion process and therefore one of the most important chemical reactions involving iron. The second reaction, also removing hydrogen from the cathodic area on the metal surface, is that of atomic hydrogen with oxygen to form water. In the third chemical reaction, oxygen reacts with water and electrons to form hydroxyl ions. This is an extremely important reaction from a coating standpoint since hydroxyl ions are strongly alkaline. When they are concentrated on the cathode area of a metal, any coating on that metal must be strongly alkali-resistant or it will tend to saponify and disintegrate.

The Electrolyte

The third element in the corrosion cell, the electrolyte, is also very important. The electrolyte is the solution that is on, surrounds, or covers the metal. The conductivity of the solution on the metal surface is the key to the speed of the corrosion process. A solution with a high conductivity or low resistance makes for rapid corrosion.

Pure water, even though a relatively poor conductor, still contains ions (H+ and OH) so that corrosion will and does take place, although rather slowly, in pure water. Examples of this are often noted in high mountain lakes where tin cans have been thrown in the water. The conductivity of snow water is also relatively low; however, the oxygen content is high and the tin cans form active anodes wherever the iron is exposed to water. In the case of seawater, corrosion cells are formed readily since seawater is almost 100% ionized and is a very good conductor.

The External Circuit

The fourth element, the external circuit, is also important. Where the anode and cathode are on the metal surface, the metal itself acts as the external circuit. If there are two pieces of metal, they must either be in contact or must have an external connection in order for the corrosion process to take place. The conductivity or resistance of the external circuit also helps determine the rate of the corrosion process.

Table 2.4: Electromotive Force Series

Electrode Reaction	Standard Electrode Potential E (V), 25 °C
$K = K^{+} + e-$ –	−2.922
$Ca = Ca^{++} + 2e-$ –	−2.87
$Na = Na^{+} + e-$ –	−2.712
$Mg = Mg^{++} + 2e-$ -	−2.34
$Be = Be^{++} + 2e-$	−1.70
$Al = Al^{+++} + 3e-$	−1.67
$Mn = Mn^{++} + 2e-$	−1.05
$Zn = Zn^{++} + 2e-$	− 0.762
$Cr = Cr^{+++} + 3e-$	−0.71
$Ga = Ga^{+++} + 3e-$	−0.52
$Fe = Fe^{++} + 2e-$	−0.440
$Cd = Cd^{++} + 2e-$	−0.402
$In = In^{+++} + 3e-$	−0.340
$Tl = Tl^{+} + e-$	−0.336
$Co = Co^{++} + 2e-$	−0.277
$Ni = Ni^{++} + 2e-$	−0.250
$Sn = Sn^{++} + 2e-$	−0.136
$Pb = Pb^{++} + 2e-$	−0.126
$H2 = 2H^{+} + 2e-$	0.000
$Cu = Cu^{++} + 2e-$	0.345
$Cu = Cu^{+} + e-$	0.522
$2Hg = Hg^{++} + 2e-$	0.799
$2\ Ag = Ag^{+} + e-$	0.800
$Pd = Pd^{++} + 2e-$	0.83
$Hg = Hg^{++} + 2e-$	0.854
$Pt = Pt^{++} + 2e-$	ca1.2
$Au = Au^{+++} + 3e-$	1.42
$Au = Au^{+} + e-$	1.68

Source: G.L. Clarke, G.G. Hawley, *Encyclopedia of Chemistry,* "Electrochemistry" (New York, NY: Reinhold Publishing Co., 1957), p, 338.

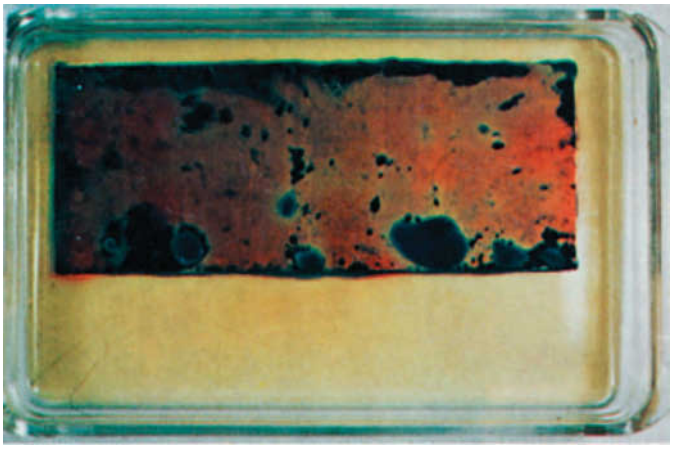


FIGURE 2.7: The corrosion of a steel specimen submerged in a gelatin bath is represented by the blue anodes and pink cathode.



FIGURE 2.8: Sandblasted steel in a gelatin bath shows blue anodes and pink cathodes. Scratches and areas of previous corrosion become strong anodes.

Oxygen as a Factor

Oxygen can be considered the fifth element in a corrosion cell. While corrosion may begin with the presence of only the first four factors, without oxygen, the process soon slows down or stops altogether. Oxygen is extremely important in most all corrosion reactions in order to remove the hydrogen ion from the cathode and to allow additional electrons to be neutralized. When hydrogen accumulates on the surface as a hydrogen film, the electrons can no longer be easily neutralized and the corrosion cell is said to be polarized.

Anode–Cathode Relationship

The formation of an anode-cathode relationship on steel may be easily demonstrated through the use of a gelatin bath with a small amount of dissolved common salt (NaCl) to act as the electrolyte. Two indicators must also be added: phenolphthalein, in order to indicate the alkaline area where hydroxyl ions are formed; and potassium ferriferrocyanide, to indicate where the iron is going into the solution or where the iron ions are formed. Prior to allowing the gelatin solution to set, it is shaken in order to add oxygen to the solution. Then, as the gelatin begins to set, a steel plate is placed in the bath. The gelatin is then allowed to gel, and within a very few minutes, the formation of the anode and cathode areas on the steel plate becomes visible (Figure 2.7).

The steel panel in Figure 2.7 is cold rolled and otherwise untreated. The pink areas where the caustic is forming (a concentration of OH ions) are distributed randomly over the face of the steel. Note that the cathode area is much larger than the total anode, which is generally the case. The blue areas where the steel is corroding (the iron is forming ions) are also formed on the face of the panel, but are also heavily concentrated along the edges of the panel where the panel has been sheared, along any scratches that may appear on the steel surface, or around holes drilled in the panel. The steel readily forms iron ions in these disrupted areas because of the fact that the steel surface in these areas is new and the iron is more active.

It is assumed that if a sandblasted panel were put in the same test, the entire surface would be active. However, the edges, scratches, and area of previous corrosion on this surface will form the blue areas preferentially (Figure 2.8). It is important to note that corners, edges, welds, and any disrupted areas on the surface of the steel are more corrosion prone than any other area, even though protected with a special coating.

Chemical Concept of a Corrosion Cell

In the chemical concept of a corrosion cell, the iron goes into solution at the anode, reacts rapidly with negative hydroxyl ions, and precipitates. The electrons move through the metal or the exterior circuit to the cathode. At this point, the electrons are neutralized by positive ions (e.g., the positive hydrogen ion on reacting with the electron becomes molecular hydrogen leaving an excess of OH- ions in the area), or oxygen is reduced by reaction with water and electrons to form hydroxyl ions (Figure 2.9). In either case (the removal of hydrogen or the reduction of oxygen), hydroxyl ions are concentrated on the cathode.

While Figure 2.9 schematically shows the chemical reactions in an iron–copper corrosion cell, Figure 2.10 shows an actual iron-copper galvanic couple with an external connection in a gelatin indicator bath. As would be expected, the iron immediately turns blue, indicating rapid corrosion or solution of iron ions, and the copper panel becomes red, indicating the rapid accumulation of hydroxyl ions (OH) on the surface, which usually occurs at the cathode.

Electrical Concept of Corrosion Current Flow

In contrast to the chemical concept, the electrical or conventional concept of current flow is quite different, although nonetheless important since it is used extensively in cathodic protection (CP). According to this concept, the flow of electric current runs from the anode through the solution to the cathode. The anode is often described as the area of the metal surface from which the current leaves the metal and enters the solution. The cathode is used to describe the area of metal surface to which the current flows from the solution and then returns by way of the external circuit to the anode. The electrical current flow, then, is from the positive pole (cathode) through the external circuit to the negative pole (anode) and from the anode or negative pole into and through the solution to the positive pole, the cathode, to complete the circuit. This concept is obviously opposite that of electron flow, which runs from the anode to the cathode through the external circuit (Figures 2.11 and 2.12).

Corrosion engineers commonly use both the chemical and electrical or engineering concept of the corrosion cell. Table 2.3 summarizes the anode-cathode reactions and indicates the difference between the chemical and engineering concepts.

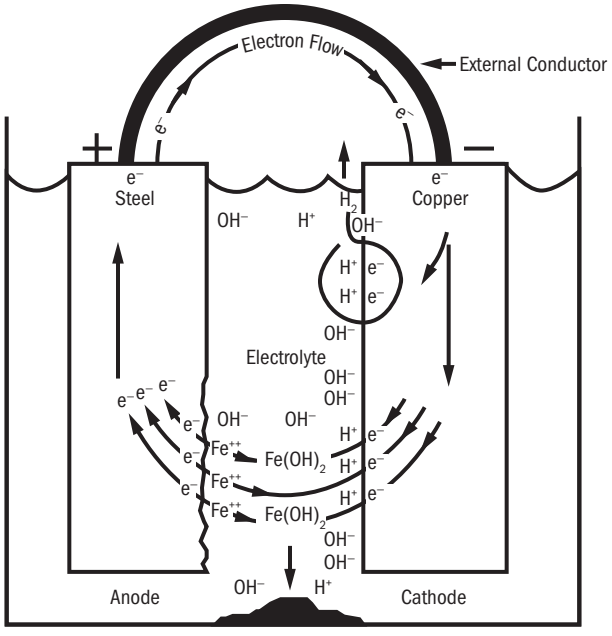


FIGURE 2.9: Electron flow (chemical concept) is an iron-copper conversion cell.



FIGURE 2.10: An iron (blue)-copper (red) couple with an external connection submerged in a gelatin bath. Note the hydrogen bubbles forming on the cathode. These are also shown schematically in Figure 2.9.

Polarization

By definition, polarization is the shift in potential caused by the passage of a current between anode and cathode half-cells. It has previously been mentioned in this text with regard to the formation of hydrogen on cathodes. The electrode potential is important to the corrosion engineer in that it measures the tendency for an electrode (metal-electrolyte combination) to gain or lose electrons. Two half-cells in combination represent a corrosion cell. The potential difference between the half-cells (i.e., the anode-electrolyte half-cell and the cathode-electrolyte half-cell) represents the driving force for corrosion and therefore the speed at which it takes place. The rate of electrochemical reactions, such as those in the corrosion process, is determined by various environmental factors. Therefore, the potential of a given half-cell is influenced by the condition of the metal, the metal ion concentration and other ions in the electrolyte, and the temperature.

Polarization is thus a very important rate-determining factor in the corrosion process. It is a process that hinders or inhibits the normal corrosion process at the electrode. It can take the form of slow ion movement in the electrolyte, slow combination of atoms to form gas molecules, or slow solvation of ions by the electrolyte. Increasing the reaction area lowers the rate of polarization and allows the corrosion processes to take place more readily by providing more surface on which the reactions can occur. Agitating the electrolytes also lowers the polarization rate by providing a maximum number of ions contacting the electrodes.

Electrolyte movement also carries away the products of reaction from the surface, thus decreasing the rate of polarization and increasing corrosion. In the case of hydrogen, agitation would remove the atomic or molecular hydrogen from the cathode surface as soon as it was formed.

Many substances that are included in the electrolytes can greatly affect the polarization of the electrodes. Oxygen and arsenic are examples of substances with opposite effects on the hydrogen electrode reaction. Oxygen effectively depolarizes the electrode or makes the reaction go more rapidly by removing the reaction product, atomic hydrogen. Arsenic, on the other hand, is an effective polarizer in that it makes the combination of hydrogen atoms to gas molecules more difficult. Increasing the temperature increases the rate of most reactions, and therefore would, in general, lower the polarization rate of the cell.

Polarization can be further defined according to its two types: activation and concentration polarization. These represent the two different methods by which electrochemical corrosion reactions are retarded. Activation polarization involves retarding the activity that is inherent in the reaction itself. The rate of the evolution of hydrogen at the cathode is, of necessity, dependent on the speed

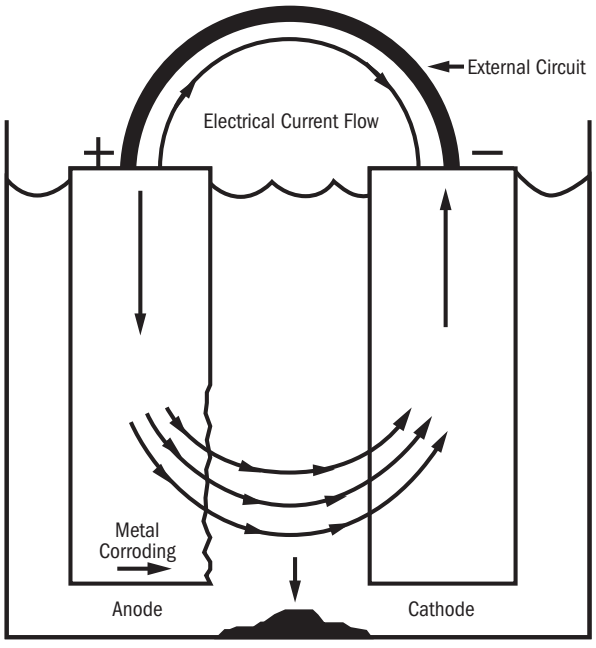


FIGURE 2.11: Electrical current flow (electrical concept) in a corrosion cell.

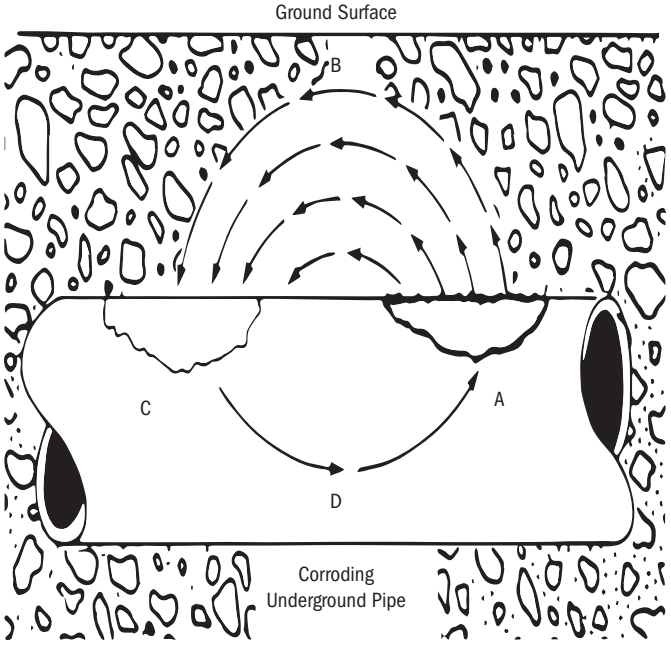


Figure 2.12: The conventional corrosion concept is a more practical illustration of the electrical concept of a corroding un¬derground pipe: (A) Anode area where current leaves the metal to enter the surrounding earth—area where metal is corroded; (B) current flow through earth from anodic area to cathodic area; (C) cathodic area where there's no corrosion of pipe surface; (D) current flows through pipe metal from the cathodic area back to the anodic area to complete the circuit. Source: *Corrosion Basics—An Introduction,* Chapter 5, "Cathodic Protection," (Houston, TX: NACE International, 1984) p. 179.

of the electron transfer from the anode. It is therefore an inherent rate depending on the anode metal. Particular metals vary greatly in their ability to give up electrons; as a result, hydrogen evolution from the cathode likewise varies.

Concentration polarization refers to the electrochemical reaction resulting from concentration changes in the electrolyte adjacent to the metal surface. In this case, if the concentration of hydrogen ions in the solution is relatively low, the neutralization of the hydrogen ion by the electrons will depend on the number of hydrogen ions available and the speed at which they diffuse through the solution. The corrosion reaction would then be controlled by the diffusion rate of the hydrogen ions. With a high concentration of hydrogen ions, the electrochemical reaction would go rapidly, as in acid solutions. While activation polarization is usually the controlling factor in corrosion by strong acids, concentration polarization usually predominates when the hydrogen ion concentration is relatively low (e.g., aerated water or salt solutions).

Knowing the kind of polarization taking place allows prediction of the corroding system's characteristics. For example, if the corrosion were controlled by concentration polarization, any change that would increase the diffusion rate of the hydrogen ion in the solution would increase the corrosion rate. Agitating or stirring the liquid would therefore tend to increase the corrosion rate of the metal. On the other hand, if the cathodic reaction is activation controlled (i.e., controlled by the number of electrons available at the cathode), agitation would have no effect on the corrosion rate. There would be little polarization, for instance, on corroding areas of the ship's water line as it passes through the water.

Oxidation and Reduction

Two terms commonly used in chemistry and important to note from the standpoint of corrosion are oxidation and reduction. Oxidation may be difficult to pinpoint since according to corrosion terminology, it can mean either the rusting of iron or development of white oxides on aluminum or zinc. In order to understand their meanings from a chemical standpoint, it is necessary to examine a chemical formula such as that for iron:

$$Fe \xleftrightarrow{H_2O} Fe^{++} + 2e^{-} \qquad (2.6)$$

This formula indicates iron in water in a state of equilibrium where no current flow exists. The "Fe" is iron as a metal, the "Fe^{++}" is the ionized form of iron, and the electrons indicate the negative charges given up when the metal changes to an ion. The movement of the iron from the metal form to the ion form is called oxidation. Therefore, in a corrosion cell, the metal is oxidized when it goes into solution as an ion. This occurs at the anode where the term *oxidation* also commonly applies to rust forms.

When proceeding in the opposite direction and adding electrons to the ionized iron, the reaction occurs in the direction of the iron as metal and is referred to as *reduction.* A metal, therefore, that has been changed from its oxidized state to the metal, has been reduced. This is what takes place when iron ore is changed to metal in a blast furnace.

Different metals have different capacities for being reduced and for being oxidized. Gold, for example, exists primarily in the reduced state (e.g., as a metal). Potassium, on the other hand, exists primarily in either the oxidized state as an oxide or in the ionic state as a salt. The symbolic reaction for iron given in Equation (2.6) and its relative potential for the electrochemical reaction shown is called an *oxidation-reduction potential.* It may also be called a redox potential, half-cell potential, or solution potential.

Galvanic Corrosion

Electromotive Force Series

When the various metals are listed according to their comparative potential, it is referred to as an electromotive force series, or EMF series. The EMF series in Table 2.4 includes corresponding oxidation-reduction potentials. As explained earlier in this chapter, hydro-

gen is used as an arbitrary reference element. The elements listed above hydrogen are increasingly more reactive, while the elements listed below hydrogen become increasingly inert, with less tendency to ionize or go into solution.

The electromotive force series can be very important in predicting the corrosion of an element in a given environment. A simple rule used for such predicting stats that: *In any electrochemical reaction, the more positive half-cell tends to be oxidized and the more positive half-cell tends to be reduced. A half-cell is either the anode plus the electrolyte or the cathode plus the electrolyte.* This means that in comparing two metals, the one with the more negative oxidation reduction potential will tend to go into solution and become an anode, while the more positive metals (or the less negative metal) will tend to be the cathode where hydrogen can be reduced from the ionic form to the atomic form.

The electromotive force series is especially important in galvanic corrosion prediction. This is because the metals that are most negative will corrode in comparison to another metal that is less negative. Thus, in the case of iron and zinc, it could be determined from the EMF series that the zinc would ionize and go into solution or become the anode as compared to the iron that would be the cathode. Similarly, lead would be expected to go into solution if it were in contact with silver in an electrolyte solution. Also, the farther apart the two metals are in the series, the greater the potential difference between the two and the greater the corrosion that will take place on the more negative metal. Aluminum, for example, rapidly corrodes when in contact with copper.



FIGURE 2.13: Zinc and copper coupled by an external connection to an indicator solution.

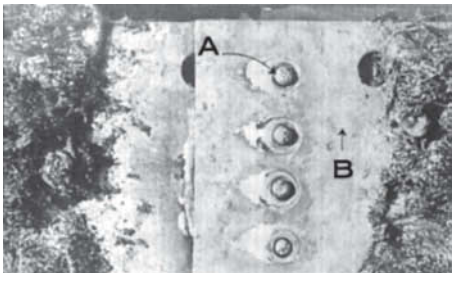


FIGURE 2.14: A large cathode (B-copper) coupled to a small anode (A-Steel) shows intense attack on the steel rivets (A), with little or no corrosion on the copper (BV). Source: N.B. Greence, NACE Basic Corrosion Course, Chapter 3, "Corrosion Related Chemistry and Electrochemistry" (Houston, TX: NACE International, 1971), p. 3-14.

Table 2.5 Galvanic Series in Seawater Flowing at 13 fps (Temperature ~25 °C)s

Material	Steady-State Electrode Potential, V (Saturated Calomel Half-Cell)
Zinc	−1.03
Aluminum 3003-(H)	−0.79
Aluminum 6061-(T)	−0.76
Cast Iron	−0.61
Carbon Steel	−0.61
Stainless Steel, Type 430, active	−0.57
Stainless Steel, Type 400, active	−0.53
Stainless Steel, Type 410, active	−0.52
Naval Rolled Brass	−0.40
Copper	¬−0.36
Red Brass	−0.33
Bronze, Composition G	−0.31
Admiralty Brass	−0.29
90Cu10Ni, 0.83Fe	−0.28
70Cu30Ni, 0.47Fe	−0.25
Stainless Steel, Type 430, passive	−0.22
Bronze, Composition M	−0.23
Nickel	−0.20
Stainless Steel, Type 410, passive	−0.15
Titanium[A]	−0.15
Silver	−0.13
Titanium[B]	−0.10
Hastelloy C	−0.08
Monel 400	−0.08
Stainless Steel, Type 304, passive	−0.08
Stainless Steel, Type 316, passive	−0.05
Zirconium[C]	−0.04
Platinum[C]	+0.15

[A]Prepared by power-metallurgy techniques (i.e., sheath-compacted powder, hot rolled, sheath removed, cold rolled in air.

[B]Prepared by iodide process.

[C]From other sources.

Source: F.W. Fink et al., The Corrosion of Metals in Marine Environments, Battelle Memorial Institute, DMIC Report 254, distributed by N.T.I.S. AD-712 585-S, 1970, pp. 7, 13.

The electromotive force series actually applies only for metals in solution of their own salts. In other electrolytes (e.g., seawater), performances may vary. The general relationships of metals in the EMF series, however, still hold. Table 2.5, a galvanic series of metals and alloys in seawater, serves as an example. While many of the alloys are not listed in the previous series (Table 2.4), and the potentials are different since the metals are in a different electrolyte, the general orientation of the metals in the two lists is similar.

Galvanic Couples

In any galvanic couple, the metal near the top of the galvanic series will be the anode and will ionize and go into the solution or corrode, while the one closer to the bottom of the list will be the cathode and receive galvanic protection. This is illustrated by the metal couples in the corrosion demonstration. (Figure 2.13). The speed at which galvanic corrosion takes place depends on the difference in electrical potential between the two metals. Metal coupled to another relatively close to it in the series will corrode more slowly than when it is coupled with a metal farther down in the series. Zinc coupled with aluminum in a NaCl solution will have a potential of over 700 mV. The greater the potential difference between the two metals, the greater will be the driving force for the more negative metal to corrode. Table 2.6 gives some practical examples of galvanic couples in seawater, showing those that have no chance of working together as well as some that can be combined with reasonably good results.

The rate of galvanic corrosion is not only determined by the relative position of the metal in the EMF series, but also by the exposed area of the two metals. This is particularly important for metals like carbon steel, where the corrosion rate is usually controlled by the total cathodic area available, thus the ratio between the area of the cathode and anode is very important. A small anode coupled to a large cathode of copper both immersed in seawater will result in very rapid attack of steel. This may have been the case where two copper plates were fastened together with steel rivets as shown in Figure 2.14.

Galvanic couples are actually an integral part of modern daily activity. Aluminum, magnesium, and other more noble alloys are combined in the construction of aircraft; aluminum deck houses are used on steel ships; and steel fittings are often incorporated into copper pipelines in the construction of household piping systems. Such couples are both necessary and useful. In order to control or prevent the accelerated corrosion attack that is perpetrated by such galvanic couples, precautions should be taken with at least one of the coupled metals. One possibility is to break the electrical circuit by installing an insulating barrier at the union of the two metals. This is often done in pipelines through the use of an insulating flange or an insulating coupling. A plastic sheet may also be placed

Table 2.6: Examples of Galvanic Couples in Seawater		
Metal A	**Metal B**	**Comments**
Couples That Usually Give Rise to Underwater Results on One or Both Metals		
Magnesium	Low Alloy Steel	Accelerated attack on A. Danger of hydrogen damage on B.
Aluminum	Copper	Accelerated pitting on A. Ions from B attack A. Reduced corrosion on B may result in biofouling on B.
Bronze	Stainless Steel	Increased pitting on A.
Borderline, May Work, Uncertain		
Copper	Solder	Soldered joint may be attacked, but may have useful life.
Graphite	Titanium or Hastelloy C	
Monel 400	Type 316 SS	Both metals may pit.
Generally Compatible		
Titanium	Inconel 625	
Lead	Cupronickel	

Source: F. W. Fink, et al., *The Corrosion of Metals in Marine Environment,* Battelle Memorial Inst., DMIC Report 254, distributed by N.T.I.S. AD-712 585-S, 1970, pp. 7, 13.

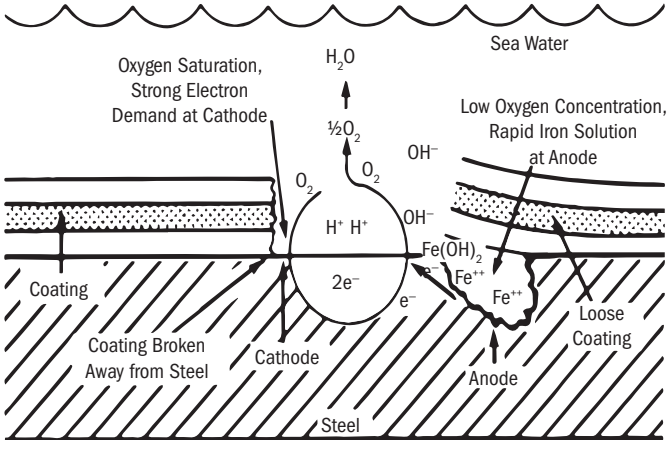


FIGURE 2.15: Oxygen concentration cell found on a ship bottom.

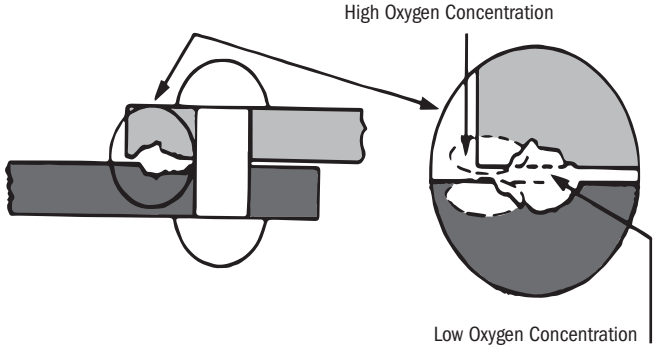


FIGURE 2.16: Schematic of oxygen concentration cell formed in a crevice.

between the two dissimilar metal plates.

If it not possible to isolate the two metallic surfaces, a break in the electrical conductivity of the electrolyte can be achieved by completely coating both metals. In this case, it is important for the applied coating to thoroughly cover both surfaces, particularly the junction between the two. If it is not feasible to coat both metals, the cathodic member of the couple should be covered with a nonconductive protective coating. The corrosion of the anode is controlled by reducing or completely coating the cathodic area. Never, under any circumstances, should the anode alone be coated, since any defect or holiday in the coating would then create a small anode and a very large cathode, which would result in catastrophic corrosion at the break in the coating.

Corrosion damage resulting from two dissimilar metals in immersion conditions can be considerable even if the two metals are a long distance apart. A ship's hull is a common example of this since the bronze propeller is strongly cathodic to the hull. This aggravates the corrosion at any coating damage, even if it is some distance toward the bow. Such corrosion also occurs on magnesium, zinc, or aluminum anodes hung between the legs of offshore platforms where the actual contact distance between the two metals could be 100 ft (30.5 m) or more. On the other hand, where two dissimilar metals are in contact in the atmosphere, galvanic corrosion is confined to a small distance of usually only a fraction of an inch between the junction of the two metals.

Cathodic Protection

Galvanic coupling can also aid in the prevention of corrosion through its role in what is known as CP. In this method, metals with more negative potentials (i.e., higher in the electromotive series) are used to protect metals farther down in the series, or the less negative ones. Examples of the use of CP abound and are generally found wherever metals are buried or immersed. Magnesium, zinc, or aluminum, for example, are commonly coupled to steel structures to provide an excess of electrons on the steel surface, which in turn prevents any of the iron from going into solution as an ion.

Automotive construction necessitates the use of many different metals and alloys for CP. Leonard C. Rowe, in a paper on automotive engineering design, reference provides a good list of recommendations for galvanic corrosion prevention. These are applicable to most

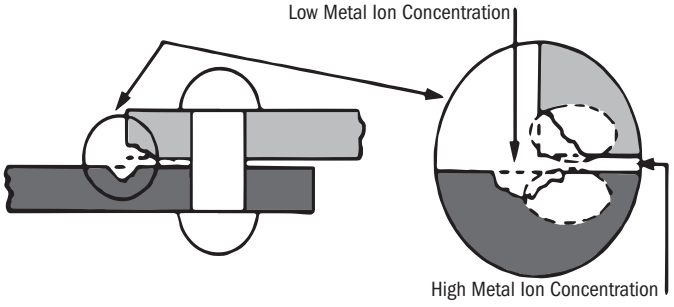


Figure 2.17: Metal ion concentration cell.

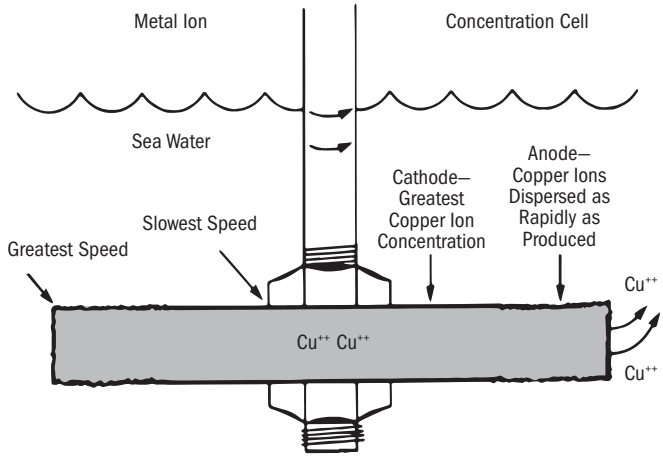


FIGURE 2.18: Spinning copper disc in seawater.

situations where different metals are combined in a structure.

1. Avoid the use of combinations of metals that have potentials that are widely separated in the galvanic series.
2. Avoid those combinations where the area of the anodic metal is small compared with that of the cathodic metal. Use metals for rivets, bolts and fasteners that are cathodic to the surrounding metal.
3. Insulate joints of dissimilar metals when possible; even paint or plastic coatings will be helpful.
4. Paint or coat all surfaces when possible. Avoid painting the anodic metal only, because corrosion may be accelerated at imperfections or breaks in the coating.
5. Seal faying (close-fit) surfaces.
6. Apply metallic coatings to reduce the potential difference between dissimilar metals.
7. Avoid threaded connections when dissimilar metals are used.[7]

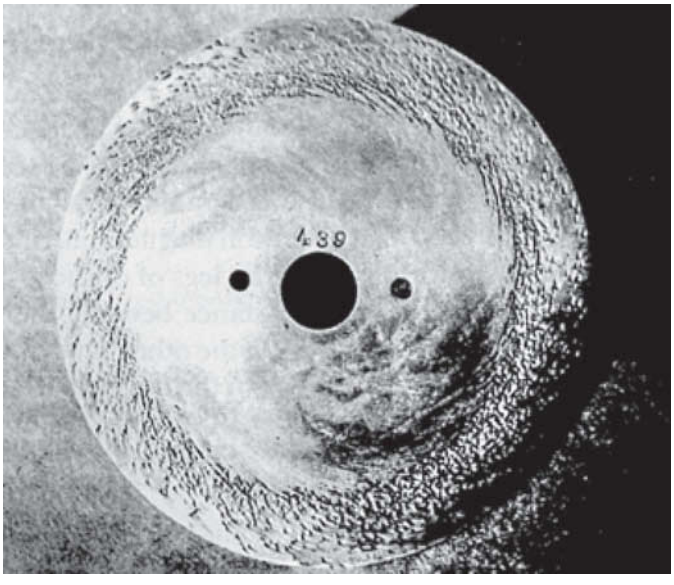


Figure 2.19: Brass disc after spinning in seawater. Source: F.L. LaQue, NACE Basic Corrosion Course, Chapter 2, Introduction to Corrosion (Houston, TX: NACE International, 1971), p. 2-12.

Oxygen Concentration Cells

Other types of corrosion cells may also develop under immersion conditions. One often very destructive type is the oxygen concentration cell. As was previously discussed, oxygen is an important element in the corrosion process, particularly in depolarizing the cathode and thus initiating rapid corrosion at the anode.

An oxygen concentration cell commonly develops where two steel plates overlap. Bolted tanks, for example, used particularly in the oil industry to store water and other corrosive solutions, may be made with overlapped plates. Similar conditions conducive to oxygen concentration cell development exist under cocked rivets, washers slightly loosened from the surface, and even on surfaces under a loose paint film like that often found on the bottom of a ship (Figure 2.15). In fact, wherever a crevice exists in immersion conditions with ample oxygen in the solution, the crevice will corrode rapidly. As shown schematically in Figure 2.16, the area outside the crevice forms a large cathode, with the oxygen depolarizing the area and making it very active. A relatively small anode is formed under the crevice, causing the metal to go into solution rapidly.

Similar conditions even exist in tanks or areas where trash accumulates. A pile of sand on a metal surface will likewise create a condition where the metal ions go into solution under the sand because of the greater oxygen content in the solution surrounding it. The accumulation of mud or sand along with some corrosion on the bottom of a water tank can create an oxygen concentration cell. In this case, the sidewalls act as a large cathode because of their easy access to oxygen in the solution.

Metal Ion Concentration Cell

Corrosion can also be influenced by the concentration of the metal ion in solution. Thus, if the concentration of metal ions corroding from a metal in one place is greater than at another point, the metal at the point of highest metal ion concentration will become the cathode. The area of the metal in contact with the lower concentration will then become the anode. This is a logical development since the area with the greatest metal ion concentration would have less tendency to ionize or go into solution than in areas with less metal ion concentration (Figure 2.17).

Evans, in a work, *The Corrosion and Oxidation of Metals,* discusses the concept further.

> The value of the potential of the metal against a solution of one of its salts must depend on the concentration of that solution since if the balance is $M \longleftrightarrow M^{++} + = 2e^{-}$, any increased ion concentration will increase the right to left reaction while leaving the left to right reaction unchanged.

In reference to "Metal Ion Concentration Cells," Evans continues,

Local concentration differences can play a part in determining the corrosion patterns of some metals. This is more important on lead than on iron. The intensified attack sometimes met with lead pipes buried in chalky soils may be connected with the removal of the lead ion as basic lead carbonate in places where the lumps of chalk press against the lead. These places would become anodic to the rest going to the concentration cells setup.[8]

A classic experiment in this area with a spinning copper disc in seawater was conducted by the Francis L. LaQue Laboratories of the International Nickel Company. Results indicated that the metal close to the center of the disc moves slower than at the periphery of the disc. This allows the metal ions to accumulate in and under films that develop near the center of the disc, while the ones on the perimeter are rapidly swept away by the rapid movement of the metal. Severe corrosion thus results in the region of the highest velocity, and therefore of the least ion concentration (Figure 2.18). Figure 2.19, which is a photograph of an Admiralty brass disc after rotation in seawater, attests to the original results. Note the heavy metal loss on the outer edge of the disc.

This may also be the case with some pump impellers where the flow of liquid is somewhat less in the center of the impeller compared to its high velocity on the outer surface. While a metal ion concentration cell could exist under these conditions, there are also a number of other factors involved in the operation of impellers.

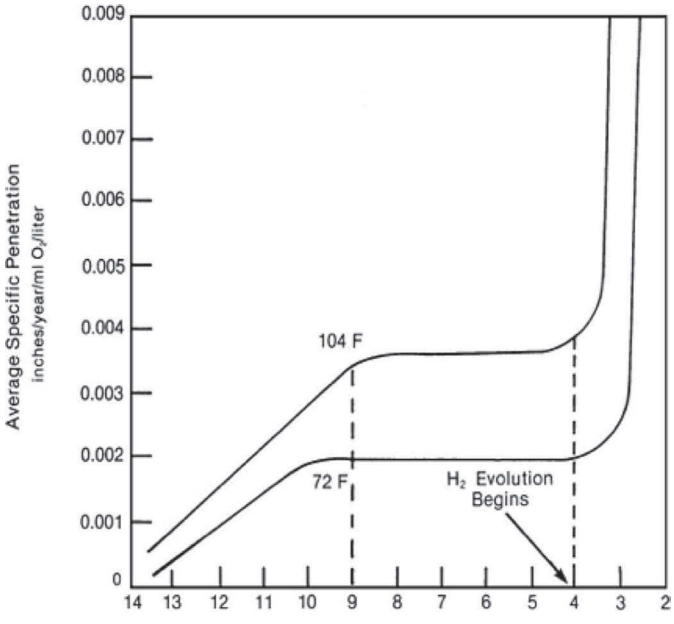


FIGURE 2.20: Effect of pH on the corrosion of mild steel. Source: U.S. Dept. of Commerce, Civil Engineering Corrosion Control, *Corrosion Control—General,* Vol. 1, Dist. by NTIS, AD/A-004082, Jan. 1975), pp. 16, 33.

While the spinning disc example does not involve a crevice, most metal ion concentration cells exist in crevices of one type or another (as do most oxygen concentration cells, which are much more prevalent). Rowe listed some practical suggestions for the prevention of crevice corrosion in a previously mentioned work on automotive engineering design.

1. Use welded joints in preference to bolted or riveted joints.
2. Caulk or seal unavoidable crevices, using durable and noncorrosive materials.
3. Minimize contact between metal and plastics, fabrics, debris, etc.
4. Avoid contact with materials that are known to contain corrosive elements or that are hygroscopic because they can accelerate the cell effect.
5. Avoid sharp corners, ledges, and pockets where debris can accumulate.
6. Where a crevice is inevitable, thoroughly coat both surfaces before they are joined.

Chemical Corrosion

Chemical corrosion is a factor in almost every type of production, ranging from the canning of fruits and vegetables and the bottling of wine, to the manufacture of heavy chemicals such as NaOH and sulfuric acid (H_2SO_4). Even many household chemicals can be extremely corrosive when removed from their original containers and allowed to contact only partially protected iron. Certain chemicals, however, may actually protect iron from corrosion. A general rule of thumb in determining the difference is that as chemicals become more acidic, their tendency to corrode iron and other metals increases. Conversely, as chemicals become more alkaline, they are less likely to corrode iron. This tendency is illustrated by the following equation:

$$\begin{array}{ccccccc} & H^+ \text{ Increased } H^+ & & \text{Decreased } Na^+ & \\ & \text{Acid} = \leftarrow & & \rightarrow = \text{Alkaline} & \\ Cl^- & \text{Corrosion of Iron} & OH^- & \text{Corrosion of Iron} & OH^- \\ & & \text{Water} & & \end{array} \qquad (2.7)$$

This does not mean, however, that a 100% ionized strong alkali solution (e.g., NaOH) cannot be corrosive under certain conditions.

pH

Another method of explaining the corrosive characteristics of chemicals is in reference to the pH scale. Technically, pH is the negative logarithm of the hydrogen ion concentration in a solution. In this case, water, which consists equally of both hydrogen and hydroxyl ions, has a pH of 7. The relative amounts of these two ions determine whether any solution has the familiar sour taste, the ability to turn blue litmus paper red, and other acid characteristics; or whether it has a bitter taste, soapy feel, the ability to turn red litmus paper blue, and other alkaline characteristics; or whether it is chemically neutral, neither alkaline nor acid. If hydrogen ions are in excess, the solution reacts as an acid; if hydroxyl ions are in excess, the solution reacts as an alkali; and if both ions are present in equal amounts, the solution is neutral. More specifically, acids are identified as substances that, when dissolved in water, increase hydrogen ion concentration; alkalies as those substances that, when dissolved in water, increase hydroxyl ion concentration.

The pH varies depending on the chemicals dissolved in the water. Pure water has a pH of 7. Acids have a pH of less than 7 down to zero, while alkalies range in pH from 7 to 14. Figure 2.20 indicates the reaction of various hydrogen ion concentrations on mild steel. As the acid concentration becomes stronger, reactivity on iron becomes greater until massive amounts of iron can be dissolved in a short time (e.g., acid pickling of steel). Note that hydrogen evolution starts at an approximate pH of 4 and increases as the pH moves toward 1.

pH is not a factor in chemical plant corrosion alone; rather, it is an important measure of chemical activity, which is an integral part of our everyday lives. pH is a factor in everything from the food we eat and the stomach acid that helps digest it, to the chemical deter-

Table 2.7: Relative pH pf Common Chemicals and Substances	
pH14	Strong Alkali (NA + OH) Sodium Hydroxide
13	0.1 N NAOH
12	0.001 N NAOH
11	0.1 N Ammonia
10	Saturated Megenta
9	0.1 N Borax, Sodium borate (washing detergent)
8	Sodium Bicarbonate (urine)
pH 7	Water (H+OH) (milk, blood plasma)
6	Saliva (tuna, beans)
5	0.1 Boric acid (turnips, sweet potatoes)
4	Saturate Carbonic Acid (soda water, tomatoes)
3	0.1 N Acetic Acid (wine, grapefruit, apples)
2	0.0 HCl (lemons)
1	0.1 NHCl (limes)
pH0	Strong Acid (H+Cl) (stomach acid)

gents used to wash dishes. Some of the most commonly encountered substances are listed according to pH in Table 2.7. Note that most of the familiar substances are on the acid side of water, which means they tend to be more or less corrosive. Some solutions, however, like NaOH, can be stored in common steel tanks for several years without appreciable corrosion. Some of the stronger organic alkalies, such as amines, can even be used in various processes as corrosion inhibitors.

Acids

Chemicals can be divided into a number of groups, each with its own corrosive characteristics. The first and most corrosive chemical groups consist of acids. Concentrated and highly ionized acids can corrode metal without the presence of oxygen. Some such acids, when in contact with iron, produce hydrogen as a gas, as shown below:

$$2HCL\ (H^{+}Cl^{-})\ \text{hydrochloric acid} + Fe \rightarrow FeCl_2 + H_2 \qquad (2.8)$$

$$H_2SO_4\ (2H + SO_4^{-})\ \text{sulfuric acid} + Fe \rightarrow FeSO_4 + H_2 \qquad (2.9)$$

$$2HNO_3\ (H^{+} + NO_3^{-})\ \text{nitric acid} + Fe \rightarrow (NO_3)_2 + H_2 \qquad (2.10)$$

Some acids, such as H_2SO_4 and phosphoric acid (H_3PO_4), are nonvolatile, while others, such as nitric and hydrochloric acids, are volatile and therefore much more corrosive. Nitric and hydrochloric acids, in fact, are considered two of the most corrosive acids commonly encountered. This is because volatile acids will evaporate, move through the atmosphere as a gas until they contact iron or steel, and then, if there is some moisture present, will react rapidly.

Thus, a plant manufacturing hydrochloric acid, or one that produces it as a process byproduct, is very difficult to protect from corrosion. Only extremely well-applied, strongly acid-resistant materials or coatings can protect the piping and equipment in such plants from rapid failure. When specially designed coatings are used for immersion in strong acid solutions, it is imperative that they be applied according to specifications and are holiday free, since any imperfection in the manually applied coating would invite rapid corrosion and failure of the basic structure. Volatile acids (gases in solution) easily penetrate many organic materials, and coatings are no exception. Heavy plastic sheet or rubber linings are the only surface materials that provide satisfactory protection against such strong acid solutions.

In addition to volatile acids, there are also oxidizing acids, which can be even more aggressive, particularly toward any material that has some tendency to oxidize. Sulfuric acid in strong concentrations (above 50%) is highly oxidizing with most organic materials. Furan resin cements, for example, are used to coat pickling tanks for steel since H_2SO_4 is used as a pickling agent. While the furan cement lasts four years under hot pickling conditions, it is not satisfactory for concentrations of H_2SO_4 above 50%, as it is sensitive to oxidizing conditions. Nitric acid, in addition to being a volatile acid, is also an oxidizing acid in strong concentration. Perchloric acid is so oxidizing that its combination with organic materials may become explosive.

Organic acids fall into another group that has highly individualized characteristics. One of the most common acids in this group is acetic acid. It is volatile, can rapidly attack many metals, and can also act as a solvent for some organic coatings. Naphthenic acid, however, consists of rather large molecules so that its corrosive effect can easily be checked through the use of coatings. Highly acidic petroleum products should not be contained in galvanized or inorganic zinc coated tanks, as they slowly react corrosively with zinc. Butyric, stearic, and linoleic acid are other examples of organic acids that are used in the manufacture of paint and soap.

Salts

Another class of compounds important to a discussion of corrosion is that of salts. Salt is classified as either acid, neutral, or alkaline. A salt is formed by the reaction of an acid and an alkali. An acid salt (e.g., ferrous sulfate) results from the action of a strong acid (e.g., O_4) with a mild alkali (e.g., $Fe(OH)_2$). This type of material is relatively soluble and can act as a salt as well as an acid. Neutral salts are a combination of strong (or weak) acids and strong (or weak) alkalies, such as hydrochloric acid and sodium hydroxide. This particular combination yields common table salt, which is a primary corrosive agent encountered in the marine industry as well as in many other industries. The alkaline salts are a combination of weak acids (e.g., acetic acid) and strong alkalies (e.g., sodium hydroxide). These materials are thus on the alkaline side (i.e., a pH of 7 or greater), and are generally less corrosive than either acid or neutral salts. Nevertheless, many are strongly ionized and act as an electrolyte, which can therefore create strong corrosion cells.

Many salts, such as sodium or potassium chloride, and sodium nitrate or sulfate are strongly ionized. Others range from being strongly ionized to being completely insoluble (e.g., silver chloride). Generally, as salts become less soluble and less ionized, they also become less corrosive.

Alkalies

Examples of strong alkalies, which are at the upper end of the pH scale and also may be strongly ionized, are sodium and potassium hydroxide. The amount of hydrogen ion present in these alkalies decreases as pH increases so that there is less hydrogen to react with excess electrons. This means that hydrogen is not evolved in the corrosion reaction. Oxygen, however, is normally reduced in accordance with Equation (2.11):

$$O_2 + 2H_2O + 4e^{-} \rightarrow 4OH^{-} \qquad (2.11)$$

It is thus more important to corrosion in alkaline solutions.



FIGURE 2.21: Sulfide attack on a steel petroleum production tank.

Oxidizing Salts

There are a number of alkaline salts that are also oxidizing agents and therefore extremely corrosive. Most common among them is sodium hypochlorite (NaOCl). Chlorine gas is added to sodium hydroxide during manufacturing so that the resulting solution is strongly alkaline. On the other hand, this material is unstable and slowly disintegrates into a nascent oxygen and NaCl. This makes it a strong corrosive agent. Any coating that is to come in contact with hypochlorite solution must be resistant to the penetration of nascent oxygen, as well as resistant to strong oxidizing conditions. Any imperfections in a coating will be rapidly corroded, with tubercles of rust forming at the break and deep pits forming underneath. Even dilute sodium hypochlorite solution can quickly attack coating weaknesses. Similar oxidizing salts include calcium hypochlorite, sodium perborate, and sodium perchlorate. It is important to note that even though most oxidizing salts are alkaline, they still can be highly corrosive.

Sulfides

Sulfides constitute another important factor in chemical corrosion. The presence of hydrogen sulfide, for instance, which is a gas and an acid sulfide, can be a major contributing factor to corrosion failure that often goes unrecognized. Other common sulfides include salts of hydrogen sulfide (i.e., ammonium sulfide, calcium sulfide, and sodium sulfide). There are also many complex organic sulfides (e.g., carbon disulfide), particularly in the petroleum industry.

Sulfide reactions are different from the other corrosion reactions in that they can take place even under relatively dry conditions. H_2S, for instance, reacts directly with the metal and does not require an electrolyte for the corrosion reaction to take place. H_2S not only reacts directly with iron, but also with some iron compounds to increase the corrosion rate, as is evident in the following reactions.

$$H_2S + Fe \rightarrow FeS + H_2 \quad (2.12)$$

$$H_2S + FeCO_3 \rightarrow FeS + CO_2 + H_2O \quad (2.13)$$

$$H_2S + Fe(OH)_2 \rightarrow FeS + 2H_2O \quad (2.14)$$

Figure 2.21 shows an oil field production tank that was in service for two years without being coated. Not only was the roof structure of the tank completely corroded, the uncoated tank exteriors, roof vents, steel pipes, and other structures in the same area were also severely corroded, even though the sulfide was not as concentrated as it was in the tank's interior.

H_2S reacts with most other metals in a similar way, especially with copper and silver, which turn black when sulfide is in the area (e.g., workers in sewers or other areas where sulfide is present often find that the coins in their pockets have turned black). FeS is cathodic to iron so that where it forms on an iron surface it can act as a massive cathode, provided that an electrolyte such as seawater is present. This is often a contributing factor in the deep pitting of sour crude tankers. FeS is also very reactive with oxygen. When oxygen contacts FeS, it reacts according to the following equation to form magnetic iron oxide.

$$6FeS + O_2 + 6H_2O \rightarrow 2Fe_3O_4 + 6H_2S \quad (2.15)$$

H_2S released in this reaction can in turn re-react with any additional iron in the area.

Sulfides are prevalent in many industries, including the rayon industry, which uses carbon disulfide, and the petroleum industry, which encounters H_2S in natural gas and crude oil. Sour crudes, in particular, pose H_2S problems that affect everything from the wellhead, gathering lines, and field production tanks, to the refinery structures and equipment.

The sewage industry also must contend with H_2S, which develops as a result of anaerobic bacterial action below and immediately above the surface of the sewage liquid. The anaerobic bacteria react with sulfates in the water and organic sulfides in the sewage to form H_2S gas. The marine industry is also affected by H_2S produced by decaying slimes and marine life. This is a particular problem in ballast tanks, which take on water in parts of the world with poor water quality. While normal marine corrosion may mask the formation of sulfides, they nevertheless significantly contribute to such corrosion and therefore must be considered before proper protection can be achieved.

Displacement Corrosion

Another type of chemical corrosion occurs where metals are attacked in solutions that do not contain oxygen or acids. Solutions containing copper, for instance, come into contact with iron. Since copper is more positive in the electromotive series than iron, the copper ion takes up electrons from the iron and precipitates metallic copper, while the iron goes into solution as iron ions. This reaction is called double displacement reaction (iron from metal into solution, copper from solution to the metal) and is given in the following diagram.

$$Cu^{++} + Fe \rightarrow Cu + Fe^{++}$$

or

$$CuSO_4\ (solution) + Fe\ (metal) \rightarrow Cu\ (metal) + FeSO_4\ (solution) \quad (2.16)$$

Copper will react in a similar way with zinc, magnesium, or aluminum. The proper coatings must protect all of these metals if there is

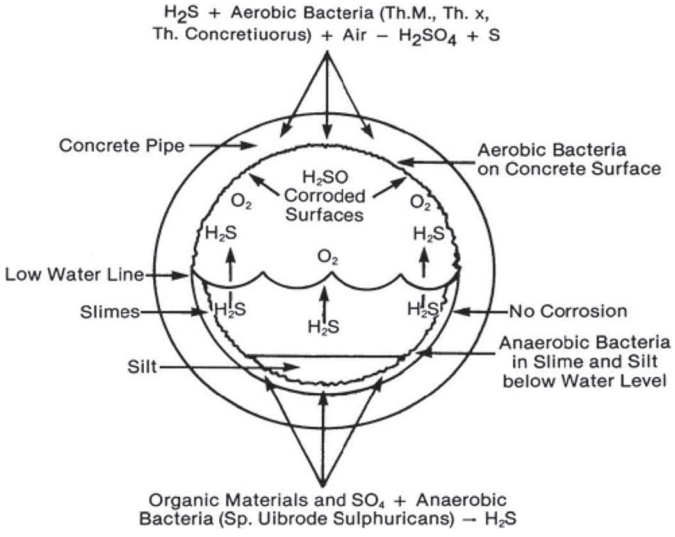


Figure 2.22: The H_2S corrosion mechanism in sewers. Source: C.G. Munger, "Sulfides—Their Effect on Coatings and Substrates," *MP* 17, 1 (1978).



Figure 2.23: Mill or blue scale steel submerged in gelatin indicator solution. Note strong blue anodes at breaks in the scale.

even a possibility of copper ion being present. The use of uncoated aluminum pipe or tanks in a copper-piped domestic or industrial water system is dangerous. The water will pick up enough copper ions so that the aluminum downstream of the copper pipe will actively corrode. Not only will the copper displace the aluminum as described, but also a galvanic cell will then form, accelerating the already precipitated corrosion.

The reduction of ferric salts is another chemical reaction that takes place without the necessity of oxygen. When ferric chloride, for example, comes in contact with iron, the following reaction occurs.

$$Fe + 2FeCl_3 \rightarrow 3FeCl_2 \quad (2.17)$$

As the iron goes into solution, it relinquishes an electron to the $FeCl_3$, which then becomes reduced to ferrous chloride. Ferric chloride will react similarly with other metals higher in the electromotive series than iron (e.g., zinc), thus necessitating their protection.

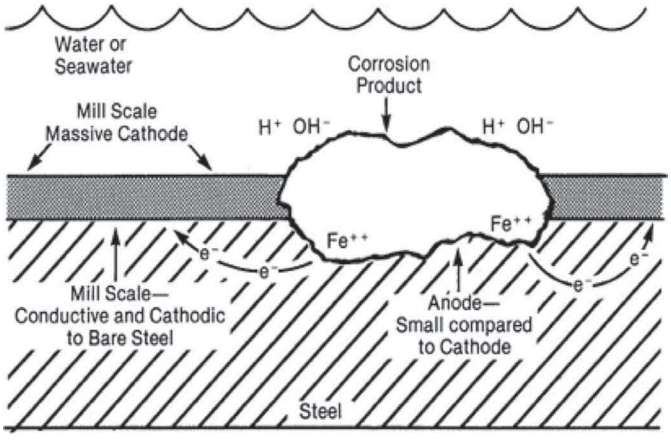


Figure 2.24: Schematic illustration of the strong electric current established between bare steel (anode) and mill scale (cathode).

Concrete Corrosion

Chemical reactions involving concrete also should be considered since concrete follows metal as a principal building material. Concrete is essentially a hydrated calcium aluminum silicate, which is strongly alkaline. Moist concrete can develop a pH of up to 13, which is one reason it is considered a good protective media for steel structures.

All acid materials react readily with concrete, due primarily to the calcium in the complex cement molecule. Cement will even react with an acid as weak as pure water with very low dissolved solids. Concrete will only stand up properly without any solution taking place if the water is somewhat hard. Thus, the acidic materials that must be considered when working with cement range all the way from pure water, fruit juices, and carbonated water, to strong acids such as H_2SO_4. Even extremely dilute H_2SO_4 will rapidly react with cement, causing effervescence and precipitation of the insoluble calcium sulfate ($CaSO_4$). This latter reaction is the one that takes place in sewers where H_2SO_4 develops from the bacteria at and above the water line. It has been measured in concentrations as high as 10%, disintegrating concrete at a rate as great as two inches per year under strongly corrosive sewage conditions. The reactions that create corrosive conditions such as these are shown in Figure 2.22.

Thus, wherever concrete is used as a structural material that may be exposed to acidic compounds, it must be properly coated to ensure the preservation of the structure. In many ways, this process can be more complex than that of coating metals (Chapter 11).

Mill Scale

Mill scale, or blue scale as it is sometimes called, forms on steel as it is hot rolled, and varies according to the type of operation and rolling temperature. It is not a complex subject, but since the majority of structural steel is hot rolled, the quantity of surface contaminated with mill scale is important.

In general, mill scale is magnetic and contains three layers of iron oxide, although the boundaries between the oxides are not particularly sharp. The thin outer layer of mill scale is essentially ferric oxide (Fe_2O_3), which is relatively stable and does not easily react. The layer closest to the steel surface, and sometimes intermingled with the steel's surface crystalline structure, is ferrous oxide (FeO). This is an unstable substance that is easily oxidized to ferric iron, resulting in a chemical change to ferric oxide. This process, accompanied by an increase in volume, results in loosening the intact mill scale, particularly during weathering or where moisture is present.

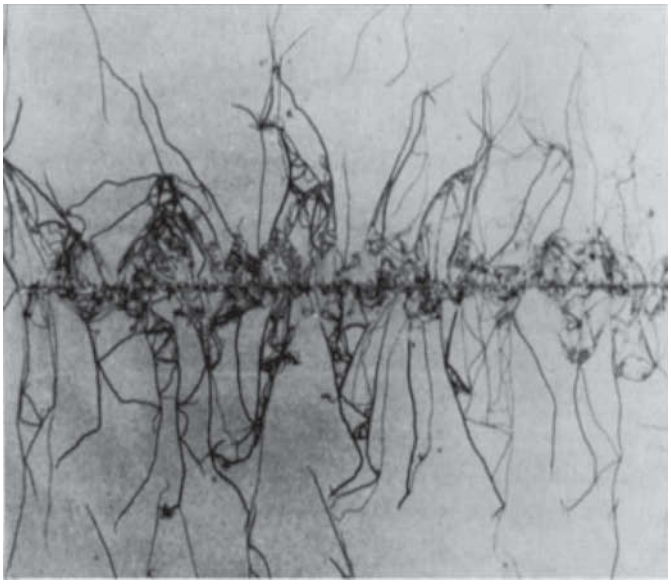


Figure 2.25: Filiform corrosion starting at a scribe on a metal panel. Source: Pictorial Standard of Coating Defects, Filiform Corrosion, Figure 8-Dense B, Federation of Societies for Paint Technology, Philadelphia, PA, 1979.

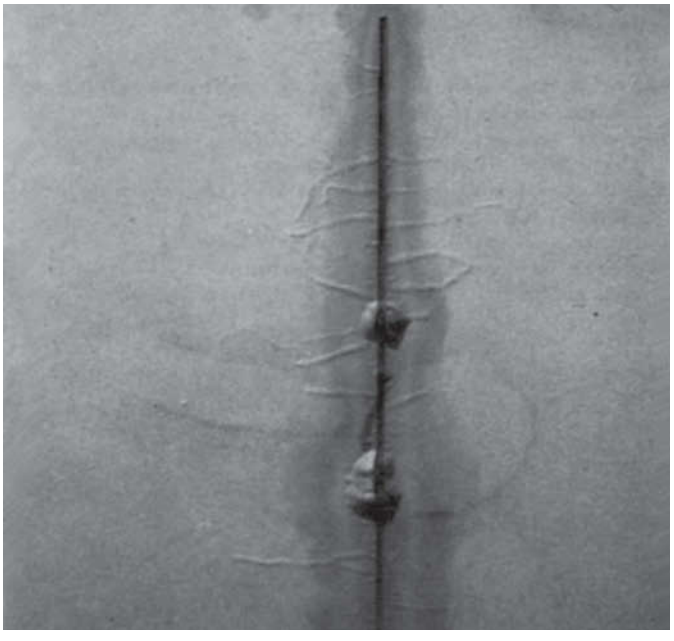


Figure 2.26: Filimentous corrosion under a pigmented coating exposed in a marine environment.

The intermediate layer of magnetic oxide is best represented by the chemical formula Fe_3O_4. The actual thickness of mill scale on structural steel, which depends upon rolling conditions, varies from about 0.002 to 0.020 in (0.05 to 0.51 mm), and consists mainly of the magnetic oxide Fe_3O_4 and the FeO layer. Much of the mill scale formed at high initial rolling temperatures is knocked off in subsequent rolling. Thus, it is the oxide that forms on the steel after rolling, while the steel is hot, that remains intact on the surface.

Mill scale is strongly cathodic to bare steel, which can be demonstrated through the use of gelatin indicator solution. Wherever there is a break in the mill scale on the steel panel, the iron goes rapidly into solution. These areas form blue anodes. The remainder of the surface covered by tight mill scale remains a pink color and forms a massive cathode (Figure 2.23). This same action is schematically shown in Figure 2.24, which indicates that a strong electric current is established between the bare steel (anode) and the mill scale (cathode). When this is coupled with the large areas of mill scale on most hot rolled plates or shapes (area relationship is indicated in Figure 2.23), a massive cathode and small anode relationship is created, which causes rapid corrosion to the base steel. The difference in potential between the mill scale and steel can amount to 0.2 to 0.3 V, which is close to the strength of many galvanic couples.

That mill scale can create a condition of very rapid corrosion was demonstrated during World War II when ships were turned out at a very rapid rate. Originally, mill scale was not removed from the bottom hull plates due to the time and expense involved. However, when ships were place in seawater, deep pitting resulted along welds and in any area where the mill scale was broken. In some cases, penetration of the hull actually took place at the outfitting dock. Pickling or blasting all of the hull plates before construction overcame this problem.

A problem is also created when mill scale is painted over. The mill scale is then unstable, and when it comes in contact with moisture tends to release adhesion or pop from the metal surface. When painted over, this reaction results in loose areas of the coating with blistering or cracking in these areas. If a steel surface is to be used under corrosive conditions, mill scale must therefore be removed prior to coating in order to obtain a viable and long-lasting coating job.

Filiform Corrosion

An interesting and unique form of corrosion that can take place on either uncoated or coated metal surfaces is filiform corrosion. It can take place when metal surfaces are contaminated with fine solid particles and the surface is exposed to humid atmospheres. It also can take place underneath coatings of various types, either pigmented or clear. It is most dramatic when it occurs under clear lacquer films applied over cold rolled or polished steel surfaces. Figure 2.25 shows filiform corrosion starting at a scribe on a metal panel.

The cause of filiform corrosion is generally thought to be mild surface contamination caused by solid particles deposited from the atmosphere or particles that remain after the metal has been processed. Rozenfeld, in the work, *Atmospheric Corrosion of Metals,*[9] lists a number of sources and surface contaminants that have caused this type of corrosion.

- Industrial Atmosphere: Iron oxide, coal dust, silica, ammonium sulfate, organic matter
- Industrial and Sea Water: NaCl, $CaCl_2$, $CaSO_4$, $MgSO_4$
- Polishing Operations: Carborundum
- Prior processing with solutions: $NaNO_3$, chromic acid, sodium nitrite, KF
- Soldering and Melting Operations: Chloride
- Pigments: Iron oxide and zinc chromate
- Corrosion Products: Iron sulfate ferric chloride[9]

It is interesting to note that some of the particles are insoluble in water, but nevertheless cause filiform corrosion. It has been stated that salts that behave normally (rapid corrosion in presence of high humidity) cause only mild filiform corrosion, if any at all, while salts with abnormal behavior (high corrosion rates at low relative humidity) always induce filiform corrosion.[6]

The mechanism of filiform corrosion is not well known; however, it apparently is similar to crevice corrosion. Sudbury, et al.[6] indicate

that the head of the filament is the anode of an electrochemical cell. The filament tube is filled with low pH electrolyte, and the resulting growth is due to an oxygen concentration difference between the anode and the cathodes (Figure 2.26).

As shown in Figures 2.25 and 2.26, the corrosion appears to have wormed its way across the surface underneath the coating. As indicated by the type of material that tends to cause filiform corrosion, it most often occurs where coatings are applied under a product finishing operation. Industrial and marine atmospheres can create this condition, as is indicated. Prevention of this type of corrosion, particularly under coated surfaces, involves making certain that the surface has been properly prepared and that the coating is applied over a thoroughly cleaned surface.

Pitting Corrosion

Pitting is often classified as a separate type of corrosion. Although it may take a variety of forms and is prevalent under many different corrosive conditions, it is primarily an aggravated form of the usual corrosion process rather than a distinctive corrosion type. Pitting corrosion is, more specifically, a concentration of corrosion in one particular area so that the metal goes into solution more rapidly at that spot than at any other adjacent area. Often, it goes directly back to the area relationship of the anodes and cathodes with a relatively small anode and a many-times larger cathode. This type of corrosion can occur where protective coatings are applied over metal and where there is a break in the coating so that the large coated area acts as a cathode, even though a very weak one.

Pitting corrosion may be caused by a number of things, including mill scale, which is a very common form of pitting corrosion. When mill scale is placed in an electrolyte, any break in the mill scale surface becomes the anode; the remainder of the mill scale, which is usually many times larger than the break, becomes a very strong cathode. Galvanic action is also a cause of pitting corrosion.

Areas where a brass valve is incorporated into steel or galvanized pipelines serve as good examples. The junction between the two areas is often badly pitted, and if the pipe is threaded, the thread in close contact with the brass valve rapidly pits, soon causing a leak. This not only occurs frequently in industry, but also in homes and on farms.

Oxygen concentration cells also can cause deep pitting, as might be expected from crevice type corrosion. Pitting also occurs on stainless and similar alloys exposed to marine life. In this case, the marine life dies after a period of time and, as with barnacles, will leave a shell on the surface. Due to the sulfides produced by the dying or dead animal, the oxide film on the metal or passivated surface is destroyed and an active pitting takes place underneath the fouling.

The deep pitting of tankers on the horizontal surfaces of cargo ballast tanks is a particularly aggravated type of pitting (i.e., pits are deep and frequent) (Figure 2.27). In this case, they are caused by frequent changes of cargo and salt water, which perpetrate an oxidation-reduction corrosion cycle.



Figure 2.27: Deep pitting in a crude oil tanker cargo ballast tank. Note the depth of the pits compared to the diameter. Source: C.G. Munger, "Deep Pitting in Sour Crude Oil Tankers," *MP* 15, 3 (1976).

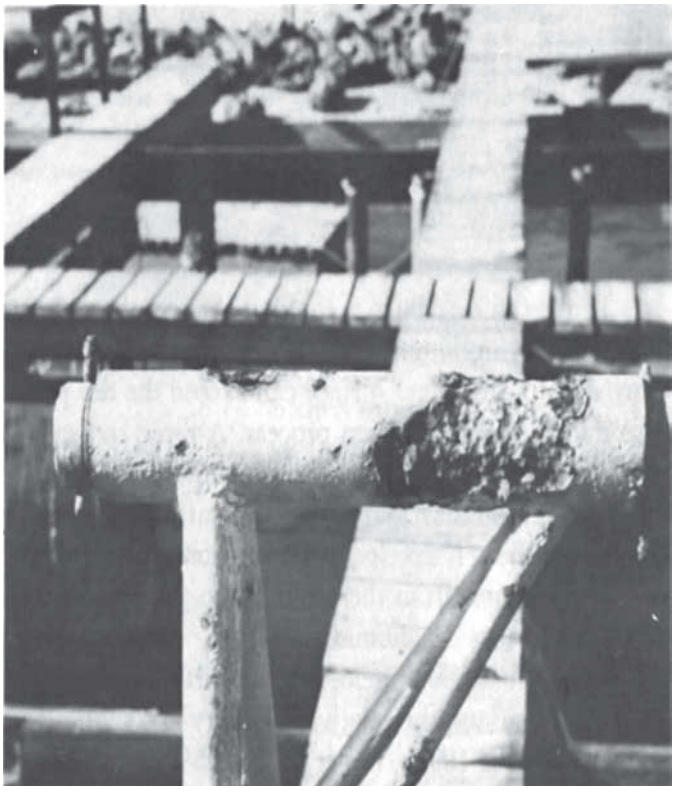


Figure 2.28 — Pitting in a marine atmosphere. Note the sharp edges on the large pitted area.

Graphitic corrosion (i.e., the preferential dissolution of iron that leaves a soft graphite residue) sometimes takes this form of attack (i.e., pitting). On underground pipelines, corrosion cells may set on the cast iron surface in such a way that the iron goes into solution, leaving the graphite, which is part of the cast iron, intact within the deep pit. The graphite in itself is cathodic to the iron, so that once the cycle starts, pitting occurs rapidly. The graphite in these pits is relatively soft and is easily cut with a knife. It usually proceeds uniformly inward from the surface, leaving a porous matrix. While there may be no outward indication of corrosion damage, in some instances, the corroding area will be covered by a large tubercle of rust. Graphitization occurs in salt waters, acidic waters dilute acids, and soils (especially those containing sulfates and sulfate-reducing bacteria). Coatings and/or CP can be used successfully to prevent graphitization.

Pitting can also take place under atmospheric conditions. The pitting, in this case, may be caused by breaks in a surface coating over a steel or other metal surface. The corrosion starts at the break and continues to undercut the coating, forming a rather heavy tubercle of hard rust or scale with the pit in the original metal underneath (Figure 2.28). These are common in the marine area as well as various

TABLE 2.8: Relative Corrosivity of Open-Hearth Steel Exposed at Various Locations

Location	Relative Corrosivity
Khartoum, Egypt	1
Ablsco, North Sweden	3
Singapore, Malaya	9
Daytona Beach, FL (Inland)	11
State College, PA	25
South Bend, PA	29
Mira Flores, Canal Zone, Panama	31
Kure Beach, NC (800 ft [244 m] from ocean)	38
Sandy Hook, NJ	50
Kearny, NJ	52
Vandegrift, PA	56
Pittsburgh, PA	65
Fordingham, U.K.	100
Daytona Beach, FL (near ocean)	138
Kure Beach, NC (8 ft [24 m] from ocean)	475

Source: *Corrosion Basics—An Introduction,* Chapter Four, "Atmospheric Corrosion" (Houston, TX: NACE International, 1984), p. 228.

industries where strong corrosive conditions exist.

Corrosion Under Insulation

Corrosion under insulation (CUI) is one of the costliest problems facing the petrochemical industry today. According to Tim Hanratty, business development manager for Sherwin-Williams Company, problems associated with CUI such as major equipment outages and unexpected maintenance costs account for more unplanned downtime than all other causes.[10] A refinery's steel piping, storage tanks, container vessels, and other process equipment are subject to temperature fluctuations. Thermal insulation applied to these structures mitigates the effects, but the presence of seams, gaps, or other discontinuities in the insulation layer makes them susceptible to infiltration by outside moisture or from the process environment itself. The insulation may be made of calcium silicate, expanded perlite, manmade mineral fibers, cellular glass, organic foams, or ceramic fiber. The insulation and cladding hides the protective coating system, so even with observation ports, less than 1% of the surface is visible, and those areas likely are not representative of the whole unit.

CUI generally stems from water and infiltration of contaminants to an insulated system that will vary in its water retention, permeability, and wettability characteristics. These corrosive elements enter the system through breaks or degradation in the insulation system's weatherproofing, inadequate system design, incorrect installation, poor maintenance, or a combination of the above.

NACE SP0198-2010, "The Control of Corrosion Under Thermal Insulation and Fireproofing Materials—A Systems Approach,"[11] reflects the latest insights from the CUI prevention and mitigation experience of the oil and gas industry. Coating systems incorporated into the standard have a track record of success and include thin-film, liquid-applied coatings; fusion-bonded coatings; metalizing or thermal spray coatings; and wax tape coatings.

The most common systems are phenolic epoxies, for temperatures of –50 to 300 °F (–45 to 150 °C) and novolac epoxies for temperatures of –50 to 1,200 °F (–45 to 650 °C).

The standard recommends topcoating any IOZ to extend its service life, and that it not be used by itself under thermal insulation in service temperature up to 350 °F (177 °C) for long-term or cyclic service.

The carbon steel coatings table in the NACE standard should be referenced and the coating manufacturer should be consulted for the generic coating, dry film thickness, and service temperature limits.

Atmospheric Corrosion

Atmospheric corrosion is undoubtedly the most widespread and, from a coating standpoint, the most important type of corrosion. There is more metal area exposed to atmospheric corrosion than to any other type. It is prevalent worldwide and exists not only in marine areas or in industry, but in many rural areas as well where high humidity and damp conditions exist. Table 2.8 gives relative corrosion rates for a number of areas around the world, ranging from those of practically no corrosion to severely corrosive areas.

It has been estimated that half of the total cost of corrosion protection in the United States is spent on protection against atmospheric corrosion. In some countries, the extent of this type of corrosion would be considerably less; on the other hand, there are also countries with primarily marine conditions where this ratio would be much higher than the 50% in the United States. Generally, the more arctic areas are comparatively less corrosive than those in temperate or tropical zones. This does not mean, however, that there are not isolated areas in any climate that differ from the norm.

Barton describes the nature of atmospheric corrosion in the work, *Protection Against Atmospheric Corrosion*,[12] as follows:

> Atmospheric corrosion is an electrochemical process that occurs in a limited amount of electrolyte. The electrolyte is neutral or slightly acidic (or under exceptional conditions slightly alkaline), and its properties are influenced chiefly by the chemical composition of the atmosphere and the properties of the corrosion products formed. The neutral or slightly acidic nature of the electrolyte and its variable presence on the corroding surface promote the formation of solid corrosion products on all metals that remain unpassivated for thermo-dynamic reasons. This is easily understood, since the solubility product of the reaction product is easily exceeded in the small volume of approximately neutral electrolyte, and so new phases are formed in the system. The properties of this reaction layer are not constant, however, since the temporary presence of the electrolyte layer plays an important role.[12]

Components of the Atmosphere

Even though nitrogen and inert gases are the atmosphere's major elements, they do not react with metal surfaces under ordinary circumstances. Nitrogen can be oxidized during electrical storms and is a source of some soluble nitrogen for the soil. The amount involved, however, is so small that it contributes very little to the corrosion of the atmosphere. Oxygen is the largest component of air and amounts to approximately 20% of the atmosphere. As discussed previously, oxygen is a very reactive material that has a substantial effect on the corrosive character of the atmosphere, as well as on the general corrosion process.

Water is the third most common atmospheric component and may be one of the most important in terms of corrosion. Water exists as ice and snow in its solid form, as rain or condensation in its liquid form, and as humidity in its vapor form. In each of these states, it performs a specific role in the corrosion process. In the atmosphere, water is primarily in its vapor form; that is, its individual molecules

TABLE 2.9: Absolute Atmospheric Humidity at Different Temperatures and Different Relative Humidity (expressed as g water vapor/m³)

Temperature (°C)	Relative Humidity (%)									
	10	20	30	40	50	60	70	80	90	100
0	0.49	0.98	1.47	1.96	2.45	2.94	3.43	3.92	4.4	4.9
1	0.52	1.04	1.56	2.08	2.60	3.12	3.64	4.16	4.7	5.2
2	0.56	1.12	1.68	2.24	2.80	3.36	2.92	4.48	5.0	5.6
3	0.60	1.20	1.80	2.40	3.00	3.60	4.20	4.80	5.4	6.0
4	0.64	1.28	1.91	2.56	3.20	3.84	4.48	5.12	5.8	6.4
5	0.68	1.36	2.04	2.72	3.40	4.08	4.76	5.44	6.1	6.8
6	0.73	1.46	2.19	2.92	3.63	4.38	5.11	5.84	6.6	7.3
7	0.77	1.54	2.31	3.08	3.85	4.62	5.39	6.16	6.9	7.7
8	0.83	1.66	2.49	3.32	4.15	4.98	5.81	6.64	7.5	8.3
9	0.88	1.76	2.64	3.52	4.40	5.28	6.16	7.04	7.9	8.8
10	0.94	1.87	2.82	3.76	4.70	5.64	6.58	7.52	8.5	9.4
11	0.99	1.99	2.98	3.98	4.97	5.97	6.96	7.96	8.9	9.9
12	1.06	2.12	3.18	4.24	5.30	6.36	7.42	8.48	9.5	10.6
13	1.13	2.26	3.39	4.52	5.65	6.78	7.91	9.04	10.2	11.3
14	1.20	2.40	3.60	4.80	6.00	7.30	8.40	9.60	10.8	12.0
15	1.28	2.56	3.84	5.12	6.40	7.68	8.96	10.20	11.5	12.8
16	1.35	2.72	4.08	5.44	6.80	8.16	9.52	10.90	12.2	13.6
17	1.45	2.89	4.33	5.78	7.22	8.67	10.10	11.60	13.0	14.5
18	1.54	3.07	4.61	6.14	7.68	9.22	10.80	12.30	13.8	15.4
19	1.63	3.25	4.88	6.51	8.13	9.76	11.40	13.00	14.6	16.3
20	1.72	3.44	5.16	6.88	8.60	10.30	12.00	13.80	15.5	17.2
21	1.82	3.65	5.48	7.30	9.13	11.00	12.80	14.60	16.4	18.2
22	1.93	3.87	5.80	7.44	9.67	11.60	13.50	15.50	17.4	19.3
23	2.05	4.10	6.15	8.20	10.25	12.30	14.30	16.40	18.4	20.5
24	2.17	4.34	6.51	8.68	10.85	13.00	15.20	17.40	19.5	21.7
25	2.29	4.58	6.87	9.16	11.45	13.20	16.00	18.30	20.6	22.9
26	2.42	4.84	7.26	9.68	12.10	14.00	16.90	19.40	21.8	24.2
27	2.56	5.12	7.68	10.25	12.80	15.40	17.90	20.50	23.0	25.6
28	2.71	5.42	8.15	10.85	13.50	16.30	19.00	21.70	24.4	27.5
29	2.86	5.72	8.58	11.44	14.30	17.20	20.00	22.90	25.7	28.6
30	3.02	6.04	9.05	12.10	15.10	18.10	21.10	24.10	27.2	30.2

Source: K. Barton, *Protection Against Atmospheric Corrosion,* J.R. Duncan, translator (New York, NY: John Wiley & Sons).

serve as part of the total atmospheric pressure. The content of moisture vapor in the air varies from almost zero to a point of saturation, and may vary over this entire range on a daily basis.

Water as liquid is an important element in electrochemical corrosion since it is the principal ingredient of the electrolyte that is necessary to carry on the corrosion process. It dissolves various materials from the solid matter and gases that are present in the atmosphere. The pH of water from the atmosphere can fall as low as 3, and it is always saturated with oxygen. When water is condensed or falls on a surface, any material on that surface may be dissolved in rather large amounts to form a relatively concentrated solution. This creates a very strong electrolyte.

The length of time that water is precipitated on the surface, either by rain or condensation, is a major factor in the corrosiveness of the atmosphere. A dry atmosphere, where water is only on the surface of the metal for a short period of time during any single day, will be relatively corrosion-free. On the other hand, an atmosphere where moisture condenses and is held on the surface for many hours at one period can be very corrosive. Such atmospheres are common in marine areas where humidity remains at relatively high stages for most of any daily period. Atmospheric corrosion of metals, then, progresses only in periods where there is a surface electrolyte present. The rate of corrosion during such periods is related to the corrosion activity of the surface electrolyte and the nature of the metal.

Relative Humidity

Moisture in the atmosphere is most commonly measured as its relative humidity. The relative humidity is the ratio of the absolute

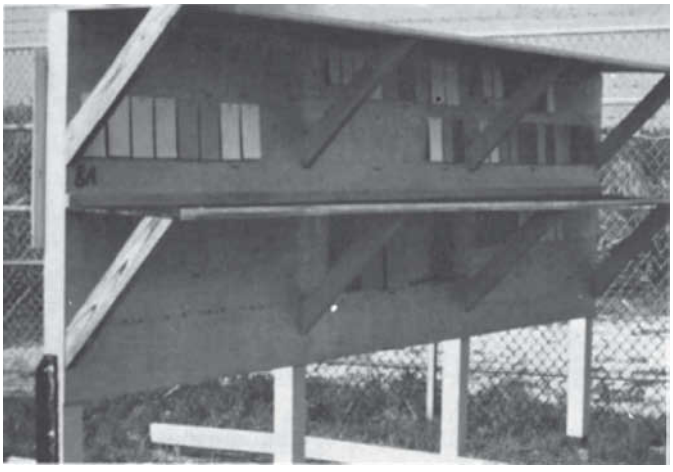


Figure 2.29: Typical sheltered exposure rack in a marine atmosphere.

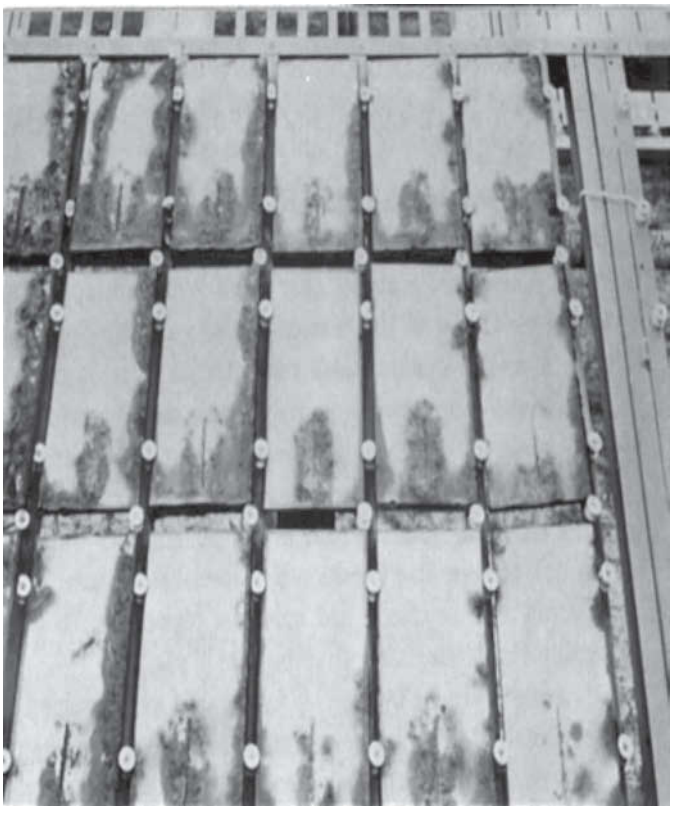


Figure 2.30: Test panels showing effect of wind on leading edges. Prevailing wind is from the right where greater corrosion is evident on most panels. This shows the need for special care when coating edges and corners.

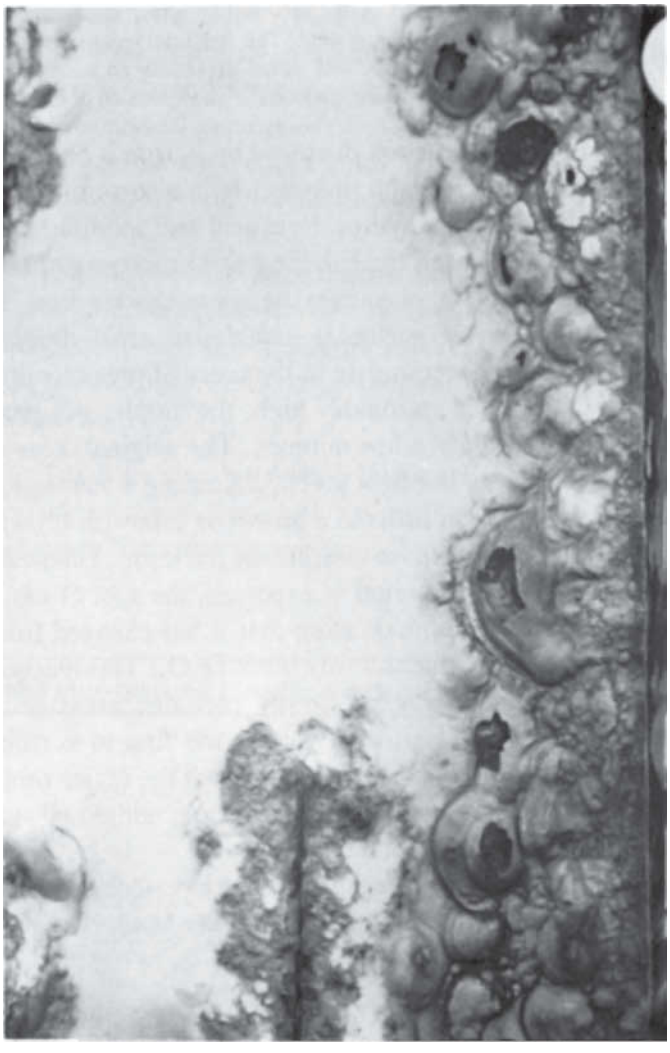


Figure 2.31: Close-up view of the leading edge of a panel exposed in a marine atmosphere. Prevailing wind is from the right where heavy corrosion is noted compared to the left edge.

humidity to the saturation value and is expressed as a percentage. Table 2.9 compares the absolute atmospheric humidity as expressed in grams of water per cubic meter at different temperatures and different humidity. This compares relative humidity with the actual amount of water vapor in a cubic meter of air. As the table indicates, the actual content of water in the air changes rapidly with temperature.

Temperature and Moisture

Extreme temperatures are of minimal significance from a corrosion standpoint. At temperatures below freezing, water is in its solid form and therefore does not act as a good electrolyte. At the other extreme, high atmospheric temperatures do not allow the moisture to condense and form a film on the surface. Atmospheric corrosion generally does not proceed rapidly, if at all, at temperatures above 25 °C (77 °F).

Temperature changes rapidly change the relative humidity. At high humidity, a rapid but small temperature drop in the metal surface can exceed the dew point, thus initiating the corrosion process. A rapid increase in surface temperature has the opposite effect in that moisture then evaporates and leaves the surface sufficiently dry so that there is no electrolyte to promote corrosion.

The distance from the ground also makes a considerable difference in humidity values. High humidity values are usually found close to the earth's surface. For example, at sunset, the relative humidity measured 5 cm above ground is 100%, but it is only 55% at a height of 200 cm. In late afternoon, for instance, the hull of a ship may change from being dry to being wet in a matter of only a few minutes. This danger must constantly be guarded against during the application of coatings at times of dropping temperatures. As the temperature drops, the air can no longer contain the moisture and the vapor condenses as water on surfaces that are at a slightly lower temperature than the air. This point at which the air can no longer contain the moisture is called the dew point.

Humidity, dew, rain, and fog are all forms of water, which contribute in a very major way to atmospheric corrosion. Although it is commonly assumed that a continually wet surface is the most corrosive, this is not necessarily the case. Compare, for example, the corrosion conditions along the Oregon coast, which is a marine area of high rainfall, and those in San Francisco, which also has a

marine atmosphere and a somewhat similar climate. Instead of rain, however, San Francisco has a much higher percentage of fog. Corrosion along the Oregon coast, therefore, is much less than that in San Francisco because rain washes the surface free of marine salts and therefore creates a more dilute electrolyte. Conversely, the salt from San Francisco's marine atmosphere is precipitated on the surface, and the foggy, very damp atmosphere keeps surfaces almost continually wet, but rarely washes them free of salts.

Corrosion is greatest where rain never washes the surface and where salt air or other contaminants accumulate and are subject to damp, humid conditions. It is true that the sheltered areas also maintain surface moisture for a longer period of time so that the concentration of the electrolyte and the time of exposure are greater. Thus, areas of a bridge exposed to rain and washing of the surface are generally less corroded than the areas that are sheltered. Similarly, unwashed sheltered screens have a much shorter life than those that are exposed and washed. Test racks are thus constructed in such a way that panels are exposed on vertical surfaces, upper horizontal surfaces, lower horizontal surfaces, and vertical sheltered areas (Figure 2.29). The underside of these panels has been observed to corrode to a greater extent than the upper side.

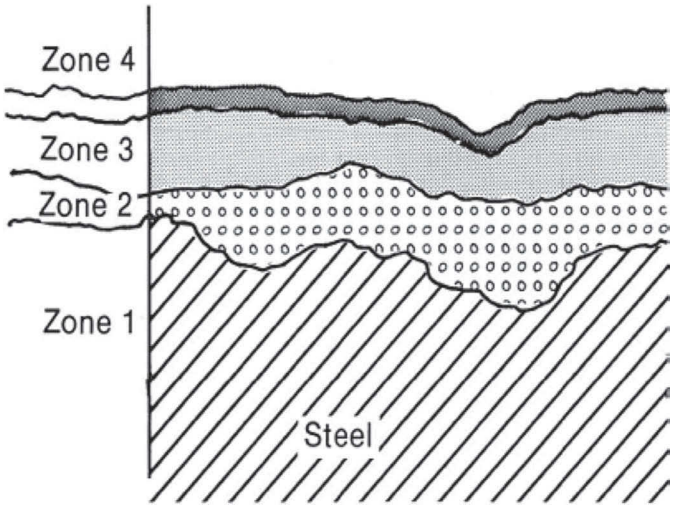


Figure 2.32: Typical rust layers found on heavily corroded steel.

Wind Direction

Wind direction can also have an effect on corrosion. At the International Nickel Company's Kure Beach test site, for example, edges of test panels that face the prevailing wind corrode more rapidly than edges of the panel turned away from the wind. In marine atmospheres, salt is impacted on the leading edge, creating a more concentrated electrolyte at that point. Corrosion is also accelerated on the windward side of a structure, which accumulates more windborne contaminates than the lee side. This is only true, of course, if a panel or structure is going to corrode within a reasonable length of time. Inorganic zinc panels, for instance, have shown no corrosion on the leading edge even after 10 years. Figures 2.30 and 2.31 illustrate this edge effect.

Hygroscopic Salts

One of the mechanisms for creating an electrolyte from atmospheric moisture vapor is the lowering of the dew point by hygroscopic water-soluble salts, which deposit and then form water-soluble metal salts on the surface. According to Barton, in *Protection Against Atmospheric Corrosion,*[12] this process is much more important than the conversion of water vapor to liquid on the metal surface.

> Water-soluble salts coming into contact with humid air after being dried take up water vapor from the atmosphere. If the equilibrium pressure of the water vapor that corresponds to a solid species (solid salt) is exceeded, further water vapor uptake occurs to give a solution whose concentration corresponds to an equilibrium value between the water vapor partial pressure over the solution and that existing in the atmosphere. Particularly in atmospheres that contain large quantities of such species, and in which the metal surface is more or less contaminated with them, this type of electrolyte formation is of special importance. This is especially true in coastal and industrial regions; in the former because of chloride, in the latter because of sulfate. Aerosol-forming hydroscopic soluble solid species convert into their dissolved forms before deposition. The electrolyte (the concentrated salt solution) falls in droplets to the surface, and these coalesce to form the electrolyte required for corrosion.
>
> Salt particles from the atmosphere are not the sole source of hydroscopic species at the metal surface. During corrosion reactions between metals and gaseous species (normally air pollutants), soluble hydroscopic products form and these lead in turn to electrolyte formation. In this respect sulfate (which arises chiefly as the conversion product of atmospheric sulfur dioxide) and chloride are particularly important. The new phases (the solid corrosion product) formed during the reaction affects the water participation in the reaction system. The fact that accumulations of more or less soluble salts, with anion depending on atmospheric type, are found in corrosion products is an expression of this.[12]

The type of reaction discussed by Barton is one quite common to marine atmospheres. It is also common in areas where there is HCl and NaOCl, as well as in the handling and processing of salt. The chloride ion is, of course, the key to this reaction. If, for example, a steel surface is sandblasted, small droplets of moisture will accumulate in the areas of previous pits. If the humidity is reasonably high, the droplet will grow in a matter of only a few minutes. The original color of the condensation is a light green, indicating a ferrous ion in solution. It soon turns to a brown or yellowish brown, however, which seems to indicate the ferric ion. Following a somewhat longer period of exposure, the spot of moisture will turn black, indicating that it has changed from chloride to oxide, undoubtedly black Fe_3O_4. This reaction partially explains why previously corroded areas on a piece of visually clean steel will be the first to corrode again. This is also responsible for one of the major problems in applying organic coatings without additional surface preparation (Chapter 9).

Moisture retention on a metal surface once corrosion products have already formed is another factor discussed by Barton.

> The anions raise the colloidal component of the corrosion products (especially rust). These colloids find the water relatively loosely in liquid form below the water vapor saturation pressure so that it is easily freed to act on the corrosion process.
>
> A corrosion process involves the existence of an electrolyte in contact with a metal. Since most corrosion processes yield solid products that contain chiefly hydroxide, hydrated salts, and oxides, part of the water is removed from the system in a more or less solidly bound form. These products also have a relatively high sorption capacity for water, which lead to finding of a further fraction of the water. Thus, on the one hand there is a partial removal by chemical processes of the very small amount of electrolyte that is atmospheric corrosion (especially at relative humidity below 100%) while on the other hand, there is a layer of corrosion products formed that can be regarded as a water reservoir, and which under some circumstances (e.g., by exceeding the sorption capacity as the humidity rises) can liberate liquid water. The reverse process is also possible.
>
> As for other cases of electrochemical metal corrosion, atmospheric corrosion should be regarded as a total process composed of simultaneous oxidation (anodic) and reduction (cathodic) reactions. Each reaction is tied to the other (i.e., the oxidation process [the actual corrosion]) could not proceed without there being a simultaneous reduction reaction though the individual mechanism of the two processes may be completely independent.



Figure 2.33: Heavy rust layering on steel exposed to marine conditions. Note the heavy rust scale (Zone 3) in both horizontal and vertical surfaces.

TABLE 2.10: Typical Layering of Rust Deposits and the Composition of Individual Layers (Rust Grown for 34 Months in an Individual Atmosphere)

	Zone			
	I	II	III	IV
Amount of Rust (mg cm^{-2})	Steel	29	40	7
Iron Content in Rust, (%) Total	–	66.9	63.9	60.5
Fe^{2+} (%) (Ferrous iron)	–	60.5	8.66	0
$(SO_4)^{2-}$ (mg cm^{-2}), Total Sulfate	–	240	1128	281
$(SO_4)^{2-}$ (mg cm^{-2}), Soluble Sulfate	–	40	87	55
Cl^- (mg cm^{-2})	–	130	186	32
Zone I: Steel.				
Zone II: removed by chemical methods (e.g., pickling).				
Zone III: spring off by bending the specimen.				
Zone IV: removed by brushing or scraping.				

Source: K. Barton, *Protection Against Atmospheric Corrosion,* J.R. Duncan, translator, (New York, NY: John Wiley & Sons, 1976) p.3.

Atmospheric Corrosion Products

Atmospheric rust is mainly composed of lepidocroicite and geothite (alpha and y-FeOOH). It also contains magnetite (Fe_3O_4), amorphous, and usually hydroxide-based components, and either ferrous sulfate ($FeSO_4 \bullet 4H_2O$) or ferrous chloride ($FeCl_2$), depending on atmospheric impurities. Impurities arise from the conversion of atmospheric SO_2, which is found along the coast in primarily industrial and chloride-containing atmospheres.

It is often possible to locate three distinct zones of rust while observing corrosion products on a steel substrate, as shown schematically in Figure 2.32. The steel itself is considered the first zone. The second zone is a dark gray and very hard, durable layer, which is difficult to remove by either sandblasting or acid pickling because of its tight adherence to the steel. The third zone, however, can easily be broken off of a surface by bending or beating the surface with steel sledges, as is often done on barge decks. This zone is also a hard layer and consists of the usual scale that forms on heavily rusted objects. It has areas of both dark gray oxides and light yellow-brown amorphous materials, which shows in the cracks and fissures of the dark materials. The fourth zone is a relatively soft amorphous, powdery material that can be brushed or scraped from the surface without much difficulty. This material, which is primarily the Fe_2O_3 form of rust (Fe_2O_3), is usually the yellowish-reddish-brown color that is typical of most rusted surfaces.

While these zones exist on almost any rusted surface, it is only possible to isolate the distinct corrosion layers on heavily corroded steel (Figure 2.33). Although marine conditions provide some of the obvious examples of layered corrosion, some industrial areas are equally severe.

Barton analyzed rust formed in an industrial atmosphere where there was obviously both sulfate and chloride contamination. The heaviest concentrations of both sulfate and chloride anions are found in Zone III, since Zone II is extremely dense. Zone III, however, is hard scale that is heavily cracked and fractured so that it is able to hold the greatest amount of soluble materials. Zone IV, on the other hand, is thin and powdery. Table 2.10 gives the composition of the three zones in more detail.

The chemical composition of the corrosion products of various metals is a complex subject. Not only do they contain miscellaneous oxides and carbonates, but also various crystal forms with their combined water as well as complex sulfates, chlorides, and sulfides. Table 2.11 lists the various chemical compounds commonly found in the atmospheric corrosion products for various metals. The metals listed in this table are the ones normally involved in atmospheric corrosion in both industrial and marine areas.

Atmospheric Dusts

The corrosion process can also be strongly affected by solid particles known as atmospheric dust. This dust accelerates the corrosion of metal surfaces exposed to the atmosphere. These solid particles may consist of soil picked up by wind, smoke, and soot particles, or they may be organic particles of vegetable origin, including microorganisms such as fungi. Many chemical compounds such as ammonium sulfate, coal dust, fly ash, or NaCls also may be included in the dust, depending on the type of industry in the area. For example, in various industrial districts in England where coal was used as a primary fuel, the release of dust particles approximated 1.2 to 1.4 kg of soot and dust per m^2 every year. Atmospheric dust measured in Pittsburgh, Pennsylvania had a composition of organic matter, 35%; mineral (primarily Fe_2O_3), 14.5%; insoluble mineral matter, 3.85%; and soluble matter (mostly sulfates), 9.2%.

The various solid particles that settle as dust can act in several different ways. As discussed previously, the soluble salts, such as ammonium sulfate or NaCl, are corrosion active since they readily make strong electrolytes.

There are also dusts that are not particularly corrosive, but that are capable of absorbing active gases from the atmosphere. These

TABLE 2.11: Compounds Found (Frequently) in Atmospheric Corrosion Products

Metal	Compounds	Notes
Iron	a-FeOOH, y-FeOOH, B-FeOOH $Fe(OH)_2$ Fe_3O_4, (Fe_2O_3?)	B-FeOOH only in atmosphere containing chloride
	$aFeSO_4 \cdot bFe(OH)_2 \cdot cFe(OH)_3$ $FeSO_4 \cdot 4H_2O$, $FeSO_4 \cdot TH_2O$	
	$FeCl_3$	In industrial atmosphere In marine atmosphere
Copper	CuO, Cu_2O, $CuCl_3 \cdot 2Cu(OH)_2$	
	$2CuCO_3 \cdot Cu(OH)_4$	
	$CUSO_4 \cdot 3Cu(OH)_2$, $CuSO_4 \cdot 2Cu(OH)_2$	In industrial atmosphere
	$CuSO_4 \cdot 5H_2O$	
	Cu_2 (OH_3) Cl	In marine atmosphere
	CuS	
Zinc	ZnO, -Zn(OH)2, β-$Zn(OH)_2$, $ZnCO_3$	
	$ZnCO_3 \cdot Zn(OH)_2$	
	$ZnCO_3 \cdot 3Zn(OH)_2$, $ZnCO_3 \cdot 3Zn(OH)_2$	
	H_2O	
	$ZnCl_2 \cdot 4Zn(OH)_2$, $ZnCl_2 \cdot 6Zn(OH)_2$	In marine atmosphere
	$ZnSO_4 \cdot 4Zn(OH)_2$, $ZnSO_4 \cdot H_2O$)	In industrial atmosphere
Cadmium	CdO, $Cd(OH)_2$, $CdCl_3$, $2CdCO_3 \cdot 3Cd(OH)_2$	
	$CdSO_4 \cdot H_2O$, Basic sulfate (?)	In industrial atmosphere
	$CdCl_2 \cdot H_2O$, Cd(OH)Cl	In marine atmosphere
	CdS	
Aluminum	$Al(OH)_3$ gel, γ -Al_2O_3 γ AlQOH,	
	∂-$Al(OH)_3$	In extremely SO_2 polluted atmosphere
	Amorphous basic sulfate	
	Amorphous basic chloride	In marine atmosphere
Lead	PbO, $Pb(HCO_3)_2$, $PbSO_4$, Basic sulfate	
Magnesium	MgO, $Mg(OH)_2$, Basic carbonate,	
	$MgSO_4$ MgCl, basic chloride	

Source: K. Barton, *Protection Against Atmospheric Corrosion,* J.R. Duncan, translator (New York, NY: John Wiley & Sons, 1976), p.3.

include various forms of carbon such as soot or even coal dust. Coal dusts often promote severe corrosion because of their absorption of SO_2 and because of their sulfur content. They have very small particle sizes and any contained sulfur is oxidized in the atmosphere to SO_2. Soots often absorb SO_2 from stack gases and also can be very corrosive. This is obvious on the decks of tankers that burn high sulfur crudes in their boilers. When the stacks are blown, soot particles settle out on the deck. These particles are strongly acidic, and wherever they contact bare steel, an active corrosion cell is created. Decks and equipment subject to such fallout require coating with a chemical-resistant coating. The acid in the soot is strong enough to penetrate and pit most IOZ coatings where soot particles have landed.

Rock dust, silica, and so on represent another type of solid material that also settles on surfaces, but is nonreactive in it. When such materials accumulate, however, they can create corrosion by absorption and retention of moisture on metal surfaces.

While there are a variety of factors that contribute to atmospheric corrosion, the ones that exercise the strongest influence are: (1) water or moisture that form the surface electrolyte; (2) soluble accelerating ions, such as chloride and sulfate ions, which are primarily responsible for the conductivity of the electrolyte; and (3) temperature. In general, the higher the temperature, the greater the corrosive activity (as long as the electrolyte is present).

Areas of Atmospheric Corrosion

There are essentially three areas commonly identified with atmospheric corrosion: rural, industrial, and marine. In a rural atmosphere, there are little or no soluble ionic materials to cause a strong electrolyte. The term rural indicates an area away from both industrial and marine conditions, so that corrosion in these areas depends primarily on temperature, humidity, and retention of moisture on metal surfaces. In desert areas where humidity is low, water retention on any metal surface is very short, even during periods of rainstorms. Under these conditions, steel will discolor and zinc will change to a dull gray, but very little corrosion will actually take place. In more humid atmospheres, however, where moisture is retained for long periods, corrosion does occur, but at a relatively slow rate.

In cities or in industrial areas, the corrosion rate also depends on the three factors of temperature, humidity, and moisture retention. In addition, it depends on the amount of soluble ionic materials in the atmosphere, which are retained in the moisture layer on the metal surface. In areas where moisture is retained for long periods of time, corrosion can be so severe that heavy rust scale is formed where bare steel is exposed.

Zone of Marine Corrosion

Marine atmospheres, on the other hand, are consistently severely corrosive environments. The degree of severity, however, depends on several variables. The humidity in a marine atmosphere is generally high, but the temperature is variable depending on the climate (tropical, temperature, or arctic) and the amount of sunlight. The chloride content is also variable, depending on the distance from the shoreline.

Three primary areas for the corrosion of marine structures such as offshore platforms can be isolated. The first is the submerged area where corrosion is relatively uniform from the mean low tide area downward. Even at great depths, there is often a sufficient quantity

TABLE 2.12: Corrosion Factors for Carbon Steel Immersed in Seawater

Factor in Seawater	Effect on Iron and Steel
Chloride ion	Highly corrosive to ferrous metals. Carbon steel and common ferrous metals cannot be passivated. (Sea salt is about 55% chloride.)
Electrical conductivity	High conductivity makes it possible for anodes and cathodes to operate over long distances, thus corrosion possibilities are increased and the total attack may be much greater than that for the same structure in fresh water.
Oxygen	Steel corrosion, for the most part, is cathodically controlled. Oxygen, by depolarizing the cathode, facilitates the attack; thus high oxygen increases corrosivity.
Velocity	Corrosion rate is increased, especially in turbulent flow. Moving seawater may: (1) destroy rust barrier, and (2) provide more oxygen. Impingement attack tends to promote rapid penetration. Cavitation damage exposes the fresh steel surface to further corrosion.
Temperature	Increasing ambient temperature tends to accelerate attack. Heated seawater may deposit protective scale or lose its oxygen; either or both actions tend to reduce attack.
Biofouling	Hard-shell animal fouling tends to reduce attack by restricting access of oxygen. Bacteria can take part in the corrosion reaction in some cases.
Stress	Cyclic stress sometimes accelerates failure of a corroding steel member. Tensile stresses near yield also promote failure in special situations.
Pollution	Sulfides, which normally are present in polluted seawater, greatly accelerate attack on steel. However, the low oxygen content of polluted waters could favor reduced corrosion.
Silt and Suspended Sediment	Erosion of the steel surface by suspended matter in the flowing seawater greatly increases the tendency to corrode.
Film Formation	A coating of rust, or rust and mineral scale (calcium and magnesium salts) will interfere with the diffusion of oxygen to the cathode surface, thus slowing the attack.

Source: F.W. Fink, et al., *The Corrosion of Metals in Marine Environment,* Battelle Memorial Inst., DMIC Report 254, distributed by NTIS, AD-712 585-S, 1970, pp. 7, 13.

of soluble oxygen in the water, which means that corrosion can and does readily take place. A number of factors that influence the corrosion of steel in seawater have been listed by Fink[13] as shown in Table 2.12.

The second area is the tidal, or splash zone. This is an area of maximum corrosion, as it is alternately exposed to seawater and air with maximum oxygen content in the strong electrolyte. The third area is that above the splash zone. It is less corrosive than the splash zone, but is nevertheless a very strong atmospheric corrosion area often characterized by large tubercles of rust and deep pits. Corrosion is most severe in the area close to the tide level and becomes less severe with the height of the structure above the water. This reduction occurs because of two things: (1) the farther into the atmosphere, the less precipitated salt spray there is to form the electrolyte; and (2) the farther above the water level, the higher the temperature is and the less humidity there is.

Figure 2.34 illustrates the corrosion that took place in two of the three zones on an offshore production platform after eight years in the Gulf of Mexico. The graph of the structure indicates the nature of the corrosion in the two areas. Maximum corrosion occurred at the splash zone where the average corrosion was almost as great as the maximum average pit depth. The totally submerged area exhibited more uniform average corrosion, but with many deep pits. The graph shows little or no corrosion in the upper atmospheric area; however, the structure was coated in this area and therefore somewhat protected.

Figure 2.35 shows the three marine corrosion zones schematically, indicating the type of corrosion and the coatings required for corrosion protection of an offshore drilling or production platform. There is nothing particularly unique about corrosion on offshore equipment, except that severe damage to coating is the general rule rather than the exception, since they are continually exposed to severely corrosive conditions for years or even decades. Repair of such excessive damage is extremely difficult and costly, therefore maximum corrosion resistance must be designed into the marine service platforms.

Marine corrosion aboard a ship is very similar to that of an offshore platform. The zones and conditions are the same, as well as the coating systems generally used (Figure 2.36). The major difference is that ships are mobile, and thus may be exposed to a variety of climates (e.g., tropical, temperate, or arctic) and special conditions, such as tropical hurricanes or arctic flow ice. On the other hand, their mobility gives them one great advantage; it allows corrosion repairs to be made on a timely basis and under relatively favorable repair conditions. Surfaces can be abrasive blasted or otherwise cleaned and coatings can be applied under other than open sea conditions.

Methods of Corrosion Control

As discussed earlier, the corrosion process takes place because of the natural tendency for materials, particularly the metals commonly used for structures, tanks, ships, and other structures, to revert from the metallic state to the more stable oxide of the metal. The material is no longer useable in this condition, and if a major metal reversion has taken place, the structure fails. This kind of destruction must therefore be prevented. Several methods of ensuring the continued viability and usability of various structures at a minimum cost may be considered.

1. Selecting and using specific corrosion-resistant[1] materials of construction.
2. Changing or altering the environment.
3. Using a barrier between the structural material and the environment.
4. Using CP.
5. Using the principal of corrosion allowance or overdesign.

There are advantages, disadvantages, and areas of the most economical use for each of these methods. An ocean vessel, offshore structure, industrial plant, or underground pipeline all have numerous, different, and specific areas of corrosion susceptibility. For

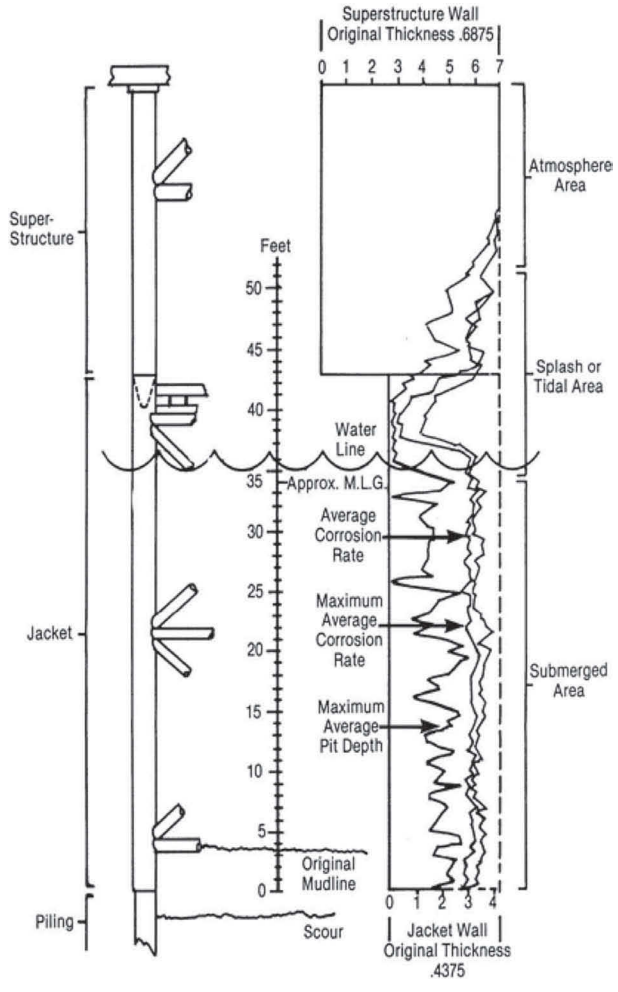


Figure 2.34: Corrosion of an offshore structure after eight years of service in the Gulf of Mexico. Source: O.L. Grosz, "Important Methods of Corrosion Control in Offshore Operations," Chevron, USA, New Orleans LA. Reprinted from *Offshore*, June-July 1958.

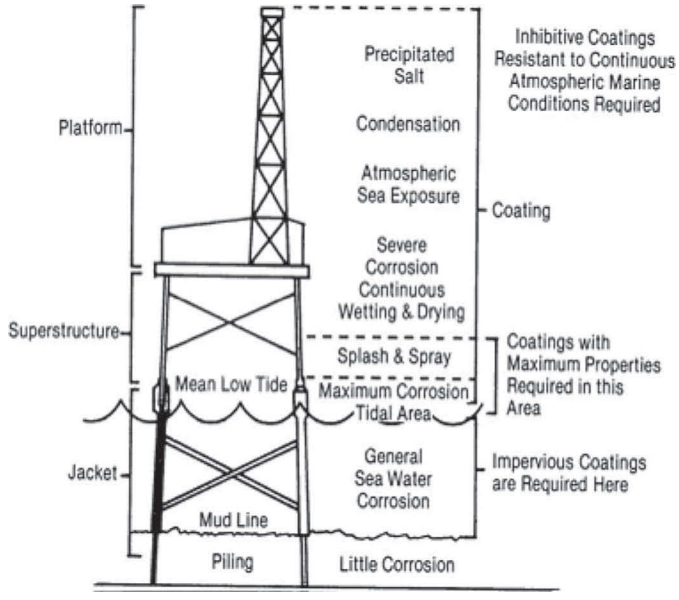


Figure 2.35: Typical corrosion zones on offshore platforms. Source: F.L. LaQue, *Marine Corrosion: Causes and Prevention,* (New York, NY: John Wiley & Sons 1975) pp. 298-299.

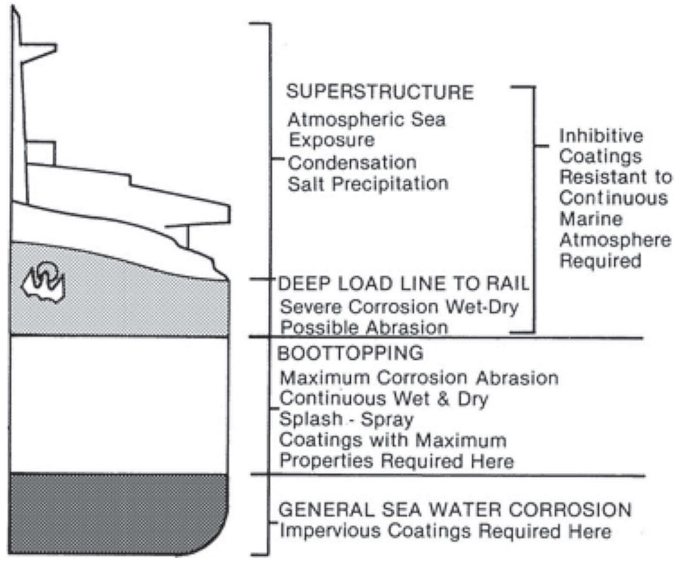


Figure 2.36: Typical corrosion zones aboard ship. Source: F.L. LaQue, *Marine Corrosion: Causes and Prevention* (New York, NY: John Wiley & Sons, 1975), pp. 298-299.

example, many industrial sites such as paper plants and refineries are a composite of micro atmospheres, each of which may pose a unique corrosion problem. A drip under a pump is certainly a different problem than a tank that contains the liquid being pumped. Similarly, the atmosphere in the area of a blow-down pit in a paper mill is different from that in the area where the pulp is bleached.

Therefore, no single method is universal or serves as a cure-all for corrosion problems. Each problem or situation must be individually studied and the specific requirements of that situation taken into consideration, along with such additional factors as the available down time, operating temperatures, appearance, age, and potential life of the area, before a decision can be reached as to which is the best method. If the structure is a new one, the method used or the design engineer most often determines the material selected. Errors in judgment made at this design development stage could be avoided by consultation with the corrosion engineer to assure that the most practical and cost effective of the above methods will be selected.

Corrosion-Resistant Materials

The use of corrosion-resistant materials is most often indicated in the original design of a structure or piece of equipment. These materials are usually selected for very specific purposes to withstand a particular corrosion condition or to prevent contamination of a contained liquid. In the case of an oxidizing acid solution containing radioactive material, a stainless tank or structure may be the only answer to the problem. High temperatures may also indicate specific materials rather than the ordinary structural grade of steel or concrete. A stack, for instance, may be lined with corrosion- or acid-resistant brick and mortars to prevent the serious breakdown of the structural concrete by fumes and condensation. Certain chemicals can only be kept in reinforced plastic containers.

Most often, the selection of specific materials is necessitated by a severe corrosion condition. In such cases, the additional material costs are entirely justified by the additional life obtained through their use. Examples of the use of such specific materials in our modern society range from stainless steel pots and pans in the kitchen and in food processing plants, to special alloys used in seawater

TABLE 2.13: Comparison of Corrosion Control Methods

Method	Examples	Principal Advantage	Disadvantages
Altering the environment	Changing process, humidity, or temperature. Use of inhibitors.	General simple changes. Many times low cost. Usually retrofit to existing facility.	May not completely eliminate problem. Inhibitors limited to immersion conditions.
Corrosion-resistant materials	Copper, nickel, chromium, molybdenum alloyed with iron or steel	Long lifespan, applicable to only certain situations.	High initial work cost, workability
Cathodic protection	Ship hulls underwater, underground pipelines	Simplicity, effective in presence of good electrolyte	Limited usefulness in damp or dry areas. Immersion required.
Barriers	Brick linings, protective coatings, plastic sheeting, monolithic toppings	Most effective and versatile, reasonable cost.	Careful analysis of corrosion problems necessary. Proper surface preparation and application essential.
Overdesign	Heavier structural members or thicker plates than required		Neither exact length of life nor replacement cost can be predicted. Higher initial cost. Ineffective. Increased weight.

condensers or materials such as Hastelloy or lead used under strong acid conditions.

The decision to use this type of protection compared to other methods of corrosion control largely depends on the severity of exposure and the ultimate cost of alternate methods. The use of special materials normally cannot be economically justified for the majority of structural areas within a plant, even though some corrosion may be present.

There are many other types of materials that may be selected in addition to metals and metal alloys. Plastic materials can be used in many corrosive conditions such as the piping of corrosive solutions. They are also used as ducts for corrosive fumes (e.g., in rayon plants) and as corrosion-resistant gratings. They can be reinforced with synthetic fiber or glass to provide sound structural properties in addition to corrosion resistance, and with such reinforcement, are often used as tanks and scrubbers and in large fume processing areas.

Both inorganic and organic mortars are used with acid-resistant brick and tile for specific corrosion-resistant areas. These may be used in such areas as pickling tanks in steel mills or as corrosion-resistant flooring materials in chemical or food plants. The category of corrosion-resistant materials is thus a broad one, with every industrial plant having some use for them.

Changing the Environment

Changing an environment can involve such procedures as the alteration of a piece of equipment in order to prevent splash, spray, or fumes from a corrosive solution coming in contact with adjacent equipment or structural areas. It can also involve a change in humidity by increasing the air flow through the area or by increasing the temperature. It may involve the ducting of corrosive fumes away from their source or the piping of a corrosive liquid rather than allowing free flow to an open floor drain.

The use of chemical inhibitors is also a method of changing the environment. These are often used in steam and condensate return lines, brine lines, petroleum transportation lines, heat exchangers, and cooling towers. They are most often used in closed systems, although the cooling water that is continually reused in a cooling tower is an important exception. Inhibitors must also be used with some caution, as some may be considered toxic, and improper selection and maintenance of an inhibitor system may accelerate rather than retard corrosion. Nevertheless, if properly used in the areas where they can be effective, inhibitors can provide a simple and relatively low cost answer to corrosion control.

Barriers

The barrier principle represents the most common and widespread use of corrosion prevention. This method utilizes corrosion-resistant materials to isolate concrete, steel, or other structures from a corrosive environment. The variety of barriers available include acid-proof brick and tile construction on the interiors of tanks or floors; the use of plastic sheeting that is either applied to structures with an adhesive or is fabricated into a unit that may be placed on the interior of a tank to contain corrosive solutions; troweled or sprayed-on plastic cements; and, of course, protective coatings. Since each of these barrier methods is characterized by usefulness, a careful analysis of the problem is required in order to choose the one that would be the most effective and economical.

Cathodic Protection

Of necessity, CP—a reversal of the corrosion process whereby sufficient electrons are maintained on any metal surface to prevent the metal from going into solution—can only be used for immersion or underground conditions. The cathodic current can be supplied either by an externally impressed current or by sacrificial metals used as anodes. CP can be an extremely effective method of corrosion control where proper and practical conditions for use exist.

Design Allowance

Overdesign for corrosion conditions is becoming less common as other corrosion prevention methods have become more practical and less costly. Overdesign of a structure through the use of heavier structural members or thicker plates does not eliminate the corrosion problem. It merely adds considerable weight requiring heavier construction. Even though corrosion is anticipated, specific conditions are often difficult to predict. The unprotected structure using the overdesign principal may therefore corrode much faster than anticipated or may corrode much more rapidly in certain areas, thus consuming the corrosion allowance and endangering the

life of the structure.

It used to be a common practice in the shipping industry to add a corrosion allowance to hull plates and bulkhead structures. The additional tonnage, however, required additional energy during transportation. These corrosion allowances have thus largely been eliminated by the use of long-lasting protective coatings that are effectively resistant to the type of corrosion found on the interiors of the tanks and the exterior of the hull.

These five corrosion control methods are summarized in Table 2.13. Each of these methods has its own sphere of usefulness, although, under many conditions, a combination of methods may be even more effective. Some stainless steels, for instance, are affected by the chloride ion, which results in surface pitting. Thus, the combination of stainless steel and an effective chloride-resistant coating often provides a more effective system than the stainless steel alone.

CP, more often than not, is also combined with various protective coatings in order to reduce the cost of impressed current or to reduce the number of sacrificial anodes used. In other cases where the surface may be both wet and dry, a combination of cathodic protection and coatings is most effective. A severely corrosive environment may similarly be changed by the combination of additional ventilation and protective coatings.

In the words of Frank LaQue,

> Knowledge of the reactions involved in the corrosion of steel combined with a knowledge of how a paint system can impede these reactions... can serve as an effective guide to the most effective use of paint to protect steel.[14]

Thus, because no single method is the cure-all or is effective under all conditions, proper selection of a corrosion control method must be preceded by a careful analysis of many factors.

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3 Essential Coating Characteristics

Protective coatings are unique specialty products that represent the most widely used method of corrosion control. They are used to give long-term protection under a broad range of corrosive conditions, extending from atmospheric exposure to full immersion in strongly corrosive solutions. Protective coatings in themselves provide little or no structural strength, yet they protect other materials so that the strength and integrity of a structure can be maintained. They are the skin over the skeleton that both protects and beautifies the bone and muscle of the world's essential structures.

Coating Function

The function of a protective coating or lining is to separate two highly reactive materials; that is, to prevent strongly corrosive industrial fumes, liquids, solids, or gases from contacting the reactive underlying substrate of the structure. This is another way of saying that a coating or lining acts as a barrier to prevent either chemical compounds or corrosion current from contacting the substrate. This physical separation of two highly reactive materials, the atmosphere and substrate, is extremely important.

That coatings or linings are, in general, a relatively thin film separating the two reactive materials indicates the vital importance of the coating and the concept of a corrosion-free structure. The coating must be, according to this concept, a completely continuous film in order to fulfill its function. Any imperfection becomes a focal point for corrosion and the breakdown of the structure, or a focal point for the contamination of a contained liquid. This relatively thin continuous film concept takes on even greater significance when it is understood that most protective coatings are manually applied to very large areas of structural steel (e.g., tank surfaces, ship hulls, drilling structures, and pipelines). A single coating application may thus involve an area of many thousands of square meters.

Essential Coating Properties

Water Resistance

To perform effectively, a corrosion-resistant coating must be characterized by many essential properties. These may vary, depending on the specific use of the coating, but there are several basic characteristics required by all coating materials.

Resistance to water is perhaps the most important coating characteristic since all coatings will come in contact with moisture in one form or another. Water, which affects all organic materials in one way or another, is actually the closest thing to a universal solvent. It is no small wonder, then, that a resistance to it is difficult to achieve. Even rock and concrete gradually dissolve or erode away due to their contact with water, and both iron and steel rapidly oxidize under even normal acidic water conditions. Thus, there is no one coating that can be effective under all water conditions; there are too many different types of structures and forms of water for overall resistance to be that easy.

The protection of iron and steel pipe, for instance, is quite a different problem from the one encountered in aboveground storage tanks leading to the pipe. Similarly, dam gates and trash racks require a different solution from the concrete flume bringing water into the dam. Filters, clarifiers, and floculators present an even different set of conditions that must be addressed. Industry adds its share of difficult situations by requiring deionized water for some processes. This requires the use of special deionization equipment, storage tanks, and piping.

These mechanical problems are multiplied by the different types of water encountered. Swamp water, which may be pure enough to drink, is ordinarily acidic and will corrode both steel and concrete. Sulfide water, which is prevalent in many areas, reacts readily with most metals (e.g., iron, steel, brass, and copper). High conductivity water or seawater leads to rapid formation of anode-cathode areas on steel, which results in severe pitting. Pure water from fields of snow will dissolve the calcium out of concrete at a rapid rate, leaving the aggregate exposed. Water with high oxygen content will also create anode-cathode type corrosion areas. The problem is thus a very complex one because no single type of material will provide a universal answer.

The water molecule is an extremely small one with the ability to penetrate into and through most organic compounds. It does this by passing through the intermolecular spaces of the organic material, and can either remain there in an absorbed state or can pass through the compound. Generally moisture will come to equilibrium, with as many water molecules passing into the organic material as evaporate out of the surface. This maintains relatively constant water content in the organic material, depending on the moisture vapor pressure at any given time. Because of this highly penetrating characteristic, water has more of an effect on organic compounds

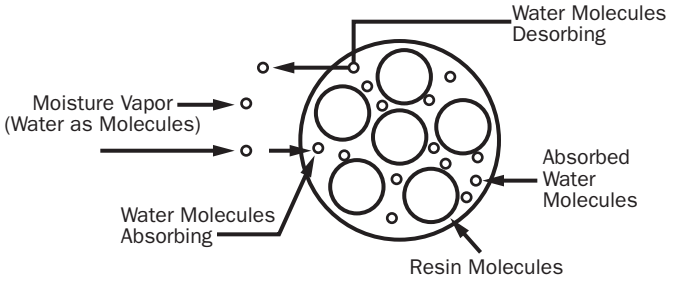


Figure 3.1: Water absorption. Source: F. L. LaQue, *Marine Corrosion: Causes and Prevention,* Chapter 16, (New York, NY: John Wiley & Sons, 1975) pp. 285–287.

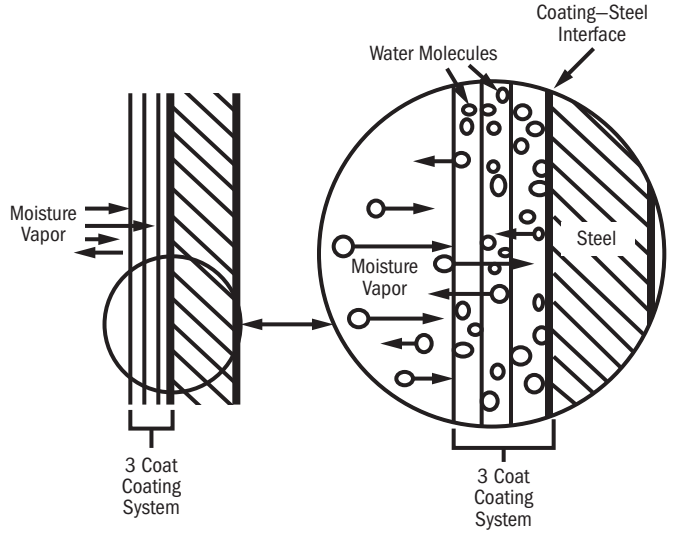


Figure 3.2: Water absorption by a coating.

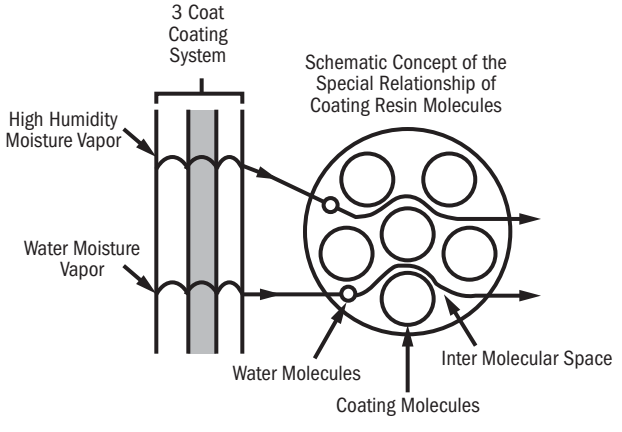


Figure 3.3: Moisture vapor transfer rate. Source: F. L. LaQue, *Marine Corrosion: Causes and Prevention,* Chapter 16 (New York, NY: John Wiley & Sons, 1975), pp. 285–287.

than any other single material. Since most coatings are organic in nature, they must have the highest possible moisture resistance in order to maintain their properties and be effective over a long period of time.

Water can also affect the permeability of other molecules, depending on their size. Some of the very small molecules (e.g., ammonia [NH_3], carbon dioxide [CO_2], and hydrochloric acid [HCl]) are also extremely penetrating and are aided by water vapor in their penetration into organic compounds. NH_3 is an extremely difficult material to deal with in terms of coatings. Since it is a gas, NH_3 becomes alkaline when it is combined with moisture. Its resulting high penetration characteristics cause blistering in many coatings. HCl is also very penetrating since it is both a gas and a small molecule. It not only has a strong affinity for water, but in areas of poor adhesion (even with heavy organic lining materials), it will penetrate and accumulate underneath the lining, causing accelerated corrosion.

CO_2 is also very penetrating. In the early days of the automobile, it was considered the ideal gas for inflating tires. Because of its small molecular size, however, CO_2 could not be prevented from penetrating the inner tube and, within a matter of a few hours, causing a flat tire.

Organic materials can, therefore, be permeated by many of the very small molecules such as water. This is particularly true where there is an interface or poor adhesion under a coating where the water vapor can accumulate and possibly condense.

The larger molecules, such as sugar, sodium hydroxide (NaOH), and even sulfuric acid (H_2SO_4), do not penetrate the organic molecules. In some cases, they even tend to draw water out of the organic coating by an osmotic reaction. A concentrated sugar solution or NaOH solution will pull the water out of the coating and into the concentrated solution so that solutions of these materials have little tendency to blister coatings.

For a high-performance corrosion-resistant coating to also have excellent water resistance means that it must not only withstand continuous immersion in water or seawater, but it must do so without blistering, cracking, softening, swelling, or loss of adhesion. It must also withstand repeated cycles of wet and dry conditions, since such coatings are normally exposed to an atmosphere of condensing dew in the evening and night hours and sun drying during daylight hours.

Water Absorption

Water absorption refers to the amount of water that is picked up and retained within the molecular spaces of the coating. Once the coating has formed, the water content comes to equilibrium with the atmosphere, desorbing (or evaporating) water under dry conditions and absorbing water when subject to high humidity or immersion (Figure 3.1).

Each coating also has its own level of water absorption. Since the water in the coating is in equilibrium with the moisture in the atmosphere, it is not, in itself, in a critical condition in terms of corrosion. If a coating is strongly adhesive and there is no interface between the coating and the substrate, the moisture absorbed into the coating will remain there in a relatively inert state. At any given moisture vapor pressure, as many molecules leave the coating as enter into it. Thus, the number of absorbed molecules in the intermolecular areas remains constant for each coating type (Figure 3.2).

On the other hand, moisture vapor can contribute to corrosion when combined with other factors, such as the very small molecules of HCl, NH_3, or similar materials. Thus, the best corrosion-resistant coating generally has the lowest water absorption.

Moisture Vapor Transfer Rate

The moisture vapor transfer rate is the rate at which moisture vapor will transfer through a protective coating when there is a difference in moisture vapor pressure on one side of the coating compared to the other side (Figure 3.3). Each coating and resin has its own characteristic moisture vapor transfer rate. Table 3.1 gives some laboratory-measured rates for individual coatings. (Note that these should not be considered standard rates for any generic type of coating.) Depending on the formulation, an epoxy could have a much higher moisture vapor transfer rate than the figures given, while an alkyd could have a lower rate. It is gen-

TABLE 3.1: M.V.T. Rates for Specific Coatings

Coating Type	Permeance Perms[A]	Test Thickness (DFT)	Grams/100 in^2 (24 h)
Epoxy Polyamide	0.16	8.0	0.17
Amine Catalyzed Epoxy	0.19	7.5	0.30
Vinyl Chloride Acetate	0.31	5.5	0.83
Vinyl Acrylic	0.54	5.0	0.83
Alkyd (Short Oil)	2.4	5.0	3.7

[A]Perm = Grains of moisture/1 h/ft^2/P (in of Hg).

erally held that the lower the moisture vapor transfer rate, the better the protection provided by a corrosion-resistant coating.

In considering the passage of water through a resin film, it should be noted that such passage is not through open pores in the coating. Rather, it is through and into the intermolecular spaces between the resin molecules, with the spatial relationship of the very large resin molecules contributing to moisture absorption and passage. These circumstances are very different from physical imperfections in the coating, such as pinholes and voids, which allow moisture to penetrate through the opening just as it would in air. In this case, the moisture has easy access to the substrate where it can actively promote corrosion or release the adhesion of the coating.

The transfer of moisture through a coating, as stated previously, depends on the difference in pressure between the two sides of the coating. If a coating has excellent adhesion, then there is no difference in pressure from one side to the other and the coating soon comes to equilibrium with the moisture in the air or the water on the surface of the coating (Figure 3.4). The water molecules merely penetrate into the coating and are absorbed while an equivalent number are evaporated from the coating so that the amount of moisture in the coating (moisture absorption) remains constant.

If the coating has poor adhesion, however, either inherently or because it has been applied over a contaminated surface, there is an interface between the coating and the steel, and moisture vapor can transfer into this area. Soon after the coating is applied, there is little moisture vapor pressure in this area so that there is a tendency for moisture to pass in the direction of the poor adhesion. Moisture can condense in this space or, if the temperature of the coating increases, the moisture vapor within the void can develop sufficient pressure to create a blister (Figure 3.5). With poor adhesion, the moisture vapor can penetrate between the steel and the coating, expanding the blister.

Blisters 6 to 8 in (152 to 203 mm) in diameter and containing so much water that the coating actually hangs down like a bag have been observed on the exterior of tanks. In this case, water, as moisture vapor, penetrated the coating from driving rain and continuing high humidity.

The moisture vapor pressure within the coating or in a void beneath the coating is dependent on the temperature and would be the same moisture in a vapor, liquid, or condensed vapor form. Moisture vapor and condensed vapor are both pure water forms. The only time there would be a difference in the moisture vapor pressure would be where moisture in contact with the coating contained considerable soluble salts. Pure water, however, has the maximum penetrating power, while water with dissolved salts has a somewhat lesser penetrating force.

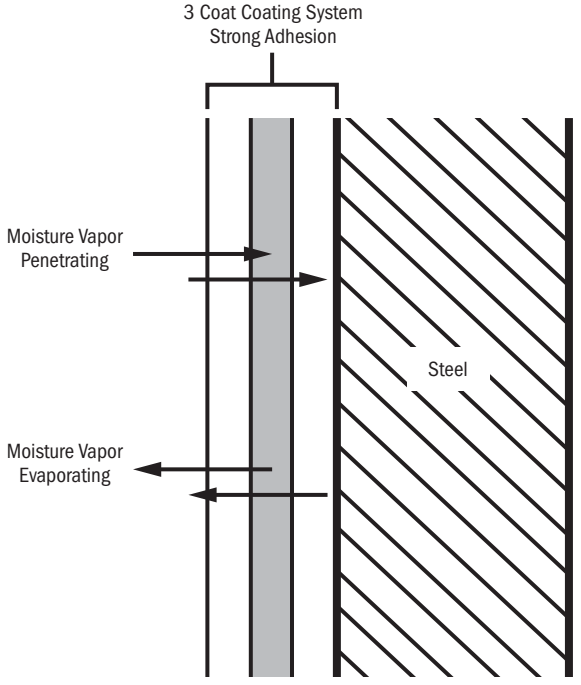


Figure 3.4: Moisture transfer through a coating with excellent adhesion.

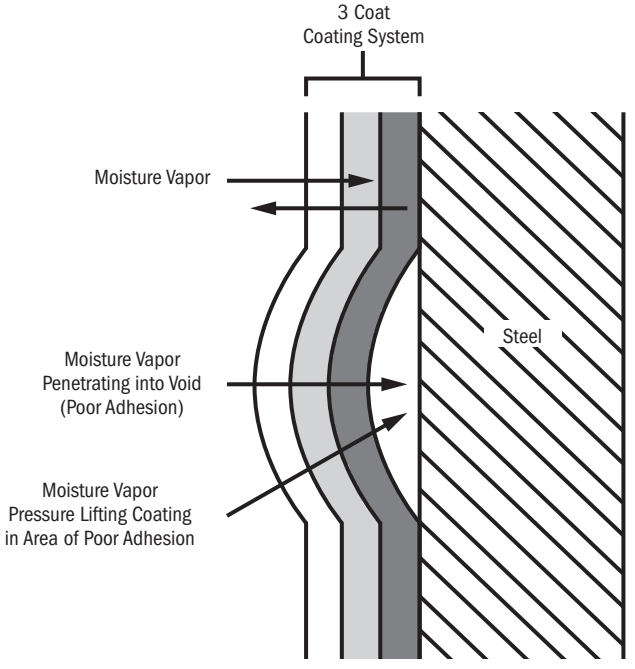


Figure 3.5: Penetration of moisture vapor into and area of poor adhesion under a coating.

Thermal Gradient Across Coating

Another mechanism of moisture as it is in contact with a coating concerns a thermal gradient across the coating. This is where the

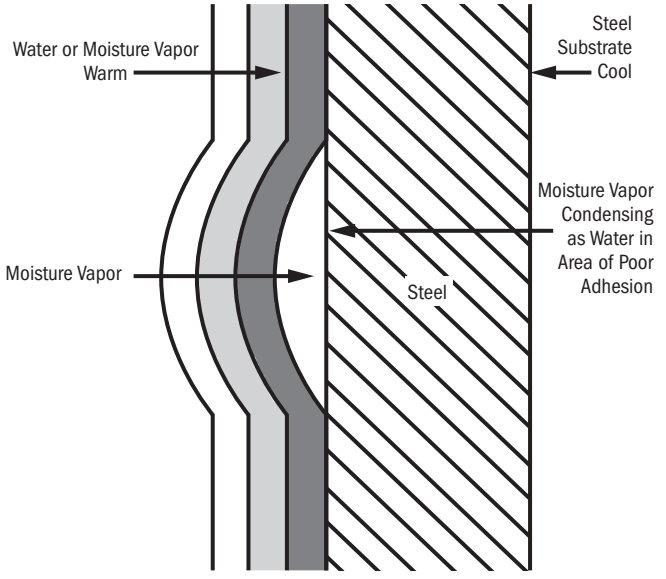


Figure 3.6: The thermal gradient effect on a coating with poor adhesion.

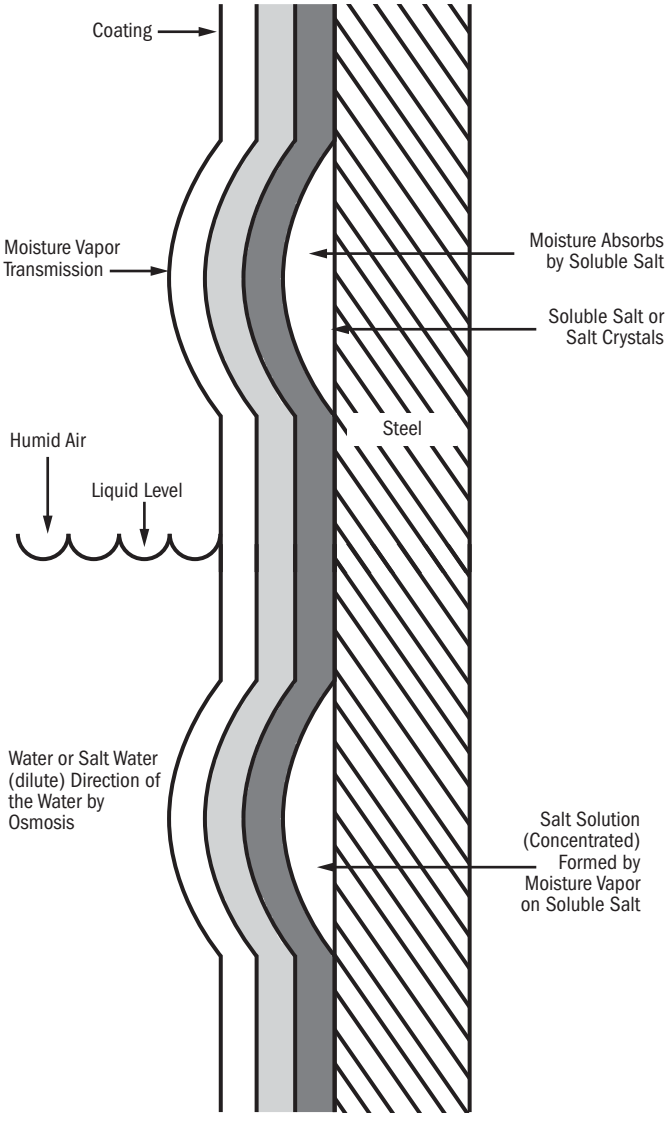


Figure 3.7: The principle of osmosis as it affects coatings. Source: F. L. LaQue, *Marine Corrosion: Causes and Prevention,* Chapter 16 (New York, NY: John Wiley & Sons, 1975), pp. 285–287.

metal or steel substrate is at a lower temperature than the moisture vapor or water on the exterior of the coating. This temperature gradient effect is the basis of what is known as the Cleveland Coating Tester, which involves forcing moist, warm water to condense on the coating while the steel substrate is exposed to the cooler outside air. The temperature on the inside of the tester is approximately 100 °F (38 °C), while the temperature on the exterior is ambient, thus causing the thermal gradient. This serves as an excellent test for a coating's adhesion characteristics; the warm moisture vapor used in the test will penetrate the coating and tend to condense on the cooler steel substrate underneath the coating, thus creating a water-filled blister.

This same principal is utilized in what is known as the Atlas tester, which is used for testing tank linings. In this case, the liquid that is put in contact with the coating is warmer (or hot), while the exterior substrate is at air temperature. This thermal gradient mechanism should also be considered wherever a tank or pipe containing a warm liquid is lined, or where the exterior of a tank is coated and the liquid on the interior is considerably cooler than the exterior temperature (Figure 3.6).

Osmosis

The mechanism of osmosis also concerns the passage of moisture through a coating. More specifically, osmosis is the passage of water through a semipermeable membrane from a solution of less concentration to one of greater concentration. All organic coatings will transmit moisture vapor, which makes them semipermeable membranes and therefore subject to this mechanism (Figure 3.7).

Osmosis is an important phenomenon wherever coatings are subject to water immersion, condensation conditions, or even high humidity. Chloride deposition on steel, for example, is not uncommon in marine areas. Contamination can come from a variety of circumstances, including a handprint on the steel surface, a drop of sweat, or poor initial cleaning of a contaminated surface. Once the surface contaminant has dried, it may not be noticed during the application of the coating. Thus, as soon as the coating is put into service under immersion conditions or high humidity, moisture vapor again transfers through the film and, when it comes into contact with chloride or other soluble contaminants, forms a concentrated solution at that point.

Since osmosis transfers moisture from the side of the coating with the least concentration to the area of greatest concentration, moisture is pulled through the coating toward the area of contamination. This principle is a general physical-chemical one that applies in every case where there is a solution concentration differential across a semi-permeable film. It is the same principle that applies to reverse osmosis in the purification of water and which affects the cell wall during biologic activity where water is absorbed by plants from the soil or air. Thus, where a coating is to be immersed or subjected to high humidity, a clean surface is essential to prevent the mechanism of osmosis from occurring.

Electroendosmosis

Moisture vapor is the key reactant in yet another mechanism. Electroendosmosis is defined as the forcing of water through a semipermeable membrane by an electrical potential in the direction of the pole with the same electrical charge as the membrane. While this may seem to only relate to an isolated series of circumstances, it should be noted that coatings are generally negatively charged and the metal around even a small break in the coating contains an excess of negative electrons, therefore making it a negative surface. Water then tends to be forced through the coating toward the cathode. Thus, wherever a break in a coating occurs, the mechanism of electroendosmosis is possible. The series of circular

blisters around a small break in Figure 3.8 shows the effect of electroendosmosis. Figure 3.9 illustrates this mechanism schematically.

The most common example of coating failure by electroendosmosis is where a coated surface is also under cathodic protection (CP). Failures of underground pipe coatings in moist soils have occurred due to excessive cathodic potentials used in the CP system. The same has been true of ship bottoms. Most of these failures have occurred because of poorly operated and controlled impressed current systems. Zinc and aluminum anodes do not develop potentials that are damaging to most coatings. In fact, coatings with strong adhesion, good dielectric strength, and a low moisture vapor transmission rate, along with controlled cathodic potentials of under –1.0 V, provide an excellent corrosion protection system.

Water-related reactions cannot be stressed enough as the mechanisms behind the success or failure of any coating. Water is present in one form or another wherever a coating is used to protect a surface. In addition to having a strong effect on coatings due to its highly penetrating characteristic, water also serves as an electrolyte, which is required for a corrosion reaction. Moisture can also affect a number of other key coating properties, although less directly than those already discussed.



Figure 3.8: Coal tar coating in a water tank showing typical electroendosmotic blistering. Note the concentric circles of blisters.

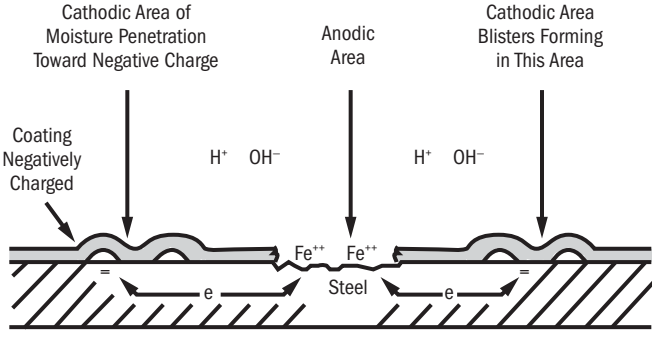


Figure 3.9: Electroendosmosis. Source: F. L. LaQue, *Marine Corrosion: Causes and Prevention,* Chapter 16 (New York, NY: John Wiley & Sons, 1975), pp. 285–287.

Dielectric Strength

Dielectric strength is a key coating property since the coating must break the electrical circuit set up during a corrosion reaction in order to be corrosion-resistant. It does so by resisting the passage of any electrons and thus preventing any metal from going into solution at the anode. If the electrons cannot travel to the cathode, the corrosion mechanism is not possible. Dielectric strength is also a key characteristic wherever coatings are to be used with CP, since such protection produces a strong excess of electrons on the metal. If, however, a coating has sufficient dielectric strength, it can break the electrical circuit and thus prevent the cathodic current flow. Since the dielectric strength of a coating can be affected by moisture absorption, the lower the moisture absorption, the more favorable the dielectric strength.

Resistance to Ionic Passage

In order for a coating to be effective, it must have a strong resistance to the mechanism of ionic passage. If chlorides, sulfates, sulfides, or similar ions were readily transferred through the coating, it would have little resistance to corrosion, but they would also reduce the dielectric strength in the coating, making it more conductive and, therefore, less corrosion resistant. Normally, ionic passage is the transfer of ions from the exterior of a coating to the substrate. A reverse situation, however, can also take place: the transfer of electrons through the coating from the substrate to the surface. This is most common where a coating is subject to an impressed cathode current and the calcareous or other salt deposits build on the exterior coating surface. The only way the deposits could form on the exterior of an intact coating is if electrons passed through the coating from the substrate, causing the precipitation of calcareous salts on the coating surface.

A coating with a very high molecular weight and dense molecular structure would have the greatest resistance to ionic transfer through the coating. It appears that the same would be true for electron transfer. An example of this type of material is a high-temperature baked phenolic coating, which has a very strong cross-linked structure with excellent water and acid resistance. Such coatings have been used for many years as tank linings and linings for oil well tubing where aggressive solutions are involved.

Coating resins have varying degrees of resistance to ionic and electron passage. Individual coating formulations, even where the same resin binder is used, can also have individual resistance and quite varying properties in this respect. Moisture absorption and moisture vapor transfer rate must also have a bearing on this coating characteristic. Properly formulated vinyl and epoxy coatings both have good resistance to ions. Epoxy coatings have shown some tendency to pass electrons. Alkyds, on the other hand, may have good resistance to ionic passage during the first portion of their life, although as they continue to react in the weather, they become more permeable over a period of time.

Chemical Resistance

Resistance to ionic passage is also a contributing factor to chemical resistance, although the two properties are not necessarily the same. A phenolic coating, for example, which is highly cross-linked and resistant to ionic passage, is not resistant even to reasonably dilute alkali solutions. Although the coating resists the passage of ions, it is rapidly destroyed because of its reactivity with alkalies.

Chemical resistance is the ability of the coating, and particularly the resins from which it is formulated, to resist breakdown by action of chemicals to which it is exposed. Vinyl coatings have a very broad range of chemical resistance. In fact, they probably have the broadest range of any of the coating resins. They are resistant to most acids, alkalies, and salts and to oxidizing conditions, as well as to many solvents such as alcohol. On the other hand they are readily dissolved by other chemicals. The difference is that while vinyl coatings are generally resistant to inorganic reactions, they are less resistant to the activity of organic materials.



Figure 3.10: This feather edge demonstrates excellent coating adhesion, with some of the steel substrate adhering to the coating curl.

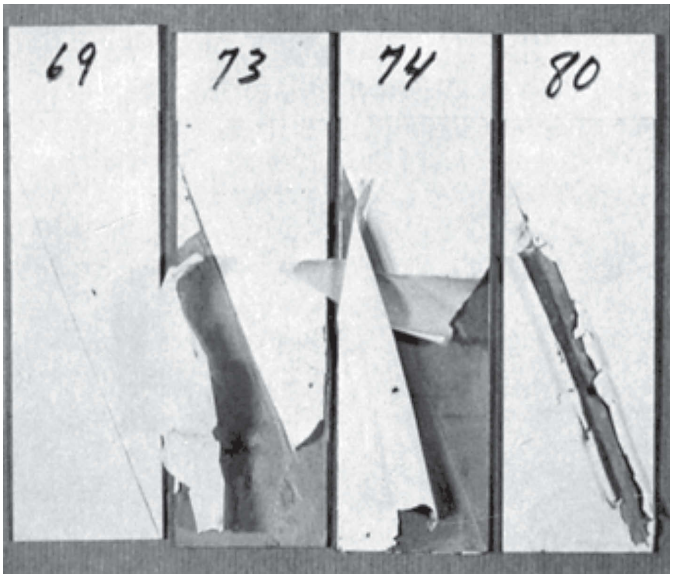


Figure 3.11: Test panels showing the importance of physical roughness to coating adhesion. All panels are cold-rolled steel. Panel 69, however, was blasted and demonstrates excellent bonding, even along the scribe. Source: F. L. LaQue, *Marine Corrosion: Causes and Prevention,* Chapter 16 (New York, NY: John Wiley & Sons, 1975), pp. 285–287.

Furan materials, which are used as cements for acid-resistant brick floors and tanks, also have a broad range of chemical resistance to acids, alkalies, and salt, but are rapidly attacked by oxidizing materials. Epoxies have excellent resistance to alkalies and generally to water, but are less resistant than the vinyls to most acid solutions. Epoxies are more resistant than vinyls to many solvents.

Chemical resistance, therefore, depends on both the coating's formulation and on the resins from which the coating is produced. Generally, a coating that is considered chemical-resistant and which would be used for corrosion resistance in a chemical atmosphere should be resistant to salts, acids, and alkalies of a rather wide pH range. It should also be resistant to organic materials such as diesel oil, gasoline, lube oil, and similar materials, since these are compounds found in almost all industrial operations.

Alkali resistance is, of course, extremely important in a primer. Since one of the chemical reactions in the corrosion process is the development of strong alkali at the cathode, any primer that is not highly resistant to alkali will tend to fail in the cathode area, resulting in undercutting of the coating and spreading of corrosion underneath the coating.

Proper Adhesion

A corrosion-resistant coating must also be highly adherent. Since the property of adhesion is essential in preventing the effects of water on the life of the coating and in preventing the problems caused by a temperature gradient across the coating, osmosis and electroendosmosis, adhesion is probably the key requirement in a corrosion-resistant coating. Irrespective of most of its other properties, the coating with very strong adhesion to the surface will retain its integrity much longer than one with less adhesion but other strong characteristics. Adhesion, in fact, has been the sole subject of many books, since each coating is unique in terms of this property.

Adhesion is created by physical and chemical forces, which interact at the interface of the coating and the substrate. The early vinyl coatings, which were composed of vinyl chloride-vinyl acetate copolymers, had little or no adhesion to the surface and were only practical where the surface was extremely porous. The addition of a third monomer created a limited number of organic acid radicals on the polymer. These had a strong affinity for metal surfaces and provided a bond between the polymer and the metal surface. Epoxies also have chemical radicals within the molecule that have a strong affinity for metal surfaces. These are often called polar molecules. (Strongly polar materials often have the characteristics required for adhesion.) From the standpoint of the corrosion engineer, adhesion is more a physical problem of applying a coating to a given surface in such a way that the inherent adhesion of the coating will be fully utilized. This involves applying the coating to a clean surface with adequate roughness or tooth, and making sure that the coating adequately wets the surface. This wet film application is necessary so that the liquid coating can come in intimate contact with the substrate. The coating shown in Figure 3.10 demonstrates such adhesion. When cut as shown, there was no evidence of chattering or breaking away along the edge of the cut. The cut was smooth, with a feather edge right down to the substrate and no evidence of any improper interface. This coating has proven to have excellent adhesion even under immersion conditions.

Physical roughness can be an important factor in adhesion. Blasted surfaces serve as a good example. As compared to a smooth, cold-rolled surface, a blasted surface has several times the area on which to adhere in addition to its physical roughness or tooth. This can make a substantial difference in the adhesion of a coating under almost any exposure condition, as shown in Figure 3.11. All four panels in this figure were coated with the same coating.

Three were cold-rolled metal and the fourth was sandblasted, cold-rolled steel. Equal thicknesses of coating were applied to each panel. They were all scribed and then immersed in water. The coating with the best adhesion (i.e., applied over a substrate with a greater surface area and some physical roughness) shows no tendency to disbond from the steel. Those surfaces that were not sandblasted, however, disbonded in the area of the scribe.

Undercutting

Undercutting is a measure of adhesion. The term applies to the corrosion at a break in the coating, growing back underneath the surface of the coating away from the break (Figure 3.12). To have resistance to undercutting, a coating must be strongly adhesive and must maintain its adhesion even at a raw edge between the coating and the steel. Examples of the undercutting of coatings can be seen on

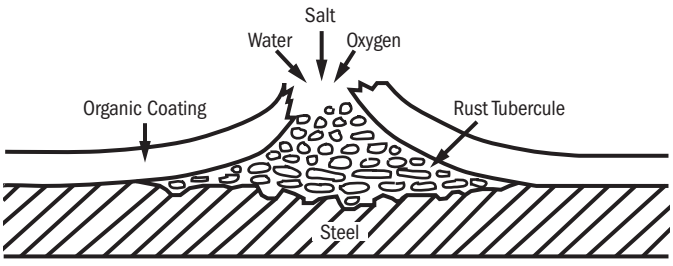


Figure 3.12: Undercutting.

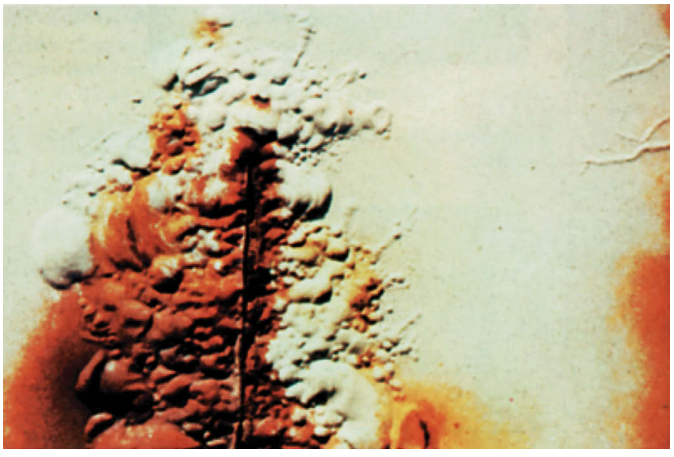


Figure 3.13: Undercutting of an organic coating in a marine atmosphere with filiform corrosion starting at the right edge of the panel.

almost any industrial or marine structure. Edges are particularly prone to this type of coating failure since the coating is usually thinner at this point. In fact, extreme cases of undercutting have been observed where the corrosion extended under the coating several feet from the original break.

Part of this bond is physical, but the remainder has to do with compatibility and the ability of the coating to thoroughly wet the substrate surface. Figure 3.13 shows the results of corrosion starting at a scribe and undercutting an organic coating that otherwise had good resistance to a marine atmosphere.

As compared to many organic coatings, inorganic zinc (IOZ), galvanizing, or even ceramic coatings have a chemical bond in addition to a physical bond between the coating and the steel. This combined bond is much more durable and is not subject to undercutting because of corrosion at breaks in the coatings. The fact that the IOZ coatings have a chemical bond and do not undercut is one of the reasons for their excellent corrosion resistance. Thus, they are often used as a permanent primer over which organic coatings can be applied. Epoxies are often chosen for priming over IOZ due to their excellent adhesion and undercutting resistant properties.

Abrasion Resistance

Coatings that are applied to ships, helicopter decks, barges, offshore platforms, and other similar areas are excellent examples of why many corrosion-resistant coatings also require abrasion resistance. In these areas, coatings are subject to the movement of heavy equipment, foot traffic, possible wheel traffic, and damage by tools and equipment. In order to withstand this type of service and remain effective as a corrosion-resistant film, a coating must be tough, extremely adhesive, hard, and resistant to shock.

Another type of abrasion is the result of sand, which is windblown or carried in waves. In this case, the coating is scoured and worn through to the substrate. Sand abrasion occurs most often where waves impact sheet piling close to the sand surface. It has also been observed that when ship bottoms periodically touch river sand bars, their bottom coating is often scoured to the base metal. The scouring, in some cases, is so even and uniform that at the interface between the abraded coating area and the steel, each coat is easily visible.

Organic coatings, which range from soft and rubbery to very hard durable ones, have a wide span of abrasion resistance. Hardness, however, is not a measure of abrasion resistance. Abrasion-resistant organic polyurethane coatings, particularly the elastomeric versions, have good resistance to impact, scouring, and abrasion. IOZ coatings, however, because of their good adhesion to the steel surface and because of their silicate and zinc composition, have proven outstanding when applied on the decks of barges and ships and on the boot-topping of ships.

Ability to Expand and Contract

Each coating material has a different coefficient of expansion. Any coating that is to withstand corrosive conditions must also have the property of expanding and contracting with the substrate. Thermoplastic coatings, in general, have little difficulty in this area. Inasmuch as thermoplastic coatings are temperature sensitive, the warmer they get, the more plastic they become and the easier they follow the expansion and contraction of the underlying surface. Since they generally also have good adhesion, the combination of the two properties allows them to withstand most normal expansion and contraction without difficulty.

Thermosetting or cross-linked coatings, such as epoxies or even alkyds, may, after some considerable aging, become brittle and cease to expand and contract with the substrate. This can lead to cracking and spalling from the surface because of the temperature cycling. This reaction is more pronounced when a coating is applied in excessively thick films.

Temperature cycling need not be merely from a reaction vessel that heats and cools, but more normally is the result of change in the temperature of surfaces subject to direct sunlight. Dark coatings on a steel surface can rise to a temperature of 65 °C (150 °F) in daylight and drop to as low as freezing at night under certain conditions. A proper corrosion-resistant coating must withstand such temperature changes without loss of adhesion and without checking or cracking. IOZ coatings have proven to have exceptional resistance to such changes in temperature.

Weather Resistance

Temperature cycling is also a part of weather resistance. Corrosion-resistant coatings should be thoroughly weather-resistant since many of the surfaces that require corrosion protection are located in unprotected, weather-exposed areas. Weather resistance requires the combination of a series of very different properties. A weather-resistant protective coating must withstand the sun's rays, rain, snow, hail, dew, freezing and thawing, expansion and contraction of the substrate, chemical fumes, dusts and particulate fallout, as well as continuing wet and dry cycling—usually on a daily basis. Weather resistance combines into one property, almost all of the properties required of a coating for other more specific uses. To be weather-resistant, a coating must resist the above conditions without excessive chalking, checking, cracking, flaking, blistering, loss of adhesion, or substantial color or appearance change for a sufficient number of years to be economical.



Figure 3.14: A platform in service 14 years in the Gulf of Mexico coated with IOZ and an epoxy polyamide topcoat.

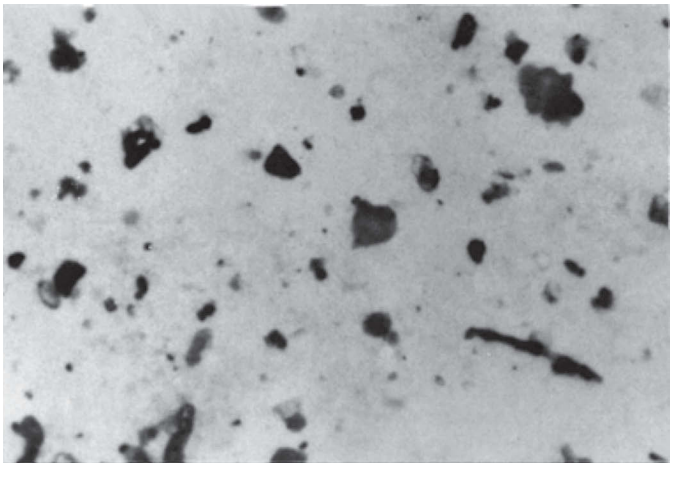


Figure 3.15: Dirt particles imbedded in paint film, original magnification 100X. Source: "Pictorial Standard of Coating Defects, Mildew Resistance," Federation of Societies for Paint Technology, Philadelphia, PA, 1979.

A small support structure for an offshore well, which is one of the most weather-affected structures in the world, is shown in Figure 3.14. It is located in a severe marine atmosphere and therefore subject to all of the above conditions. Coated with an IOZ primer and an epoxy polyamide high-visibility topcoat, it remained in good condition after 14 years of exposure.

Resistance to Dirt Pickup

Dirt pickup is a property that concerns appearance more than anything else. Each coating is distinct in this regard. Some coatings will tend to pick up dirt and grime from the atmosphere and hold it very tightly on their surface. Others will tend to be unaffected by dirt and grime, with the result that their surfaces stay bright and clean, except for extremely dirty conditions. Dirt pickup is undesirable from a corrosion standpoint as well. Where dirt accumulates, so do corrosive deposits such as chlorides, sulfates, fly ash, and similar materials that create a good electrolyte and, therefore, a favorable atmosphere for corrosion. Normally high-gloss coatings resist dirt pickup better than semi-gloss or flat coatings until such time as normal weathering or chalking reduces the glazed finish, thus making dirt pickup more likely, as shown in Figure 3.15.

Resistance to Bacteria and Fungus

There are two ways in which bacteria and fungus can affect a coating. First, where they settle on any dirt that has accumulated on the surface of a coating, they tend to live and thrive. This increases dirt buildup and dramatically detracts from the appearance of the coating. They also attack the coating itself and form colonies or areas that not only become unsightly, but which may actually be penetrated by corrosive conditions. Almost everyone is familiar with the dark, blotchy fungus growth on some coatings, particularly on the shady side of a structure (Figures 3.16 and 3.17). These fungus colonies are living on one or more of the coating ingredients and this can eventually lead to premature coating breakdown. The susceptibility of coatings to such biologic activity can often be offset by the addition of bactericides and fungicides to the coating itself during manufacture. Coatings that do not contain any oils or hydrocarbon by-products in their film structure are generally more resistant to bacteria and fungus growth (for example, waterborne latex/acrylics). Under some conditions, catastrophic coating failures can occur because of biologic activity. One such failure occurred when a polyamide coating was applied to a concrete sewer manhole. Polyamide epoxies have good resistance to water and good adhesion to concrete. In this case, however, the coating became mush within nine months to a year due to bacterial action. An amine-cured epoxy, however, was unaffected by the same atmosphere. The difference is that the polyamide part of the molecule is vulnerable to biologic attack (it becomes a food source for the bacteria), therefore making polyamide coatings unsatisfactory for sewer conditions.

Underground conditions can also lead to coating breakdown due to bacteria attack. If a coating contains organic sulfides, they are often subject to breakdown by anaerobic soil bacteria (sulfate-reducing bacteria [SRB]). Sulfur cements were used to join sewer pipe until it was discovered that sulfur-active bacteria used the cements for food with the development of additional quantities of hydrogen sulfide (H_2S) gas. These bacteria can also cause metal corrosion by any or all of the following:

1. Creating differential electrolyte concentration cells on the metal surface;
2. Creating a corrosive environment due to their life cycle and decomposition products;
3. Acting as either anode or cathode depolarizers; and
4. Generating sulfides, which react directly with the metal to form metal sulfides.

Extensive testing was done in this area during World War II to develop coatings that could be used in tropical climates where biologic activity created some serious problems. It was found that coatings for use in any area suspected of fungus or bacterial growth should be formulated with resins, pigments, plasticizers, and so on, which in themselves cannot be used by biologic organisms for food. For the more severe conditions, it is not enough to rely on bactericides and fungicides.

Pleasing Appearance

The earlier-mentioned characteristics of weather resistance, dirt retention, and biologic action all contribute to a coating's appearance. Although a coating is primarily used to prevent corrosion and protect the basic structure, it should also be pleasing to the eye and maintain its color, especially since appearance is, in fact, one of the most obvious properties of a coating, whether it is applied to an automobile, tank, ship, or pipe. If a coating does not serve its purpose of creating a pleasing appearance, it can only be used in seldom seen, unexposed areas, even though its other properties may justify a much broader use. Thus, if it does not look good, it is considered a poor coating in the eyes of the person who must use it.

Age Resistance

To feasibly provide corrosion resistance, a coating must provide protection for a reasonable period of time. If it does not have a sufficient lifespan to be a sound economic investment, the coating is not worthwhile. Corrosion-resistant coatings should therefore have the ability to maintain protection effectively over a period of many years under widely differing corrosion conditions. If the coating is defective in even one property, however, such as weather or abrasion resistance, it may not be able to do so. Thus, in order to be age-resistant, all of the properties previously described must be optimally applied.

Easy Application

Application is one of the most important coating characteristics, especially when dealing with intricate structures with many corners, edges, recesses, and similar areas. If a coating is somewhat difficult to apply, these are the areas that suffer and break down first in a corrosive atmosphere. Most structures, tanks, and offshore platforms are reasonably difficult to coat, even under the best conditions. There are many welds, corners, and edges, which are focal points for corrosion, so that if the application is not easily and properly accomplished, the corrosion resistance of the coating suffers.

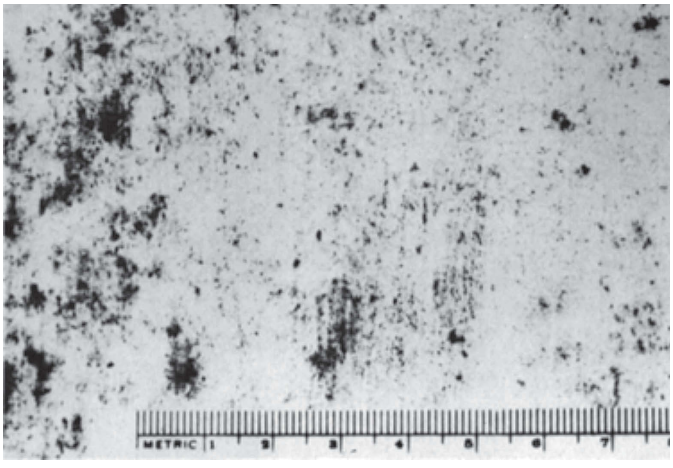


Figure 3.16: Typical appearance of a coating susceptible to fungus attack. The fungus feeds on ingredients in the paint film. Source: "Pictorial Standard of Coating Defects, Mildew Resistance" (Philadelphia, PA: Federation of Societies for Paint Technology, 1979).

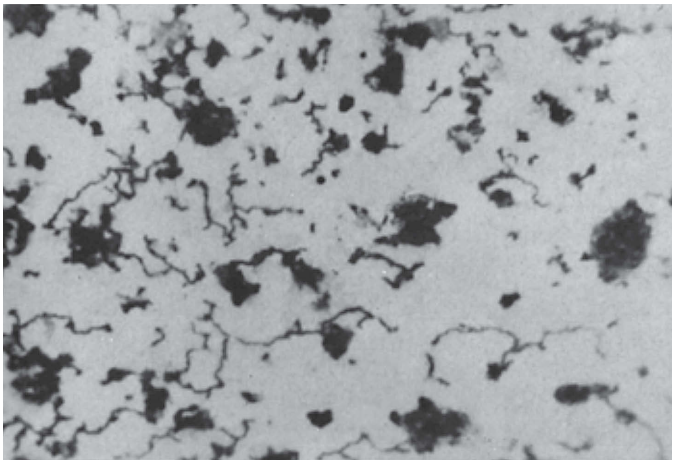


Figure 3.17: Mildew on a coating, original magnification 50X. Source: "Pictorial Standard of Coating Defects, Mildew Resistance" (Philadelphia, PA: Federation of Societies for Coating Technology, 1979).

Additional Coating Properties

Resistance to Extreme Temperatures

For the most part, any corrosion-resistant coating should have the majority of the properties already described in this chapter. Some coatings, however, are used for specific purposes that may necessitate unique requirements. The following are some additional properties that fall into this more specific coating use category.

While all coatings are subject to temperature and some temperature cycling, these conditions are generally moderate. Temperature, however, can be a key factor in coatings used for stacks, pipes, the exterior of process vessels, and for other similar uses. Where coatings are used for excessively cold temperatures (below those that would be found in normal atmospheric conditions), the three general characteristics to be considered are adhesion, shrinkage, and brittleness.

Adhesion is liable to deteriorate under excessively cold conditions, particularly when the cold varies from normal down to very cold temperatures. Brittleness is closely affected by adhesion. When organic compounds are exposed to excessive cold, they tend to become more brittle and may shatter on impact or because of loss of adhesion.

Shrinkage is also a factor that can affect both adhesion and brittleness. There may be adhesion problems where a coating shrinks to a greater extent than the underlying surface. Thus, with impact or abrasion, the coating can shatter from the surface.

In order for a coating to withstand excessive cold, it should have excellent adhesion. The coating should also be somewhat resilient and retain its plasticity in cold temperatures. Coatings with this characteristic generally do not have shrinkage problems since they follow the expansion and contraction of the underlying surface. Butyl rubber and polyisobutylene polymers aid in the retention of cold weather adhesion.

Cold or heat can also change the corrosion characteristics of various atmospheres. The rate of chemical reaction, or rates of corrosion reaction, change dramatically as temperatures rise and fall. Epoxy resins that cure well at 20 °C (70 °F), cure very slowly at 5 °C (40 °F). If temperatures are 38 °C (100 °F), some epoxy coatings have been known to react so fast that application was impossible without keeping the mixed (catalyzed) coating in iced containers. Soils also show a marked change in resistance due to temperature changes, thus causing a change in the corrosion rate. Figure 3.18 indicates the rapid increase in soil resistance as the temperature drops below freezing. (As soil resistance increases, the corrosion rate drops.)

High temperatures create additional problems. There are a number of things that happen to coatings at high temperatures or cyclic high temperatures. Chloride-containing polymers, such as vinyl chloride and chlorinated rubber, tend to break down over a period of

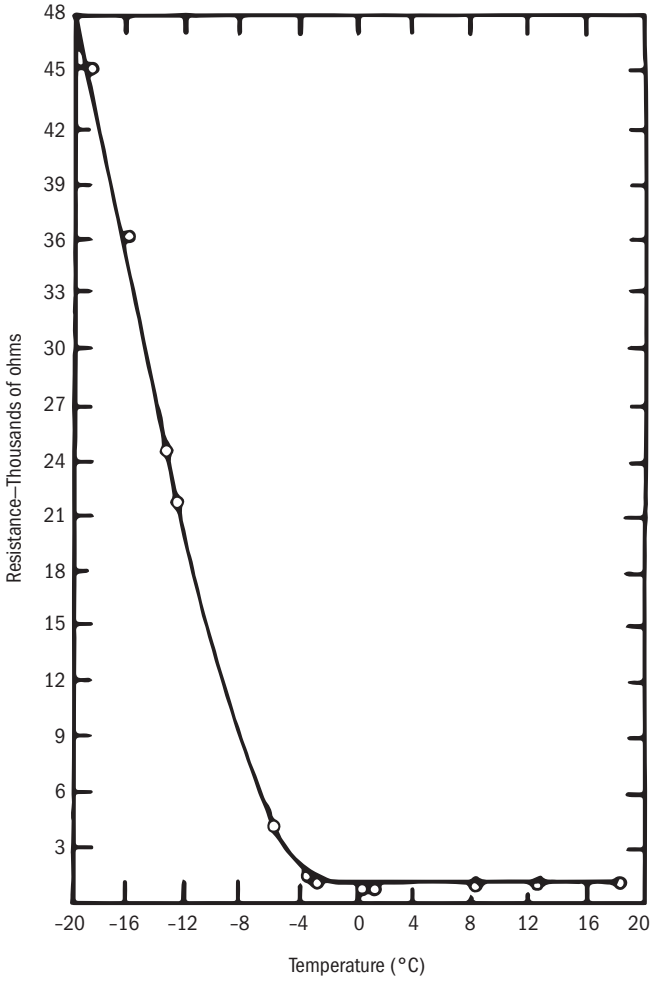


Figure 3.18: Changes in soil resistance due to temperature. Source: U.S. Dept. of Commerce, *Civil Engineering Corrosion Control, Corrosion Control—General,* Vol. 1, Distributed by NTIS, AD/A-004082 (1975), p. 30.

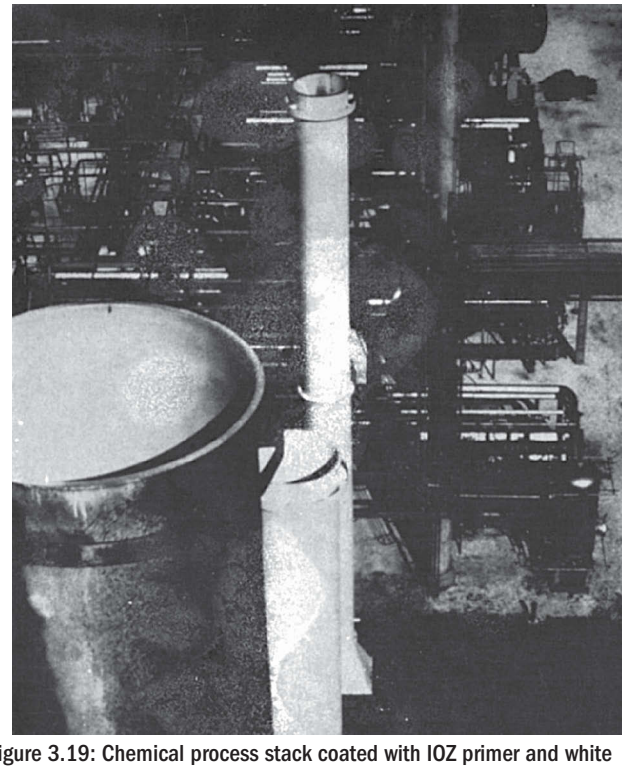


Figure 3.19: Chemical process stack coated with IOZ primer and white inorganic topcoat after several years operation at high temperatures.

time (depending on the temperature), releasing HCl, which can severely aggravate a corrosive condition. There are other polymers that do not contain a chloride atom in the molecule that may tend to depolymerize and even appear to evaporate from the surface. Some styrene polymers exhibit this characteristic. Other cross-linking polymers, such as epoxies, can over cure at temperatures in excess of that recommended by the manufacturer and become very brittle, shrink, and lose adhesion.

The IOZ compounds are quite stable to temperatures in the area of 370 °C (700 °F) and have been used continuously at such temperatures quite effectively. Silicone polymers also have excellent heat resistance in the same temperature range. For relatively short time exposures (e.g., days or weeks, but not continuously), inorganic coatings coated with silicone aluminum topcoats have been exposed to 520 °C (968 °F) and have maintained their effective coating characteristics. Some non-zinc coatings have also shown good resistance to higher temperatures and alternate high and low temperatures (Figure 3.19). Some newer polysiloxane coatings pigmented with inorganic pigments have shown selected temperature resistance up to approximately 2,000 °F (1,079 °C).

Table 3.2 gives some of the common coating types and their comparative temperature resistance. Depending on its formulation, each coating type may vary considerably either up or down in its temperature characteristics. (These figures are essentially for comparison between the coating types and are not to be considered for the specific coating.)

Radiation Resistance

With the advent of atomic energy and atomic power, coatings have been used extensively for protection against the radioactive contamination of various substrates including steel, concrete, stainless steels, and so on. In order to be effectively used on such installations, coatings must be able to withstand varying amounts of radiation. Some coatings harden, become very brittle, shrink, and crack under heavy doses of radiation; others will tend to depolymerize and become sticky and soft; while still others blister and lose adhesion. Such coatings obviously are not suitable for use under these conditions.

Many coatings have been tested under high-density radiation sources. Table 3.3 shows the comparative radiation tolerance of the principal corrosion-resistant coatings. The inorganic coatings are apparently unaffected by radiation as they show no change after high exposure. Organic coatings, however, appear to be more stable and more resistant if they are strongly cross-linked. The thermoset coatings appear more radiation-resistant than those that are thermoplastic.

Resistance to Soil Stress

Soil stress is particularly important in connection with underground pipeline coatings. The pipe expands and contracts due to changes in temperature, as well as to the swelling and contraction of the soil as the water content varies. This is particularly a problem in high clay soils, which expand to a great degree when damp and shrink an equal amount when dry. Clay soils move substantially, which is evident by the large cracks that form as the soil dries out. This cyclic action tends to pull the coating away from the pipe or structure, creating cracks, voids, or thin spots.

Coatings are often damaged due to poor backfill procedures, which allow rock or clods to impact the pipe. Nonuniform backfill pressure caused by clods or rocks, whether in the soil or in the backfill, can cause breaks in the coating. Rocks may be round, irregular, or broken with sharp points or edges. The weight of the pipe and the weight of the backfill can cause coating breaks at the points of highest pressure. Roots are also known to ei-

Table 3.2: Comparison of Temperature Characteristics for Some Corrosion Resistant Coating Types

Coating	Immersion °C (°F)	Non-Immersion °C (°F)
Vinyl Copolymer	38 (100)	65 (150)
Chlorinated Rubber	38 (100)	65 (150)
Coal Tar	50 (122)	65 (150)
Coal Tar Epoxy	50 (122)	95 (203)
Epoxy	50 (122)	95 (203)
Urethane	38 (100)	120 (250)
Epoxy Phenolic	82 (180)	120 (250)
Baked Phenolic	82 (180)	120 (250)
Inorganic Zinc	–	370 (698)
Silicone	–	370 (698)

ther penetrate the coating or to surround the pipe and grow to such an extent that they create sufficient pressure to cause the coating to flow, creating thin spots. Roots surrounding plastic pipe have been known to crush the pipe after a period of time. Coatings used under soil stress conditions must therefore have strong adhesion, high impact resistance, a low tendency to creep or move under pressure, and the ability to resist the abrasion of soil movement.

Resistance to Cathodic Disbonding

Cathodic disbonding is a type of failure characteristic of CP. In many ways, it is related to electroendosmosis. The coating must resist the electrical potentials used under CP. Most coatings will withstand cathodic potentials of approximately –1.0 V, with an optimum potential of –0.85 V. Potentials of –1.1 V and above can create conditions for cathodic disbonding, depending on the coating, its thickness, dielectric strength, water resistance, and other factors. The coating must have a low moisture vapor transfer rate and very high adhesion to help resist cathodic currents. Coal tar epoxies have good resistance to cathodic disbonding, as do many of the heavier pipe coatings, which use butyl rubber as a bond coat. Advanced versions of 100% solids epoxy coatings have shown very good resistance to cathodic disbondment as have some specially formulated 100% solids polyurethanes, polyureas, and polyurethane/polyurea hybrids. Figure 3.20 shows a coating that disbonded due to excessive cathodic current. Large blisters, at times many inches across, are the usual indication of cathodic disbonding.

Friction Resistance

Some coatings are subject to friction, particularly when they are used as faying surfaces where two sections of metal are riveted or bolted together to form a friction joint. Inorganic coatings have proven to be very satisfactory under such conditions, while most organic coatings are unsatisfactory. Table 3.4 shows the comparative friction coefficient of various surfaces.

Types of Exposure

There are three essential types of exposure that corrosion-resistant coatings and linings are subjected to: atmospheric exposure, immersion, and underground exposure. Each of these has a different priority from the standpoint of the coating characteristics described previously.

Atmospheric

The obvious major difference between atmospheric exposure, immersion, and underground use is that of weather resistance.

Table 3.3: Radiation Tolerance of Corrosion-Resistant Coatings

	Maximum Allowable Radiation Dose in Air	
Coating	On Steel (Rads[A])	On Concrete (Rads)
Chlorinated Rubber	1×10^8	1×10^8
Epoxy Amine	1×10^9	1×10^9
Epoxy Coal Tar	5 x 10	5×10^8
Epoxy Polyamide	1×10^{10}	NA
Inorganic Silicate Finish	1×10^{10}	1×10^{10}
Inorganic Zinc	2.2×10^{10}	NA
Epoxy Phenolic	1×10^{10}	1×10^{10}
Silicone (Baked)	1×10^{10}	NA
Urethane	5×10^8	6×10^9
Vinyl	1×10^8	–

[A]Rad: The unit of absorbed radiation. For most organic material one roentgen = 1 Rad (ANSI N 5.12, 1973).
Severe Exposure = Greater than 4.5×10^9 Rads
Moderate Exposure = 5×10^8 to 4.5×10^9 Rads
Light Exposure = Less than 5×10^8 Rads
Source: Kirk-Othmer *Encyclopedia of Chemical Technology,* C.G. Munger, "Coatings Resistant," Vol. 6 (JNew York, NY: John Wiley & Sons, 1979).



Figure 3.20: Cathodic disbonding of a coating under excessive CP potentials (1.2 V in seawater). Note white deposits on un-perforated blisters.

Table 3.4: Coefficient of Friction of Various Surfaces When Used as a Faying Surface

Surface Condition	Coefficient of Friction
Solvent-based IOZ	0.52
Rusted and wire brushed	0.51
Water-based IOZ	0.48
Rusted	0.48
Sandblasted	0.47
Mill scale	0.30
Galvanized	0.25
Rust prevention paint	0.11
Red lead paint	0.06

Note: A coefficient of friction less than that of sandblasted steel is not recommended for riveted or bolted joints.

Coatings that are immersed or designed for underground applications are not usually exposed to weathering conditions. On the other hand, weather resistance is the major consideration from the standpoint of atmospheric exposure. A coating under atmospheric exposure must withstand a multitude of conditions that include ultraviolet attack, actinic radiation, heating and cooling, maximum exposure to oxidation, fallout from airborne chemicals, and alternate wetting and drying, in addition to the more basic requirements of strong adhesion, low moisture vapor transfer rate, the need for some inhibitive properties to reduce corrosion and undercutting at damaged areas, general chemical resistance, and the requirement to maintain a good appearance.

Atmospheric coatings are usually relatively thin films, which makes the retention of the above properties and the general aging of the coating extremely important. The conditions of exposure for an atmospheric coating are extremely broad, ranging from coatings used in very hot, dry atmospheres and those used under tropical conditions to those that are used essentially in cool or cold climates.

Because of their use in such a very broad range of conditions, atmospheric coatings require careful development and formulation, as well as application, in order to obtain the corrosion resistance needed. Good examples of this are the coatings for automobiles, which undoubtedly are the most highly engineered coatings in present use. They are required to maintain their appearance and prevent corrosion to the underlying surface for many years when exposed to all types of atmospheric conditions, temperatures, humidity, and chemicals. Their application is controlled to a much higher degree than that of almost any other coating. The surface is very thoroughly prepared, and is pretreated so that the highest degree of adhesion is obtained with a minimum of undercutting due to road damage. They are undoubtedly the finest coatings made for use under the broadest conceivable atmospheric conditions.

There are other coatings that are more effective under more specific atmospheric conditions, such as in marine atmospheres (e.g., ship hulls and barge decks) or in industry where the coatings are exposed to chemical fumes, splash, or spillage.

Immersion

Immersion coatings, as compared with atmospheric coatings, are primarily subject to water solutions ranging from very pure water to ones containing high concentrations of various chemicals. Examples range from snow water or deionized water used in various industries, to seawater and on to higher concentrations of various materials such as acids, alkalies, and salts, or organic solutions such as sugars or glycols. There are, of course, specific immersion situations, such as the lining of petroleum and solvent tanks, where water solutions are not encountered. Water, however, is the key factor in most immersion conditions, since the effect of water on most coating materials can be quite severe.

The primary coating requirements for immersion, then, are adherence and resistance to moisture vapor transfer, ionic penetration, osmosis, chemicals, cathodic disbondment, and varying temperatures. Immersion coatings, for the most part, do not require any specific weather resistance since, once under the surface of a liquid or water, solar radiation, air oxidation, and similar conditions do not apply. They are, however, subject to continuous contact with water and/or various chemicals, either alone or dissolved in the water. This means that water absorption, the absorption of various ions, and the passage of moisture through the coating are all at their maximum driving force and the coating must be designed to withstand these immersion forces.

Snow water, distilled water, or deionized water are close to, if not the most penetrating of all of the chemicals in which a coating is immersed. On the other hand, as the salt content of water is increased, it becomes more aggressive from other standpoints. It is more conductive and therefore corrosion can take place at a rapid rate. It is generally conceded that seawater is more aggressive than pure synthetic seawater. Polluted fresh water is more aggressive than pure fresh water and can be more destructive to some coatings than seawater.

Corrosion engineers must be prepared to determine which coatings are best under the particular conditions that exist. As an example, coal tar epoxy coatings are very effective under many water conditions, including contaminated water. On the other hand, they are not satisfactory for potable water because of possible taste and odor contamination. IOZ coatings can be used for continuous exposure to refined oil and various solvents, while they are not particularly satisfactory for immersion in water or seawater without topcoats. Polyamide epoxies have excellent water permeation resistance and are widely used in potable water tanks. Certain epoxy coatings have good resistance to many organic chemicals, and yet are not satisfactory for many dilute acid solutions.

Thus, wherever a coating is to be used under immersion conditions, the conditions should be precisely determined prior to the selection of any coating. Solutions with minor contaminants, which were scarce enough to be deemed unimportant, have caused many coating failures under immersion conditions. A good example is minor quantities of naphthenic acid in diesel oil (acid value of more than 0.5). IOZ coatings exposed to such conditions react rapidly with the naphthenic acid, forming zinc naphthenate, which contaminates the diesel fuel.

Underground

The coating requirements for underground conditions are quite similar to those for immersion: adhesion, moisture vapor transfer, resistance to ionic passage, and resistance to osmosis. Underground conditions are in many ways similar to immersion, or actually can be immersion conditions where a pipe is subjected to submarine conditions or to high groundwater tables. Groundwater, then, is the key element to be protected against in underground conditions. Coatings must have an extremely high water resistance and resistance to moisture vapor transfer in order to be effective. On the other hand, other factors such as soil stresses come into play and can be extremely damaging. Biologic damage also can exist here, due to the activity of SRB or various fungus conditions.

TABLE 3.5: Comparison of Coating Characteristic Required for Atmospheric, Immersion, and Underground Exposure

Coating Characteristic	Atmospheric	Immersion	Underground
Weather resistance	1	–	–
Water resistance			
M.V.T. rate	5	2	2
Adsorption	–	–	–
Osmosis	–	3	–
Ionic passage	6	4	3
Electroendosmosis	–	3	4
Adherence	2	1	1
Undercutting	4	–	–
Inhibition	3	–	–
Temperature resistance	–	8	–
Temperature cycling	7	–	–
Thermal gradient	–	–	–
Chemical resistance	9	6	9
Dielectric strength	–	5	5
Cathodic disbondment	–	5	5
Biological damage	–	–	8
Thickness	–	9	10
Resistance to soil stress	–	–	7
Radiation resistance	–	–	–
Abrasion	–	–	–
Appearance	8	–	–
Dirt pick up	–	–	–
Age resistance	10	10	–
Easy application	–	–	–
Easy repair	–	–	–

NOTE: "1" indicates best resistance required; "10" indicates comparatively lesser resistance is needed. Characteristics without numbers may be critical under special conditions

Coating thicknesses, however, are probably more important underground than in either of the other two coating exposures. Pipes or structures underground are subject to varying backfill conditions, varying soil movement, and expansion and contraction due to more or less moisture in the soil. Soil forces can be strong enough to actually pull the coating from the surface of the metal, which then cracks it and allows other external forces to react on the metal itself. Both cathodic disbonding and electroendosmosis are factors contributing to underground coating failure. High dielectric strength is also a requirement. Thickness is important since rock points and damage during backfill are quite common. Thickness also helps contribute to moisture impermeability as well as to the impermeability of various soil chemicals.

In general, many coatings applied to pipe and underground structures are thicker than atmospheric coatings or linings. Many pipes have an extruded plastic coating, which may vary from 50 to 250 mils (1,250 to 6,250 μm) in thickness. Pipe wraps of various types using hot-melt coatings are commonly used to build a reinforced laminated coating over pipe surfaces. Thin coatings are generally less satisfactory and less durable underground than the heavier built-up coatings or those that are extruded over the exterior of the pipe. Fusion-bonded epoxy coatings of medium film build have served very well on underground pipelines through many different soil ranges.

Again, it needs to be stressed that the corrosion engineer must understand the soil conditions under which the coating must operate in order to be able to select the best coating for the job. Many factors have to be taken into consideration. For example, a coal tar epoxy was applied to an underground pipe that was alternately subjected to steam and cooling water. The soil was soft, sandy loam containing

some, but not excessive, moisture and no particular chemicals. The coal tar epoxy coating was considered a good selection inasmuch as the temperature involved was too high for coal tar or asphalt coatings. After a short period of cycling between steam temperatures and cooling water, the pipe was perforated from the exterior because of the disintegration of the coal tar epoxy due to the cycling temperature conditions.

All conditions must be taken into consideration, even the minor ones, when selecting a coating for either atmospheric, immersion, or underground exposure since no two coating jobs are ever the same, even though the conditions may seem to be the same. Table 3.5 lists the various coating characteristics that have been described and rates from 1 to 10 (the most to the least important) the characteristics that are most important for atmospheric, immersion, and underground conditions. There are a number of coating characteristics that are not numerically identified for any of the conditions, but which may be important where specific conditions are encountered.

When the corrosion engineer intends to build or bury a structure for long service life, one that will be relatively stable and free of excessive maintenance, there are certain basic fundamentals to consider. A selection of the coating type best suited for the task to be performed must be made to also meet the design requirements of operation and maintenance.

In a paper on "Coating Fundamentals,"[1] Bellassai listed these fundamental considerations:

1. The type of environment in which the structure will be buried or submerged.
2. The characteristics of the environment as to the texture, uniformity, varying degree of moisture, or soil shrink factor.
3. Operating temperature ranges.
4. The nature of the product carried in the pipeline.
5. Can quality of backfill be controlled?
6. Use of CP and possible range of current potentials.
7. Method of application, whether in the plant or in the field.
8. The degree of handling to which the coated structure will be subjected prior to final resting location, such as loading, unloading, bending, and so forth.
9. The experience with similar materials in this environment or on paralleling structures.[1]

All of the above factors must be considered since each represents a force of deterioration that, by itself or in conjunction with any of the others, will result in the degradation of the coating system. While this list is designated for pipe, the principles are relevant for the selection of any coating application.

Measurable Coating Characteristics

For every coating material there are individual, measurable coating characteristics that are important in identifying the coating. They are: (1) specific gravity (weight per gallon); (2) total nonvolatile measured by weight; (3) total nonvolatile measured by volume; (4) viscosity; (5) fineness of grind; (6) color; and (7) solvent tolerance. These seven characteristics serve to identify the liquid coating material and indicate certain quantitative data in connection with its use. Such characteristics are determined directly on the liquid.

With the advent of government regulations on emissions of organic volatiles into the atmosphere, an additional characteristic is now seen on manufacturers' product data sheets—volatile organic compounds (VOC). VOC refers to that portion of the liquid coating that evaporates into the atmosphere during drying and curing. It is generally stated in lb/gal or g/L.

Specific gravity, or the weight per gallon, generally indicates something of the material ingredients used in the coating. A high solid coating will, for example, generally weigh more than one that is very high in solvent, and a coating that contains red lead will weigh more than one that contains carbon black.

The nonvolatile by volume figure indicates how much of the coating must be used to develop the required film thickness over a given area. Nonvolatile by volume data is useful in determining the wet film thickness required to develop a specified dry film thickness.

A total nonvolatile by weight provides a measure of the solids in the coating compared to the amount of solvent in the coating. The coating with a total nonvolatile by weight of 50% means that it would have 50% resin and pigment by weight and 50% volatile solvents by weight.

The fineness of grind indicates the degree of dispersion of the pigment in the vehicle and provides some determination as to the appearance of the coating. A coating with a very fine grind may be a high gloss or a very smooth semi-gloss finish.

The viscosity indicates the type of applications that are possible. Viscosity is generally expressed in two ways: (1) in seconds, which is the time required for a measured amount of the coating to flow through a measured orifice (this equipment is generally used for the lower viscosity coating materials such as the ones suitable for air spray); and (2) in Krebs unit, where the viscosity is determined by a one-point rotational viscosity meter. (Krebs Stormer: the viscosity is ordinarily expressed as KU value, which means Krebs units. This equipment is used for higher viscosity materials, generally those used for brushing or for airless spray. KU values in the range of 75 to 95 KU indicate brushing or spraying viscosity, and KU values in the range of 95 to 100 KU indicate a coating that may be intended for high build use.)

There are also some other terms that relate to viscosity. The first of these describes a material that retains the same viscosity no matter how rapidly it may be stirred. This is referred to as a Newtonian solution, and coatings of this type are generally the low-build, easy flowing type. The second term describes a material that appears to be very heavy when stationary, but when stirred or agitated, decreases in viscosity and is quite liquid, although it becomes heavy in consistency when the stirring or mixing is stopped. This is known as a thixotropic material. Thixotropic materials are low in viscosity as they pass through the head of the spray gun. However, as soon as the shear action of the spray equipment is finished, they again increase in apparent viscosity after being deposited on the surface. This allows the coating to remain on the surface in relatively high volume without drips or sags.

Solvent tolerance indicates a type of solvent that may be added to the coating as a thinner or type of solvent used for cleanup. Using improper solvent for thinning can be extremely damaging. As an example, vinyl coatings will tolerate some mineral spirits in the liquid form; however, once they are applied, the active solvents evaporate from the vinyl coating and leave the mineral spirits behind. These mineral spirits are gradually squeezed out and accumulate underneath the coating, leaving the coating without any adhesion whatsoever. There are many instances where this type of failure resulted when proper thinning instructions were not followed. There are equally as many instances where the use of MEK (methyl ethyl ketone) as a solvent in alkyd coatings actually degrades the resin to the point that it yellows quickly and becomes quite brittle.

In terms of color, it is essential when coating large structures to make sure that all containers of liquid coating are from the same batch. If they are not, spot checks should be made to ensure that the color is consistent.

There are also inherent coating characteristics that are not apparent in the liquid coating, but are measurable only after the coating is applied. These characteristics include gloss, drying time, time to tack-free, time to touch, time to recoat, and hardness. These are generally different for each coating material being used, and each may be an important consideration in the selection of a coating.

Whenever a protective coating is being considered as a means of dealing with a corrosion problem, the first step to be taken involves determining the desired coating characteristics. Without first analyzing the specific, essential coating requirements, improper materials may be selected that could result in costly failures.

Reference

1 S.J. Bellassai, "Coating Fundamentals," *MP* 11, 12 (1972).

4 Coating Fundamentals

The fundamentals of a coating could refer to several things, depending on the purpose or the use of the coating. For example, an antifouling paint would have the fundamental property of inhibiting the growth of animal or vegetable organisms on the coating. A fire-resistant coating must fundamentally resist burning, or at least retard the burning of the substrate. A coating to be applied over concrete must have a fundamental property of resistance to strong alkali.

All corrosion-resistant coatings, however, must fundamentally resist the corrosive atmosphere and prevent it from reaching the basic structure. Thus, there are as many variations in the types of coatings as there are in the forms of corrosion. The design of an effective anticorrosive coating is a complex task, which requires an extensive knowledge of not only corrosion principles but of the science and chemistry of coating formation as well. Without such inclusive information, the development of effective corrosion-resistant coatings would be impossible.

A coating is not a self-supporting structure. It is part of an overall system, which includes the basic structure that supports the coating. Although it is always on a substrate of one kind or another, a coating can be thought of in the same light as a building. In order to be strong, a building must have a heavy, carefully constructed foundation; in order to be durable, a coating must also have a carefully designed (formulated) and constructed (applied) foundation (substrate and primer). A building also consists of a number of interlocking parts—the foundation, the superstructure, and the roof—and each one has a different function. The corresponding parts of a coating are the primer, intermediate coats, and topcoat.

In the case of a small building with a relatively short, useful life, the foundation and superstructure may be minimal. The same is true of a coating applied only for decorative purposes where surface preparation, application, and long life may be easily overlooked. In the instance of a substantial industrial structure, however, durability, reliability, and long life are required. Again, the same holds true for an industrial corrosion-resistant coating, which likewise must be engineered with a properly prepared substrate, a sound foundation coat or primer, a strongly reinforced intermediate coat, and long-lasting weather and corrosion-resistant topcoats. In constructing a building, the substrate (the soil or ground) indicates the type and extent of the foundation since sand, clay, or rock all have different foundation requirements. The same, of course, is true of coatings. The primer must be designed specifically for the substrate, whether it is steel, aluminum, concrete, plastic, or wood. In fact, the surface over which a coating is applied may be more important from the standpoint of long life and durability than the design of the coating itself.

The fundamental concepts involved in corrosion-resistant coatings, then, include those of coating protection, component design, component function, and coating formulation. Many coatings contain as many as 15 to 20 ingredients, each of which has its own function in the overall performance of the coating.

A coating system may employ one or more of the basic coating concepts of impermeability, inhibition, and anodic or cathodic pigments. While many coating systems employ only one of these concepts, some of the most successful anticorrosive systems combine two of the concepts into one coating system.

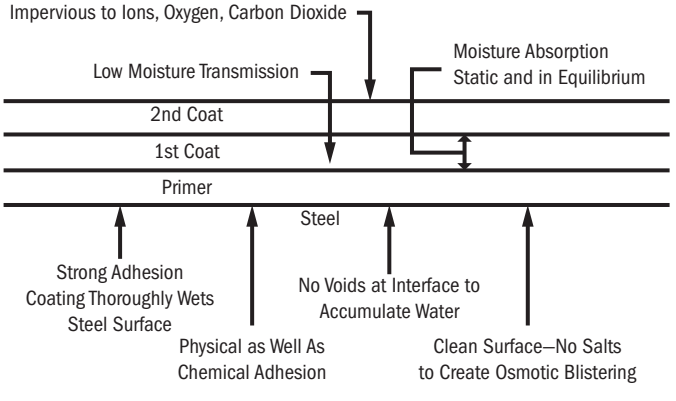


FIGURE 4.1: An impervious coating serves as an inert barrier to protect the surface. Source: C.G. Munger, C.K. Othmer: *Encyclopedia of Chemical Technology,* "Coatings, Resistant," 3rd Ed., Vol. 6 (New York, NY:John Wiley & Sons, 1979), pp. 456–457.

Basic Coating Concepts

Impermeability

Impermeability is a concept basic to most available anticorrosive coatings. While no coating is totally impermeable to moisture vapor, an impermeable coating contains no materials that will react with moisture vapor. Each ingredient is designed to be unaffected by the moisture vapor and to only allow the vapor to accumulate within the coating to the point of normal moisture absorption content.

An impervious coating is most often used as an immersion coating and must therefore be inert to surrounding chemicals. It must also be impervious to air, oxygen, carbon dioxide (CO_2), and the passage of ions and electrons. It must be dielectric and have very high adhesion to the underlying surface, and also must wet the surface well

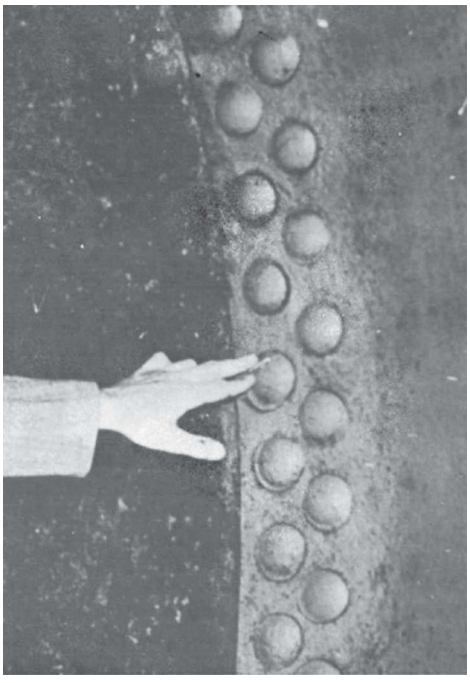


FIGURE 4.2: A vinyl coating on the interior of an electric turbine scroll case subject to continuous immersion in fast-flowing water. After five years of use, note the smooth coating without any evidence of blistering, even around the rivets.

enough to prevent any voids at the coating substrate interface. All in all, an impervious coating forms an inert barrier over the surface (Figure 4.1). This concept has been responsible for some of the most effective anticorrosive coatings available.

This type of coating prevents corrosion of steel by interrupting or providing a block to the normal processes necessary for corrosion. Coatings used for water immersion have long proven the effectiveness of this type of coating. Many hundreds of miles of steel pipe have been lined with coal tar enamel or a hot coal tar pitch applied to the interior of the pipe, usually by centrifugal means. It consists of a primer and a thick hot-melt coat of the coal tar enamel, which forms an entirely impervious coating. Many inert vinyl coatings have also been used for water immersion. Figure 4.2 shows the interior of a large scroll case that is part of a water turbine at the outlet of a dam for the generation of electricity. The scroll case is the outer portion of the hydraulic turbine, which swirls the water into the service five years, and is also fully impervious and is without any inhibitive or cathodic primer.

Inhibition

The second concept involves an inhibitor, which usually is only in the primer and consists of pigments that react with the absorbed moisture vapor within the coating. These then react with the steel surface in order to passivate it and decrease its corrosive characteristics. Inhibitive pigments are sometimes characterized as anodically active, which means that the pigments within the coating sufficiently ionize in the water vapor to react with the steel or metal substrate. This maintains that area in a passive or inactive condition.

Instead of a completely inert coating film, as with impervious coatings, the inhibitor coating uses the absorbed water in the film to aid in the passivation of the substrate (Figure 4.3).

In contrast to the coatings developed on the basis of impermeability, the inhibitive coatings are used, for the most part, in atmospheric exposures; that is, as coatings for steel or other metals that are subject to weathering but not to immersion. There are some inhibitive coatings used for immersion; however, these are few and far between compared to those used for strictly non-immersion, atmospheric purposes. This is due primarily to the inhibitive pigment's reactivity with water. Many pigments are so water sensitive that upon immersion, osmosis takes place and the inhibitive pigment solution draws so much water into the coating that blisters develop. This was one of the difficulties encountered with many of the zinc chromate inhibited marine primers used during World War II. While corrosion was generally inhibited, blistering was sufficient to limit the usability of the coating.

One of the most unique and more effective coatings was a vinyl coating developed during World War II that used the vinyl wash primer as a metal treatment. This material contained zinc chromate as well as phosphoric acid so that there was a definite reaction with the metal substrate. Intermediate coats of a special vinyl resin solution pigmented with red lead followed this primer. The red lead in the intermediate coats added to the inhibitive character of the metal treatment primer, while the final coats were primarily inert vinyl resin pigmented coatings used to provide weather resistance and color. Both the vinyl wash primer and the red lead pigmented intermediate vinyl coat have largely disappeared from use due to restrictions on heavy metals and volatile solvent emissions legislated by the federal government in the United States. Other countries around the world have also banned the use of red lead pigments, but it is still used for special purposes such as a paste form that is injected into the strands of tension cables on bridge supports that are then encased in a jacket around the cable.

Inhibitive coatings have been used in marine atmosphere applications practically as long as steel vessels have been used. These coatings were originally oil based and heavily loaded with red lead. In fact, some such coatings used today are still oil-modified. Many of the more recent coatings, however, such as the vinyl, epoxy, and urethane coatings, use an inhibitive pigment primer as a base when subject to atmospheric, marine, or industrial conditions. Figure 4.4 shows the application of a vinyl coating system to the downstream face of a large drum gate, an area subject not only to water, splash, and spray, but to weathering as well.

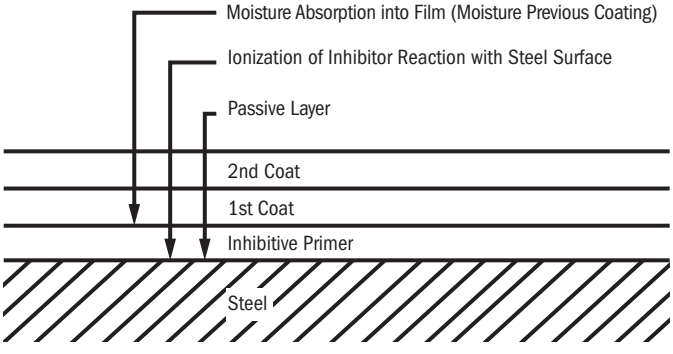


FIGURE 4.3: In inhibitive coatings, moisture penetrates to the inhibitive primer where inhibitive pigments are activated to passivate the metal substrate at the coating-metal interface. Source: C.G. Munger, C.K. Othmer: *Encyclopedia of Chemical Technology,* "Coatings, Resistant," 3rd Ed., Vol. 6 (New York, NY:John Wiley & Sons, 1979), pp. 456–457.

Cathodically Protective Pigments

The concept of cathodic pigments is, in many ways, an extension of the inhibitive primer principle. The reactions that take place, however, are entirely different. In the case of inorganic zinc (IOZ) primer or an organic zinc-rich primer, the zinc acts as an anode to the steel, and whenever there is a break in the film, the sacrificial action of the anode (zinc film) tends to protect the basic steel substrate from corrosion. Many times, where scratches or damage to an IOZ coating have occurred, the zinc reaction products have proceeded to fill in the scratch or damaged area and seal it against further atmospheric action.

The IOZ coatings (and this concept should include galvanizing)

may be used alone or as a permanent primer over which topcoats may be applied. In order to satisfactorily topcoat over a reactive base coat containing zinc, the topcoat must be highly alkali-resistant. Such topcoats would include acrylics, vinyls, chlorinated rubbers, epoxies, and coal tar epoxies. For special purposes such as high heat stacks, silicone topcoats are often applied. When zinc primers are overcoated with alkali-resistant coatings and in proper coating thickness, the zinc primer remains inactive until a break occurs in the coating. At this point, the cathodically active primer reacts to protect the steel substrate (Figure 4.5).

IOZ primers are also highly adherent, reacting with the substrate to form a chemical bond in addition to the physical bond with the steel surface. The high adhesion of the zinc primer prevents undercutting of the organic topcoats so that the breaks in the coating that occur because of abrasion or other causes do not expand and enlarge, as is the case with many organic inhibitive primer systems (Figure 4.6). Although organic zinc-rich primers protect in a similar manner, providing the zinc is in particle-to-particle contact within the primer, the organic binder is not chemically reacted to the substrate. Thus, the coating may be undercut if corrosion occurs.

Figure 4.7 shows a large offshore structure under construction that was coated with a cathodically active coating prior to being topcoated. Coating systems such as this (IOZ primer plus vinyl or epoxy intermediate and either epoxy, acrylic, polyurethane or polysiloxane topcoats) have provided long-term protection for millions of square feet of steel surface under severe marine conditions.

The concept of cathodically protective pigment can be used for coatings that are to be subject to either atmospheric or immersion conditions. Under immersion conditions, particularly marine, the zinc coatings must be overcoated, preferably with inert, impervious coating systems. This prevents the gradual buildup of zinc salts on and within the zinc coating, which inhibit its cathodic action. Proper cathodically pigmented systems, including the inert topcoats, have proven very effective under many immersion conditions.



FIGURE 4.4: Application of a vinyl coating system to the downstream face of a drum gate. Note the many corners, edges, and rivets that must be fully protected by the inhibitive coating.

The Coating System

For serious corrosion situations, the system approach (primer, intermediate coat, and topcoat) provides an excellent answer to many specific coating requirements. Figure 4.8 indicates a five-coat impervious coating system and the purpose for each of the three different kinds of coats.

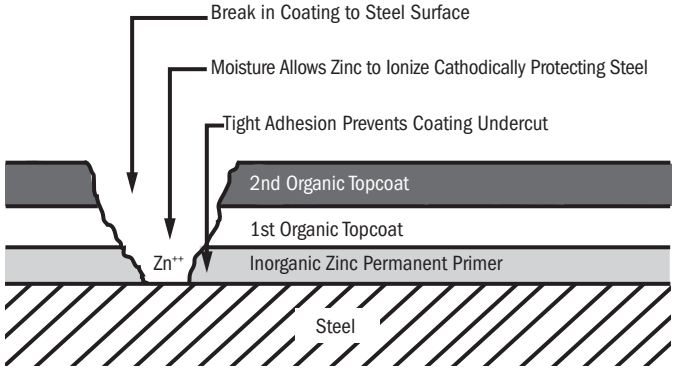


FIGURE 4.5: An inorganic zinc primer reacts to protect the steel substrate at breaks in the alkali-resistant topcoat. Source: C.G. Munger, C.K. Othmer: *Encyclopedia of Chemical Technology,* "Coatings, Resistant," 3rd Ed., Vol. 6 (New York, NY:John Wiley & Sons, 1979), pp. 456–457.

Components

Primers

The primer is universal for all anticorrosive coatings and is considered one of the most important components of the coating system. The primary purposes of a primer are listed as follows:

1. Adhesion (strong bond to substrate)
2. Cohesion (high order of internal strength)
3. Inertness (strong resistance to corrosion and chemicals)
4. Intercoat bond (high bond to intermediate coat)
5. Distension (appropriate flexibility)

The primer is the base upon which the rest of the coating system is applied. As a base, it must have strong adhesion to the substrate surface. If the coating system is an inhibitive one, it must contain the inhibitive pigments and be capable of using these pigments in a way that will passivate the metal surface and reduce its tendency to corrode. In a cathodically active primer, the coating preferably reacts to a certain extent with the steel surface in order to obtain an even greater and stronger adhesion. In addition, this primer must react with moisture and electrolytes from an outside source in order to cathodically protect the steel substrate. Primers are actually the key to the adhesion of the total coating system.

The primer must also provide a proper and compatible base for the topcoats. It must be thoroughly wet by them, and, by its generally flat, nonglossy surface, provide some physical adhesion to the topcoats. Primers, then, have dual requirements: adhesion to the substrate and provision of a surface that will allow proper adhesion of the following coats.

Primers are often applied and allowed to stand for many days or months prior to the application coats. Therefore, they must also have sufficient resistance to the atmosphere to protect the steel substrate from any corrosion during the period between the time the primer is applied and the time that the topcoats are applied. If it allows corrosion to take place during this period, it is not performing the whole purpose for which it was designed.

A primer, generally, must have the ability to stifle or retard the spread of corrosion discontinuities such as pinholes, holidays, or breaks in the film. The primer for the impervious coating systems must be, in itself, highly adherent and very inert, so it tends to stifle corrosion due to these factors. The primers using the inhibitive system contain anticorrosive pigments, which aid the coating in preventing corrosion, while the primers that use the cathodic principle inhibit the corrosion due to actually providing cathodic protection (CP) to the underlying steel surface.

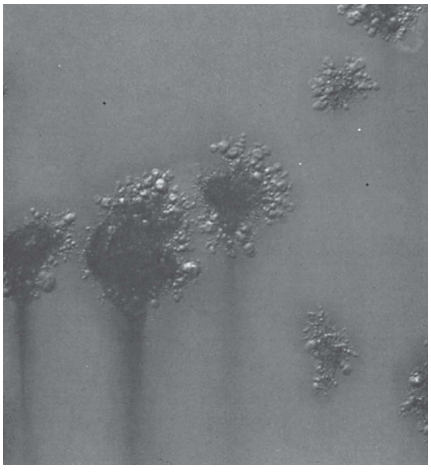


FIGURE 4.6: Blistering of organic inhibitive coating with undercutting. Even though inhibitive, this is typical of breaks in many organic coatings subject to marine or otherwise corrosive atmospheres.



FIGURE 4.7: Offshore platform coating with inorganic zinc primer.

Primers also, under certain conditions (particularly where they are used for immersion conditions or tank linings), must have chemical resistance equivalent to the remainder of the coating system in order to satisfactorily protect against the chemical solution in which it is immersed. This property is usually associated with the impervious coating system, and unless the primer is as fully resistant as the remainder of the system, the under-film breakdown would soon cause coating difficulties with rapid corrosion. Table 4.1 is a comparison of the various primer types.

Intermediate or Body Coats

Intermediate or body coats are usually used in coating systems designed for specific purposes. One old coating system that uses this principle is the wash primer, vinyl red lead, vinyl topcoat system. In this case, the wash primer is considered a metal preparation, the red lead vinyl is considered the primer, and the topcoats provide resistance to the atmosphere. A newer and more common system utilizes a thin film epoxy primer pigmented with inhibitive pigments such as red iron oxide, a thick film intermediate coat pigmented with internal film strengtheners such as glass fibers or aluminum flakes, and a topcoat of polyurethane pigmented mainly with atmospherically resistant pigments such as titanium dioxide.

Irrespective of the names applied to these coats, the principle remains the same since the intermediate provides a heavy body coat that adds thickness and resistance to the coating system. The primary purposes of an intermediate coat are to provide:

1. Thickness for total coating;
2. Strong chemical resistance;
3. Resistance to moisture vapor transfer;
4. Increased coating electrical resistance;
5. Strong cohesion; and
6. Strong bond to primer and topcoat.

The formulation of the intermediate coats is important, primarily as it increases thickness. Physical thickness improves many other essential properties of a coating, such as increased chemical resistance, reduced moisture vapor transfer rate, increased electrical resistance, increased abrasion, and impact resistance. The body coat or intermediate coat must also provide strong adhesion to the primer, as well as a good base for the topcoats. The intermediate coat usually has a rather high pigment-to-vehicle ratio, so that it is a flat or low sheen coat with physical adhesion. Without the ability of this material to properly adhere to the primer and to provide proper adherence to the topcoats, the problem of intercoat adhesion would cause early coating breakdown.

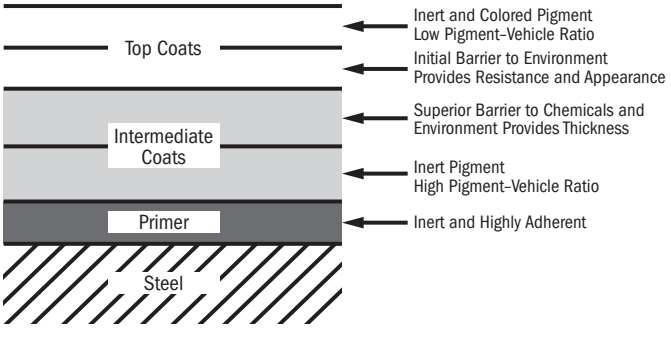


FIGURE 4.8: Five-coat impervious coating system.

Another important role of the intermediate coat is in providing a superior barrier with respect to aggressive chemicals in the environment or when immersed. The intermediate coats are usually deficient with respect to appearance properties so that they are generally not used as finish coats. They may also be used to add physical resistance. Most intermediate coats are used with the impervious type coating system.

Topcoats

Topcoats also perform several important functions in that they:

1. Provide a resistant seal for the coating system;
2. Form the initial barrier to the environment;
3. Provide resistance to chemicals, water, and weather;
4. Provide a tough and wear-resistant surface; and
5. Provide a pleasing appearance.

In the primer, intermediate coat, and topcoat system, the topcoats provide a resinous seal over the intermediate coats and the primer. The first topcoat may actually penetrate into the intermediate coat, thus providing the coating system with an impervious top surface. The topcoat is the first line of defense against aggressive chemicals, water, or the environment. It is the initial barrier in the coating system. It is more dense than the intermediate coats because the topcoats are formulated with a lower pigment-to-vehicle ratio. Although they are a much thinner coat than the intermediate coats, as would be expected from the lower pigment volume, with the higher resin ratio they provide a tough upper layer. It also provides the coating system with the characteristic of appearance through its color, texture, and gloss. There are a number of situations; however, where the intermediate coats provide the primary barrier to the environment, while the finish coat is applied for entirely different purposes. The topcoat, for instance, can be used to provide a non-skid surface, while the intermediate coat and the primer provide the barrier to the environment, as in a marine environment. The

TABLE 4.1: Primer Comparison Table

	Primer Type			
Requirement	Alkyd or Oil Primer	Inhibitive Primer (May Be Mixed Resin System)	Inhibitive Primer (Resin May Be Identical to Topcoats)	Cathodic (Zinc)
Bonding to surface	Usually wets and bonds to most surfaces. Somewhat tolerant of substandard surface preparation. May be used on metal or wood surfaces but not on concrete. Not recommended for immersion.	Adhesive properties are mahor consideration. Not as tolerant of substandard surface preparation as oil primers. Used primarily on metal. Inhibition not necessary on wood or concrete. Usually not for immersion.	Surface must be properly prepared. Primers require maximum adhesion. Used on metal or concrete. Used for immersion.	Inorganic zinc: outstanding adhesion to properly cleaned steel or iron surfaces. Chemical as well as physical adhesion. Organic zinc: Adhesion depends on base resin.
Adhesion of topcoats	Satisfactory for oil types. Usually unsatisfactory for vinyls, epoxies, and synthetic polymers. Soften and lose integrity by attack from solvent systems of synthetic topcoats.	Formulated for adhesion of topcoats. Specific coating systems may require specific primer.	Usually part of specific generic system. Primer designed for specific intermediate or topcoats.	Fits into wide range of systems. "Tie coat" may be required. Specific recommendations should be obtain for immersion systems.
Corrosion suppression	Limited. Alkali produced at cathod attacks film (saponification). Spread of underfilm corrosion results.	Usually formulated with good resistance to alkali undercut. Contains inhibitive pigment for a degress of corrosion resistance.	Relies on inert characteristics. Very strong adhesion.	Inorganic zinc: Outstanding ability to resist disbonding and underfilm corrosion. Anodic property of metallic zinc protects minor film discontinuities.
Protection as single coat	Limited by severity of exposure.	Limited by severity of exposure.	Limited by severity of exposure. Usually suppresses corrosion alone for some period of time.	Will protect without topcoat with very few exceptions.
Chemical resistance	Typical of alkyds. Not recommended for alkali exposure.	May be of lower order of resistance than that of topcoat due to inhibition.	Typical coating system.	Not resistant to strong acids and alkalies. Inorganic: Outstanding solvent resistance.

finish coat or topcoat may also provide resistance to marine fouling, such as shell growth and algae. In other cases, a topcoat may be applied for appearance alone. A summary of coating component functions is given in Table 4.2.

Variations

While a coating system is obviously only for severely corrosive conditions, modification of the numbers of coats can effectively be used for a variety of corrosive situations. Several combinations of this system have proven very effective and have provided many years of corrosion-free service on offshore platforms.

A coating system, however, need not be composed of the three different parts; even a single coat can provide a coating system, depending upon the requirements of the coating. IOZ coatings, for example, provide an excellent one-coat system for the storage of refined oil products and many solvents. A single coating formulation applied in two or more coats may provide the best answer to a specific problem. A self-adherent vinyl system, for example, has been applied to the interior of water tanks in three or four coats for many years with outstanding performance. Coal tar epoxy systems have been applied on piers, docks, and other marine structures very effectively where the only difference in the coats is some color contrast to facilitate even application of the topcoat.

A two-material system may provide the best answer under other circumstances. An epoxy-based primer, for example, topcoated with one or more coats of coal tar epoxy, provided a system with excellent resistance to water and seawater for many years, particularly in ballast tanks of ships. Since the adoption of the Performance Standard for Protective Coating (PSPC) requirements for ballast tanks by the International Maritime Organization (IMO) in resolutions MSC 216 (82) and MSC.291 (87), coal tar epoxy systems are no longer used in ballast tanks. Two- and three-coat epoxy systems are the most common ones that meets the PSPC requirements and the final coat is required to be a light color, such as white, light blue, or light green. The target useful life for PSPC ballast tank systems in this regulation is 15 years.

The three-material system (i.e., primer, intermediate, and topcoats) is often used where chemical resistance is needed. Another

TABLE 4.2: Functional Summary of the Component of a Coating System

Coat	Main Function	Specific Requirement	General Requirements
Primer	Adhesion	Adhere to substrate Bond to intermediate	Adhesion, cohesion resistance, flexibility internal bond
Intermediate	Thickness and structure	Bond to primer Bond to topcoat	Cohesion, internal bond thickness, strength, resistance —Chemical —M.V.T. —Electrical
Topcoat	Resistance to atmosphere	Atmosphere and/or environmental resistance Bond to intermediate	Seal surface Strength, resistance, flexibility, appearance, toughness

example where the three-material system has proven itself is on the face of dam gates, where the coating is subject to abrasion, immersion, and continuous weather. A vinyl system (which included a vinyl primer, vinyl intermediate coats using a silicate pigment, and vinyl topcoats pigmented with aluminum) provided a long-lasting system for the upstream faces of rotary and floating drum gates. There exists special dispensation in the USA for use of these high volatile organic compound (VOC) vinyl coatings on dam structures due to the limited usage in comparison to other generic coating systems.

Coating systems, then, may consist of any number of coats and combinations of materials. In most cases, a coating system is based on the same or similar resin combinations. Each one of the different binders in the coating system layers provides its own series of properties, characteristics, and benefits to the total coating system. Such systems are generally for specific purposes such as immersion in seawater, for use in cargo ballast tanks, or in chemical storage.

Mixing Coating Systems

There are dangers in mixing different coating systems. This situation usually occurs when individuals take it upon themselves to apply a mixed coating system. The use of a mixed coating system simply for expediency or an individual's whim is not a recommended practice, as it frequently causes problems. An attempted application of vinyl or epoxy coatings over an alkyd or organic shop primer is an example of this kind of mix. It generally does not work since the solvents from the topcoat systems penetrate and break up the alkyd so that it no longer maintains its integrity. The reverse could also occur where a vinyl primer and intermediate coat is applied, with an alkyd topcoat applied over the entire system. The alkyd, in this case, may work, but more often than not, it will check and crack away from the underlying vinyl after a certain period of time. Mixed coating systems that have been researched by the manufacturer are generally more sound and should perform as recommended. As a general rule, two-component thermosetting types of coatings should not be used over single-component coatings that cure by oxidation or evaporation/coalescence.

Basic Coating Formation

The basic formation of a coating is a highly technical reaction, and the type of reaction is extremely important to the effectiveness of the coating in its particular use. In order to produce a film that will perform practically and satisfactorily in a given environment, the coating, after its application, must convert to a very dense, solid membrane, which is resistant to that particular environment. This conversion from the liquid resin to the solid resin film is the most important reaction that takes place in the formation of a coating.

Molecular size, weight, and complexity of the coating resin often determine the type of coating film that forms. Generally, for corrosion-resistant applications, a very dense, tight, chemical-resistant film is desired. Resins that form this type of film by evaporation are of very high molecular weight, and are reacted into their finished form prior to being formulated into a coating. For the high molecular weight film to form on the surface, it is only necessary for the solvents to evaporate from the resin solution. Because of the high molecular weight of these resins, they are often difficult to put into solution, requiring strong solvents with the total coating formulation having relatively low solids.

On the other hand, resins that are of relatively low molecular weight may be liquids in themselves. These require reaction in place, either by catalytic action, reacting with other resins, or by reaction with oxygen or moisture from the air to form films. These materials, which are of lower molecular weight to begin with, have the advantage of building a higher solid combination into the coating so that there can be less volatile material or, in some cases, no volatile material in the coating. The polymerization, or condensation, creates the high molecular weight coating resin in place. In this case, the conditions during application are critical for the film-forming reaction to take place.

There are several different types of binders, or film-formers that are used to formulate protective coatings for corrosion-resistant applications. Each of these has their own characteristics and requirements for film formation. These types of binders are those formed by solvent evaporation, oxidation, polymerization (co-reaction), condensation-reaction with moisture from the air, coalescence, and the formation of inorganic coatings.

Materials that form a film may generally be classified under two categories: thermoplastic and convertible. A thermoplastic material is one that becomes soft or fluid when heated. On cooling, it regains its original physical and chemical properties. Convertible film-formers undergo a chemical change or conversion. This results in a definite alteration of their physical properties. The word convertible is used broadly to include all of the methods of conversion mentioned previously with the exception of evaporation of the solvent and inorganic materials. Since most of the film formers, regardless of class, are synthetic, a brief description of synthetic resins should serve as a background for their use in forming coating films. Unit II of the Paint Federation's Series on Coatings Technology, "Forma-

tion and Structure of Paint Films,"1 provides a general description of resins and their formation, as follows.

> **General Nature of Resins**
>
> Resins are polymers. They are made by combining single units (monomers) of chemical compounds such as styrene, vinyl chloride, vinyl acetate, ethyl acrylate, phenol, formaldehyde, and urea. Activated by heat and catalyst, the monomers unite to form molecules that are many times larger. When only one kind of monomer is used, the resin is a homopolymer. If two or more kinds are used, the resin is a copolymer. Each type and grade of resin has characteristic properties. This difference in properties determines which resin or combination of resins is most suitable for a specific purpose, and it permits a resourceful paint chemist to satisfy a wide diversity of requirements. To be capable of polymer formation a monomer must contain chemical groups that have potential chemical reactivity. Frequently resins take their names from these chemical groups. Among such groups are: hydroxyl (–OH); carboxyl (–COOH); amine ($-NH_2$); vinyl (CH_2=CH–); epoxy (–C –CH_2); and isocyanate (–N=C=O). (–CH_2) and Isocyanate (–N=C=O). The functions of heat and catalyst are to energize and direct
> O
> the reactions of polymerization. A double bond in a formula indicates unsaturation. Unless the double bond is in a benzene ring structure, it carries a strong tendency to react in a manner that replaces it with a single bond.
>
> Next to the kind of monomers, the most important feature of a resin is the degree of polymerization. With a given type of resin increasing the size of the polymer molecules, or molecular weight, results in a general improvement in film properties; greater hardness; greater film strength; better resistance to water, chemicals, and solvents; and better exterior durability. On the negative side, higher molecular weight means reduced solubility and higher viscosity or lower solids of solutions. This relationship between viscosity and film properties has great importance. It may be the deciding factor in the choice of resin for a particular purpose.[1]

During the mid to late 1990s resin manufacturers introduced newer technology in resins and reactive diluents, particularly 100% solids epoxies that permitted a wider range of viscosities and film-building properties. During the latter part of this same period, resin manufacturers introduced both aliphatic and aromatic versions of elastomeric polyurethanes and polyureas that expanded the range of both dry film thickness and resistance properties. Beginning in the early 2000s resin manufacturers introduced polyaspartic resins that took traditional thin film polyurethane technology into the realm of very high film coatings that are applicable direct to metal or over selected primers.

Film Formation by Solvent Evaporation

The resins that dry by solvent evaporation are all thermoplastic film-formers. Shellac is an old example of this type of material. The original gum shellac was dissolved in alcohol and applied to a wooden surface; the alcohol evaporated leaving the dry, continuous film of shellac on the surface. A more modern example would be a solvent vinyl solution where the vinyl resin is dissolved in ketone solvents and, when these evaporate, a smooth, clear, continuous film of vinyl resin is obtained. Film formation by solvent evaporation, which appears to be the simplest type of film formation, is actually far from simple. The film formation does not commence until the evaporation of the solvent has reached an advanced stage, which brings the molecules of the resin into such close contact that their mutual chemical attraction draws them together. Film properties are influenced by the molecular arrangement or structure within the film. A homogeneous, dense structure is promoted by a solvent that maintains maximum dispersion and mobility of the polymers during film formation. The opposite is true when the resin is precipitated out of the solvent. The attraction between the polymer molecules is not just limited to films formed from solution, but it is the underlying basis of all films, and is the force that holds the molecules together.

In order to obtain a smooth, continuous resin film, it is usually necessary to use a combination of solvents. In order to form a good vinyl resin film, for example, it is necessary to use a combination of solvents that are classed as active solvents, latent solvents, and diluents.

The active solvents are those that easily dissolve the resin and are the primary ones for putting it into solution. The latent solvents are less active, but still act as solvents, while the diluents are materials that will tend to soften the resin, but will not actively dissolve it. The combination of these three types, working together, often provide a better and stronger film than a single solvent alone. They evaporate at different rates, with the active solvent usually being the last solvent to leave the film, creating the conditions whereby the resin molecules orient themselves properly to form a smooth, clear, continuous film. The skill in mixing the three types of solvents for any given polymer is what makes a solvent evaporating coating easy to apply as a smooth film with a good gloss. The aim in mixing the solvents is to provide a uniform evaporation. If the solvents evaporate too fast when the coating is applied, the resin will tend to dry before it hits the surface and overspray or dry spray will result. Fast-evaporating solvents also eliminate any possibility of brushing. Solvent combinations that evaporate too slowly make for a very slow film formation. The film generally remains tacky and the solvent is retained for a long period of time, making the resin film less water and chemical resistant.

There is a considerable difference in the way that various resins will release the solvents from the film. In the case of vinyl resins, there is a mutual solubility; that is, the resin dissolves in the solvent but there is also some of the solvent that dissolves in the resin. The solvent that dissolves in the resin is the solvent that is retained the longest and the one that is most difficult to remove from the resin. In many ways, it acts as a permanent plasticizer. Isophorone is an example of such a solvent. Resins that hold the solvent in this way are said to have poor solvent release. On the other hand, there are other materials, such as chlorinated rubber, that have a rather rapid release of their solvents and quickly form a very hard film. The solvent formulation of the coating often has a considerable effect on the solvent release. If two solvents have the same volatility, the one with the higher solvency volatilizes more slowly from the resin itself.

Thermoplastic Film Formers

There are many thermoplastic film-forming materials. Nitrocellulose, which had a great deal to do with the automobile industry, is one example. There are also the acrylic ester resins, such as methyl methacrylate; styrene butadiene resins; vinyl acetate resins; vinyl chloride acetate resins; cellulose acetate butyrate resins; various petroleum resins, including asphalt and coal tar; chlorinated rubber; and some rubber solutions. All types of solvent combinations are required in order to properly develop films from each of these materials, and no two would require exactly the same solvent combination.

There is also a wide variation in molecular weight between these materials. As the molecular weight increases, it is more difficult to dissolve the resin in solvents, resulting in a generally higher viscosity. This limits the amount of resin that may be placed in solution

and practically applied to form a coating film. Thus, the dry film thickness of a number of the solvent evaporating coatings such as nitrocellulose, vinyls, and the acrylic esters, is rather low.

Films Formed by Change-of-Phase

Thermoplastic resins may also be formed into coatings by another method called a change-of-phase. This generally means that the resin is changed, usually by heat, from a solid to a liquid and then back to a solid again. The process is more commonly referred to as hot-melt.

Use of this hot-melt technique to form a coating dates back to the Egyptians and their method of applying rosin and tars to the bottom of their ships. Today, it is still an extensively used method, particularly in the piping field. The principal materials used in this process are asphalts and coal tars. Both of these are relatively easily converted to a liquid through the use of heat. The liquid resin can then be applied to the metal surface by daubing, a process of brushing the material on the surface while it remains in a liquid state. This method has a number of disadvantages. Because the liquid resin cools rapidly, it is particularly difficult to obtain a smooth, even film by this brushing technique.

For the interior of pipe, the hot-melt materials are often applied by centrifugal force; that is, the liquid materials are poured into the pipe while the pipe revolves. The centrifugal force of the turning pipe spreads the resin uniformly over the surface and a very smooth, even coating can be obtained.

The application of the hot resin to the exterior of pipe can also be done by pouring the resin evenly over the pipe surface, as it turns. The common method of external application, however, involves inserting a number of pipe wraps into the liquid resin as the pipe revolves. This reinforces the hot-melt resin and aids in holding it in place, while at the same time making a more uniform, even coating. Pipe wrap materials can be organic fabric, fiberglass matte or fabric, or other similar high-strength materials.

The hot-melt technique is effective wherever a basic resin can be melted to a reasonably liquid form. Since there are no solvent or volatile materials involved, 100% of the resin material is applied to the structure. Thick coatings are easily built-up from the hot-melt materials and, when done properly, the hot-melt materials wet the surface of the metal very well.

The formation of a good coating depends on the control of the temperature of the resin, the condition of the metal, the temperature of the metal, and, many times, the weather and humidity. Under most circumstances, the majority of the pipe applications are done under plant conditions where pipe is easily handled, so that a very good coating can be obtained at a relatively low cost. These materials can also be handled by over-the-ditch hot-melt wrapping machines, but only at some added expense and with less application control.

This change-of-phase or hot-melt process is similarly used for the application by extrusion of polyethylene and polypropylene coatings as on the exterior of pipe. In this case, the polyethylene/polypropylene is heated in the extruder and smoothed on the surface of the pipe by the extruder die in an even film. The film is formed and complete as soon as the polyethylene/polypropylene cools. The cooling process is often speeded up by quenching the coated pipe immediately after it leaves the extrusion station.

This change-of-phase mechanism is also used in the application of powdered coatings where the solid film-former is ground into a very fine powder. The powder is sprayed on a preheated metal surface, which is above the melting point of the resin in order to hold it in place. The metal is heated to a temperature high enough to fuse the resin onto the surface. A fluidized bed process also uses the change-of-phase principle. In this case, the fine resin is fluidized by the use of compressed air, and parts are heated and then dipped into the fluidized resin until the proper thickness is obtained. Again, the part is heated and the resin fused on the surface. In all of these change-of-phase coatings, the resin is applied at 100% solids so that no solvent evaporation is necessary to form the film.

Plastisols and Organosols

Another example of the use of this change-of-phase process for corrosion control is in the application of plastisols or organosols. In this case, the resin is dispersed in a plasticizer, which remains in the coating permanently, or in a latent solvent, which only becomes active when heat is applied. In the case of the organosols, it is possible to obtain a hard finished film, which contains little or no plasticizer. In the case of the plastisols, the resin is dispersed in a plasticizer, which acts as a latent solvent and does not tend to solvate the resin particles until a certain temperature is reached. At that temperature, the resin dissolves in the plasticizer, forming a semi-liquid gel, and then, upon cooling, becomes a plasticized resin coating. This film-forming process is often used on steel pipe, particularly in the chemical and mining industries.

Film Formation by Oxidation

The formation of films in this category is primarily from drying oils, which are natural materials of vegetable or fish origin. They are chemically classified as triglycerides; that is, compounds of one molecule of glycerin and three molecules of long-chain fatty acids.

The use of drying oils is one of the oldest methods of forming paints. The oils are applied in relatively thin films and allowed to stay in place until they have reacted with oxygen in the atmosphere long enough to become hard and dry. Originally, and for a considerable time after their original drying period, the oils are quite resistant to atmospheric conditions. They continue hardening, however, until they eventually check, crack, and chip away from the surface.

Oxygen reactions with unsaturated oils are varied and complex. The long-chain unsaturated oil molecule reacts with oxygen irrespective of whether it is attached to an alkyd, epoxy, or urethane to form the base coating film. Oxidation of an oil can isomerize, polymerize, and cleave the carbon-carbon chain, as well as form oxidation products. Blown oils of varying viscosity are manufactured through the reaction of oxygen in sufficient amounts to give what appear to be polyethers. The steps involved in film-forming from drying oils may be summarized as follows.

1. An induction period in which little visible change in physical or chemical properties of the oil occurs but antioxidants present in the film are being destroyed.
2. Oxygen uptake becomes measurable and hydroperoxides and conjugation form.
3. Decomposition of the hydroperoxides occurs to form free radicals and their concentration increases and the reaction becomes autocatalytic.
4. Polymerization and cleavage reactions begin and high molecular weight cross-linked polymers as well as low- molecular weight

scission products including CO_2 and water are formed. Oxygen absorption reaches a maximum at about the time the film forms and oxygen continues to be absorbed but at a much slower rate.[2]

Film Formation by Polymerization

There are several reactions that create large molecules out of small ones. Most often these are processes that must be carefully controlled under strict manufacturing conditions and are therefore not applicable to on site coating formation. Vinyl resins, however, are an example of a resin that is completely polymerized before it is cast into a film from a solvent. These films cannot be polymerized in place. When coating films are reacted after application, the primary consideration is the coating reaction in place. Liquid resins are converted to a solid continuous film after application to the surface. Thus, the process actually being referred to is polymerization by cross-linkage.

Polymerization by Cross-Linkage

Polymerization by cross-linkage broadly includes many types of baked coatings, such as those used on appliances of all sorts. Its meaning in this discussion, however, is limited to the cross-linkage that occurs at normal or ambient temperatures and under the conditions in which protective coatings would be applied. The polymerization takes place between a monomer and one or more polymers of different types to produce the resin film that is cross-linked, as compared to the linear polymer described under vinyl resins. In this case, a rigid, three-dimensional molecular structure is created on site to form a coating film that is thermoset (i.e., the coating becomes insoluble in its own solvents and is not softened appreciably by heat.

The two most important examples of this type of reaction are both epoxies. One is the basic epoxy resin that is reacted with a monomeric amine, such as a diethylene triamine or an amine adduct, to form a cross-linked film. This reaction takes place at ambient temperature to form a hard, somewhat brittle film. The second example is the reaction of the epoxy resin with a polyamide resin. This cross-links the epoxy through the amine groups on the polyamide resin. In this case, by varying the proportion of the viscous polyamide resin, films can be formed with a very wide range of physical properties.

Polyurethane resins that use an amine-curing agent are also of the cross-linked type. The basic resin used in this case is an isocyanate prepolymer, to which is added an amine curing agent just prior to application. The film is formed at ambient temperature and is a truly cross-linked, three-dimensional polymer. The amine in both the epoxy and the urethane is often called a catalyst. This is a misnomer, since the amine becomes a part of the much larger polymer molecule. A true catalyst initiates a reaction, but does not become part of the end product.

Cross-linked coatings are much more resistant from a corrosion standpoint than the oxygen convertible coatings. This is especially true in terms of hardness and chemical, water, and solvent resistance.

Catalyst Polymerization

Unsaturated polyester resins are good examples of catalyst film formation. Polyester resins are not generally used as coatings, but rather are often combined with fiberglass or other reinforcing materials to form highly corrosion-resistant linings. These heavy linings are then most commonly used in chemical tanks, plating tanks, and tanks for the electrolytic refining of metals.

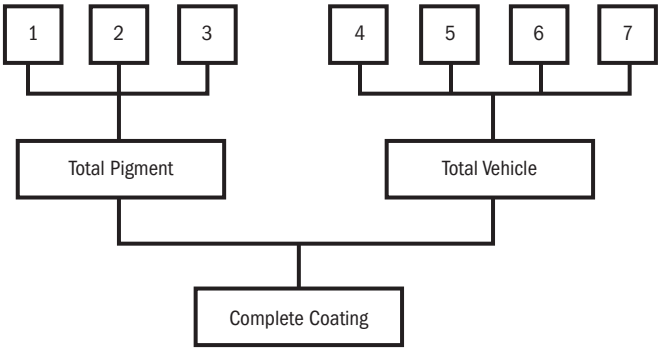
The polyester resins are made by reacting dibasic acids, such as maleic anhydride or phthalic anhydride with a polyhydric alcohol, usually propylene glycol. The resulting polyester is dissolved in styrene in order to develop a liquid solution for easy application. Styrene also reacts with the unsaturated polyester to provide a copolymer resin. In order to bring this about, a cobalt compound is added to the liquid resin, and, shortly before the application, a solution of a material such as methyl ethyl ketone peroxide (MEKP) is blended with the resin solution. These two materials catalyze the reaction between the polyester and the styrene to form a copolymer resin through the unsaturation of both components. The MEKP is a true catalyst (as is cumene peroxide [CKP]) and is not a part of the resulting polymer. Since the liquid styrene becomes a part of the compound, the polyester resin solution is essentially 100% solids. Except for the amount of styrene that evaporates initially, the entire solution converts to a solid resin film.

Most often, the polyester linings are applied as rather thick films. A thin coating is difficult to obtain because of the rapid loss of exothermic heat that occurs during the polymerization and because of the loss of styrene. The reaction of the polyester resin from a liquid form to a solid film is rapid, so that ordinary methods of application are not practical once the catalyst is mixed. The pot life is very short as the reaction increases rapidly when the material is held in volume. A two-component spray gun is therefore usually used in the lining's application, with the catalyst mixed at the head of the gun. The resulting film is three-dimensional with good chemical and water resistance. There is also extensive film shrinkage because of the continuing polymerization reaction even after the film or lining becomes solid. Depending upon environmental conditions at the time of application, including temperature and wind currents, the shrinkage of this basically solid resin film can be as high as 23%. Vinyl ester resins are applied in the same way and have many of the same characteristics as polyesters, but have greater heat and chemical resistance.

Inorganic Zinc Film Formation

The formation of a coating from inorganic or organic silicates and zinc represents quite a different series of reactions from those that takes place in organic films. While the molecules of organic films are primarily made up of carbon atoms combined into long-chain linear polymers or cross-linked polymers, the basic building blocks of IOZ coatings are silica, oxygen, and zinc. In liquid form, they are relatively small molecules of metallic silicates such as potassium silicate, sodium silicate, or organic silicates such as ethyl silicate. These essentially monomeric materials are cross-linked into a silica-oxygen-zinc structure that is the basic film-former or binder for all of the IOZ coatings. This occurs through a chain of rather complex chemical reactions, some of which take place rather rapidly while others come about slowly.

There are essentially three stages in the formation of the inorganic coating. The first reaction is a very simple one: the concentration of the silicates in the coating by evaporation after the coating has been applied to the surface. As the solvent evaporates, the silicate molecules and the zinc come in close contact and are in a position to react with each other and the base metal to which the material has been applied. This initial solvent evaporation provides for the primary deposition of the film on the surface.



1 Inhibitive Pigment (Primer Only)
2 Inert and Reinforcing Pigments
3 Color Pigment
4 Primary Resin (Binder)
5 Secondary Resin
6 Solvents
7 Plasticizers or Modifier

FIGURE 4.9: General components of a coating.

The second reaction is the ionization of the zinc metal, which initiates the reaction of the zinc ion with the silicate molecule to form a zinc silicate polymer.

The third reaction is the completion of the film reaction over a long period of time by continuing formation of zinc ions, which react to increase the size of the zinc silicate polymer and cross-link it into a very insoluble, resistant, three-dimensional structure. In the field of inorganic chemistry, this is a unique reaction since inorganic materials generally do not form a coherent thin film. The only other inorganic film is one formed by fusing the inorganic material to a basic metal in order to create ceramic enamel.

Coating Component Functions

Individual coating components may be combined into certain categories, and any one coating may be made of more than one component type, all of which serve different functions. In order to obtain a gray coating, for example, it may be necessary to use several colored pigments. Figure 4.9 shows the general components of a coating and the manner in which they are ultimately combined into the complete and finished product.

Inhibitive Pigment (Primer Only)

While the primary function of the inhibitive pigment is to react with the substrate to provide a passivated surface and therefore, cathodically protect it, they can also contribute to the overall prime color or lend opacity of the coating.

Inert and Reinforcing Pigments

The inert pigments are often added to improve the density and corrosion resistance of the coating, as well as to increase the thickness. The reinforcing pigments, on the other hand, are to do what the word indicates (i.e., reinforce the paint film so that it becomes tougher with fewer tendencies to check and crack after extended periods of weathering. Both of these pigments tend to increase the hardness and tensile strength of the film. They can also increase the chemical and atmospheric resistance. Platelet-shaped pigments such as aluminum flake and micaceous iron oxide (MIO) increase the permeation resistance of a coating film. Some inert and reinforcing pigments aid in the adhesion of the primer, although how they do so is not completely understood. It is known, however, that properly pigmented films can be substantially more adherent than a clear film of the same resin. These pigments improve the bonding surface for topcoats. They are used to build film thickness and contribute substantially to the viscosity, thixotropy, and overall workability of the coating in its liquid stage.

Color Pigment

The primary function of color pigment is to provide a pleasing and decorative color, to impart opacity, and to hide the underlying surface. Another very important function, however, is to protect the resinous binder from the penetration of the sun's ultraviolet rays into the coating itself. This is important inasmuch as many binders are rather rapidly affected by the sun's rays when used as a clear coating.

Primary Resin (Binder)

The primary resin has a number of functions. It binds the various pigments in the coating together into a homogeneous film. There must also be sufficient resins present so that the binder wets the individual pigment particles and is thus able to bind them together. In addition, the binder resin must provide the adhesion of the overall coating to the substrate. Again, there must be sufficient resin left after wetting the pigment for the resin to also be able to wet the surface of the substrate sufficiently for adhesion to be obtained. The resin is the primary barrier to all of the various materials that may come in contact with the coating, either when subject to atmospheric or to immersion conditions. It must also maintain its integrity in a corrosive environment.

Secondary Resin

While many coatings have only one primary resin as their binder, many others incorporate more than one resin in order to develop specific properties. Secondary resin is also part of the overall binder. Its function is to extend the primary resin functions, increase the amount of resin available for both wetting the surface and the pigments, aid in the adhesion of the coating to the substrate, increase the overall resistance of the coating, and build the coating thickness. One primary requirement is that it be compatible with the primary coating resin so that the two maintain a cohesive resin structure. An excellent example of the additional properties obtained from secondary resins is the addition of polysiloxane resins to an epoxy formula, thus obtaining color and gloss retention properties not available with epoxy resins alone.

Solvents

A function of the solvents is to dissolve the binder into a compatible and workable liquid. Many of the resin binders are solids and would be unworkable without proper solution. Solvents aid in the control of the viscosity of the overall vehicle. They not only aid in making the binder-pigment combination workable, but they transport the combination to the substrate. By providing a more liquid, viscosity-controlled coating, they also aid in the wetting of the substrate surface.

TABLE 4.3: Binders Commonly Found in Corrosion-Resistant Coatings and Linings

Rating: E—Excellent, G—Good, F—Fair, P—Poor

		Resistant Properties					
Binder Type	Generic Type	Alkali	Acid	Water	Weather	Temperature	Primary Use
Lacquer	Copolymer Vinyl Chloride-Vinyl Acetate	E	E	E	E	to 65 °C/150 °F	Resistant intermediate and topcoats
	Polyacrylates	F	F	F	E	to 65 °C/150 °F	Resistant topcoats
	Chlorinated Rubber	E	E	E	G	to 60 °C/140 °F	Resistant intermediate
Co-reacting	Epoxy-Amine Cure	E	G	G	F	to 93 °C/200 °F	Resistant coatings and linings
	Epoxy-Polyamide	E	F	G	G	to 93 °C/200 °F	Resistant coatings and linings
	Urethane (Two-package)	G	F	G	F	to 120 °C/250 °F	Abrasion-resistant coatings
	Urethane (Moisture cure)	G	F	G	F	to 120 °C/250 °F	Abrasion-resistant coatings
	Urethane-Aliphatic	G	F	G	F	to 120 °C/250 °F	Weather and abrasion resistant topcoat
Condensation	Phenolic (Requires added heat to cure)	P	E	E	F	to 120 °C/250 °F	Chemical and food resistant lining
	Epoxy Phenolic	F	E	E	F	to 120 °C/250 °F	Chemical and food resistant lining
	Epoxy Powder Coating (Requires high heat to fuse and cure)	G	G	G	F	to 93 °C/200 °F	Pipe coating and lining
	Inorganic Zinc Silicate	P	P	G	E	to 315 °C/600 °F	Permanent primer or single coat weather-resistant coating
	Glass (fused to metallic substrate)	F	E	E	E	to 260 °C/500 °F	Chemical and food resistant lining

Source: C.G. Munger, C.K. Othmer: Encyclopedia of Chemical Technology, "Coatings, Resistant," 3rd Ed., Vol. 6 (New York, NY:John Wiley & Sons, 1979), pp. 456–578.

Plasticizers

Not all coatings contain plasticizers. However, many resins require the addition of a plasticizing material in order to provide satisfactory coating properties. Plasticizers in many ways are permanent solvents in that they are both dissolved by and dissolve into the resins. Plasticizers provide many coatings with flexibility, extensibility, and toughness.

Basic Coating Components

Binders

In order to perform in a practical way in any given environment, a coating, after its application, must convert to a dense, solid, adherent membrane with all or most of the properties that have been previously discussed. The binder is the material that makes this possible. It provides uniformity and coherence to any coating system. Not all binders are particularly corrosion-resistant so that only a few serve as the basis of all protective coating systems. Those most commonly used are listed in Table 4.3.

The binder's ability to form a dense, tight film is directly related to its molecular size and complexity. Binders that generally have the highest molecular weight are those that form films by the evaporation of solvent only. The resin or the binder molecule is in its completed form prior to application. Additional binders must chemically react in place, and generally the molecular weight of the finished binder resin is considerably less than those that form a film by solvent evaporation or heat conversion.

Binders can generally be classified, according to their essential chemical reactions, as one of the following types:

1. Oxygen reactive
2. Lacquer (thermoplastic)
3. Heat conversion
4. Co-reactive (thermoset)
5. Condensation (thermoset)
6. Coalescent (non-immersion)
7. Inorganic

Oxygen Reactive Binders

Oxygen reactive binders are generally low molecular weight resins, which are only capable of producing coatings through an intermolecular reaction with oxygen. Metallic salts of metals such as cobalt and lead often catalyze this reaction. (The chemical reactions involved are discussed in Chapter 5.) There are several types of coatings in this category that are important to the corrosion engineer.

Alkyds

To produce alkyds, natural drying oils are chemically reacted into a synthetic resin in such a way that film curability, chemical resistance, weather resistance, and so forth, is improved over the original drying oil. Nevertheless, the drying oil part of the molecule is responsible for the conversion of the liquid coating into the solid state, and the properties of the drying oil usually dominate.

Epoxy Esters

Epoxy resins are combined chemically with drying oils to form epoxy esters. The drying oil part of the molecule determines the basic properties of the epoxy ester coating. The coating dries by oxidation in the same manner as an alkyd. The chemical and solvent resistance is less than an unmodified epoxy but greater than an alkyd or oleoresinous paint. The coatings generally are hard and have good adhesion and flexibility. Many epoxy-resin oil combinations can be made, with the properties being dependent on the type and amount of oil used in the formulation of the resin. Epoxy ester coatings have made excellent machinery enamels and interior coatings. They are not, however, entirely suitable for exterior finishes as they chalk readily and heavily.

Urethane Alkyds

Epoxy ester resins are also chemically combined with drying oils as part of the molecule that is further reacted with isocyanates to produce urethane alkyds. Upon application as a liquid coating, the resin-oil combination converts by oxidation to a solid film. The oil properties are again dominant, with the isocyanate contributing to the characteristic abrasion resistance and toughness of this coating.

Silicone Alkyds

Alkyd resins are combined with silicone molecules to form an excellent weather-resistant combination known as silicone alkyds. Heat resistance is also increased in spite of the drying oil part of the overall resin molecule. The heat and weather resistant properties are directly related to the percentage of silicone in the formula.

Lacquers

Lacquers are coatings that are converted from a liquid material to a solid film by the evaporation of solvents alone. Lacquers, in general, have a relatively low volume of solids compared to materials formed from lower molecular weight resins and then converted into a solid film.

Polyvinyl Chloride Copolymers

The principal corrosion-resistant lacquer is made from polyvinyl chloride copolymers. The vinyl molecule is a large one and will only effectively dissolve in solvent in the 20% range. The film build is therefore low (in the neighborhood of 1 to 2 mils of thickness per coat). The overall chemical resistance is broader than almost any other binder.

Chlorinated Rubbers

In order to be effective, chlorinated rubbers must be modified by other resistant resins to obtain higher solids, decrease brittleness, and increase adhesion. The chemical and water resistance of chlorinated rubbers depend on the type of modifier used. Again, the solids are relatively low, providing coatings of from 1 to 3 mils thick per coat. Low molecular weight resin modifiers have proven to be the best chemical and corrosion-resistant coatings. Alkyd or oil-base modifiers do an excellent job of plasticizing the chlorinated rubber, but these combinations suffer from reduced corrosion resistance because of the oil. Chlorinated rubber swimming pool paints have been used very successfully for over 75 years despite their high solvent content, They are still used with special precautions for this purpose because of their excellent record despite the fact that they do not meet current VOC regulations.

Acrylics

Acrylics are also of high molecular weight and may be combined with vinyls and chlorinated rubbers to improve exterior weatherability and color retention. When used alone, they have excellent color, gloss, and weatherability. However, their chemical and water resistance are not as high as that of vinyl copolymers or chlorinated rubbers.

Bituminous Materials

Asphalts and coal tars are often combined with solvents in order to form lacquer-type films. Hard asphalt, gilsonite, or coal tar is dissolved in solvents in what is called an asphalt or coal tar cut back. These provide good chemical and corrosion-resistant films, but can only be applied where appearance is not a factor.

Heat Conversion Binders

Hot-Melts

As discussed previously, hot-melts usually involve asphalt or coal tar, which are melted and applied as 100% solids in the hot liquid condition. The resin binder is generally not combined with any other resins but is used essentially as a basic coating material.

Organosols and Plastisols

As also discussed previously, organosols are high molecular weight resins that are dispersed in solvents. The solvent does not actually solvate the resin until heat is applied. It is applied as the solvent resin mixture and is heated to a point where the resin is solvated and fuses not only to itself, but to the surface as well. Plastisols are primarily high molecular weight vinyl materials dispersed in a plasticizer that also does not solvate the resin until heated. The film is formed only after the plastisol has been applied to the substrate and then heated to convert the liquid to a solid.

Powder Coatings

Powder coatings can be high molecular weight thermoplastic resins or semi-thermoset resins, such as certain epoxies, which are

usually converted to a very fine powder and applied to a heated substrate, which first slightly melts the resin. Then, the entire object is heated above the resin's fusion temperature to form the completed coating. Hybrid combinations involving acrylic and urethane resins are formulated to obtain specific performance characteristics.

Co-reactive Binders

Co-reactive binders are formed from two low molecular weight resins that are combined, usually just before application, and which, after having been applied to the surface, co-react with each other to form a solid film.

Epoxies

*Epoxy binder*s are made up of relatively low molecular weight resins in which the epoxy group is at the end of each molecule. These low molecular weight resins are then reacted with ammonia-type compounds called amines. The amines may be liquid, low molecular weight materials or they may be higher molecular weight resinous semi-liquids, with the amine groups scattered over longer chain molecules such as the polyamides. In either case, the amine group on the molecule reacts with the epoxy resin to form the solid binder. These materials not only react quickly, but also over a longer period of time to form higher molecular weight binders with good solvent and chemical resistance. As previously indicated, these materials are cross-linked and form a thermoset structure. In some cases, the epoxy materials are combined with other lower molecular weight materials, such as asphalt or coal tar. The coal tar epoxy, particularly, results in a binder that combines the good properties of both of the base materials. Water resistance is improved over the epoxy binder alone and the solvent resistance of the coal tar is improved by the reaction of the epoxy.

Polyurethanes

Polyurethanes are co-reactive binders in which relatively low molecular weight resins containing alcohol or amine groups are reacted with diisocyanates into an intermediate resin prepolymer. This urethane prepolymer is then capable of reacting with resins or chemical groups containing amines or alcohols to form the finished coating. As previously indicated, another variation exists where the isocyanate group comes in contact with water and the moisture from the air converts the binder from a liquid to a solid.

Condensation Binders

Condensation binders are based primarily on resins that interact to form cross-linked polymers when subject to relatively high temperatures. These are the so-called high baked materials, which are used as tank and pipe linings. Some powder coatings may also come into this category. Condensation is essentially the release of water during the polymerization process. The oldest of this type of coating is the pure phenolic. Thin films of a phenolic resin are applied as a coating and baked at approximately 375 °F to form an extremely hard, adherent, chemical-resistant film. Coatings of this type are modified from the pure phenolic by the use of epoxies and other reactive resins. These condensed materials are strongly cross-linked and are very chemical-resistant. The exception is the pure phenolic, which is attacked by caustic solutions. It is, however, strongly resistant to waters and acids.

Coalescent Binders

Coalescent binders include the coatings where the binders of various resin types, such as vinyls, acrylics, or epoxies, are emulsified to form a liquid binder. They are primarily emulsified with water, although some solvent dispersions have been made from various resins. In this case, the binder is in a dispersed form in the emulsion. When applied to the surface, the water or other medium must evaporate, leaving the coating in such a way that the binder resin gradually flows into itself, or coalesces, to form a continuous film. Water, chemical, and corrosion resistance are generally decreased because of the fact that the dispersed phase never forms as tight and effective a film as does a solvent solution. Coalescents work by softening the waterborne latex or acrylic resins, allowing them to fuse into continuous films. Common coalescents include ester alcohols, esters and glycol ethers.

Inorganic Binders

Inorganic binders are primarily inorganic silicates that are dissolved in either water or solvent and which, when once applied to the surface, react with moisture or CO_2 in the air in order to form an inorganic film. The type of inorganic binder depends on the form of the silicate during its curing period.

Post-Cured Inorganic Silicates

Water solutions of alkali silicates, such as sodium or potassium silicate, combined with zinc dust form very hard, rock-like films referred to as post-cured inorganic silicates. In this state, however, they cure to water insolubility at an extremely low rate. The coating must therefore be reacted with an acidic curing agent to achieve the conversion of the silicate film from the water-susceptible stage to the completely insoluble zinc silicate.

Self-Curing Water-Based Silicates

Self-curing water-based silicates are also mixtures of alkali silicates often combined with colloidal silica to improve the speed of cure. Once the material has been applied to the surface and the entrained water has evaporated, they develop water insolubility from the absorption of CO_2 from the atmosphere. The rate of cure of self-curing water-based silicates is directly related to the ratio of silicate to alkali metal composition in the silicate binder. Traditional water-based self-curing IOZs have lower mole ratios of silica to alkali metal lower than the 4.7:1 to 5.3:1 range seen in "high ratio" water-based IOZs based on modifications of the original NASA patents. This high mole ratio produces a relatively predictable curing reaction whereas the lower ratios in traditional water-based self-curing zincs are rather unpredictable because they are more dependent on environmental conditions such as temperature and absorbance of CO_2 to complete their cure.

Self-Curing Solvent-Based Silicates

Organic esters of silica, which are liquids and are converted into solid binders by reaction with moisture from the air, form self-curing

solvent-based silicates. In this final form, they are very similar to those binders formed from the water-based silicates. A major advantage of these materials is their conversion to rain or moisture resistance shortly after their application. All of these materials contain zinc, which is part of the reactive mechanism that forms the silicate binder. The zinc in the liquid coating acts as a pigment; however, once applied to the surface, the zinc also reacts with the silicate in such a way that a zinc silicate matrix is formed, which surrounds all of the zinc particles. This makes a very hard and extremely corrosion-resistant binder.

Pigments

While binders are responsible for many of a coating's primary properties, pigments also contribute several properties important to their effective use. In fact, proper or improper pigmentation can either make or break a coating in terms of corrosion resistance. Several different pigments may be used within the same coating, all of which contribute to the coating's general characteristics and perform several functions.

Primary Pigment Functions

Color

Pigment produces an aesthetic effect (decoration) and hides substrates.

Protection of Resin Binder

Pigment absorbs and reflects solar radiation, which can cause breakdown of the binder.

Corrosion Inhibition

Various borates, phosphates, and molybdates used in primers act as passivators. Metallic zinc, when in high enough concentration, gives cathodic (sacrificial) protection.

Corrosion Resistance

Proper pigmentation can increase both the chemical and corrosion resistance of a coating. Conversely, improper pigment use can seriously reduce resistance (e.g., calcium carbonate pigments in an acid-resistant coating).

Film-Reinforcement

Finely divided fibrous and plate-like particles of pigments increase hardness, toughness, and/or tensile strength of a film, as well as increases cohesive strength.

Non-skid Properties

Particles of silica, pumice, aluminum oxide, or other inorganic pigments roughen a film's surface and increase abrasion resistance.

Sag Control

So-called thixotropizing pigments prevent sagging of the wet film by providing a false body effect, which also reduces the tendency of other pigments to settle in the container during storage.

Increased Coverage

Properly selected inert pigments can increase the volume of solids (or coverage) of a coating without reducing its chemical or corrosion resistance. There is a limitation on how much inert pigment can be used with a given resin composition. This constraint is termed the critical pigment volume concentration (CVPC), and indicates the volume of pigment that can be bound by the resin without leaving voids in the film.

Hide and Gloss Control

Increasing the color pigment concentration improves hiding, while an increase in either color or other pigmentation generally decreases gloss, depending on the fineness of grind and critical pigment volume concentration.

Adhesion

Certain pigments, particularly plate-like or flake pigments, can increase coating adhesion over that of the binder alone.

In order for pigments to properly function in a coating, they must be thoroughly wet with the binder. This means that each individual particle of pigment must be surrounded by a layer of the binder resin. In other words, the pigment must be dispersed in a matrix of the binder resin. If the pigment is added to the binder in an amount greater than the critical pigment concentration, the binder will not cover the pigment and a porous flat film with little strength will be produced. Pigments vary in their wetting characteristics. They also vary in particle size and certain binders will have greater wetting characteristics for one pigment than another. Thus, each pigment-binder combination has its own critical pigment volume concentration.

A large amount of energy is needed in order for the binder to completely wet each particle of pigment. This is put into the system by milling the binder and the pigment together. Milling does two things: it breaks up the agglomerates of pigment into the individual particles, and by physical action the resin or binder is rubbed over the surface of the particle so that it is completely surrounded. While this was at one time done with two revolving granite stones, present milling operations properly disperse and wet the pigments with intensive mixers such as bead mills or high-speed impellers. Using a much more liquid mix, the high-speed mixer simply transfers enough energy into the system so that all particles are properly wetted.

Manufacturers of pigments have also increased the wettability of the pigment so that it disperses much more readily. The dispersion of the pigment makes a difference in the viscosity or thixotropy of the coating, the hiding qualities, the ability of the pigment to remain in suspension, as well as the gloss or lack of gloss of the finished coating. Unless a pigment is properly dispersed in the vehicle, the quality of the coating will be seriously impaired.

Pigment Classes

Pigments can be separated into classes such as coloring pigments, reinforcing pigments, inhibiting pigments, or metallic pigments. Its designated class depends on the pigment's purpose within the coating.

Color Pigments

Color pigments, of course, provide the pleasing color and decorative characteristics expected of a coating. While this is truer in the case of ordinary paint, corrosion-resistant coatings must also provide pleasing as well as utilitarian surfaces. Knowledge of the nature of color and its cause and effect is often helpful to the corrosion engineer, and is thus discussed in Unit 8 of the Federation Series on Coating Technology.

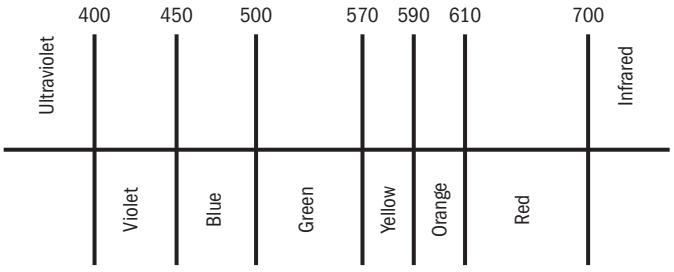


FIGURE 4.10: Wavelengths in millimicrons (mμ).

The nature of color: The usual first response to the word color is to think of it as a human reaction or color sensation. This discussion will be concerned mainly with the stimulus that evokes the sensation or the physical basis of color.

Color has its origin in light. Sunlight or white light from any source consists of the relatively narrow band of radiant energy or electromagnetic waves that comprise the visible spectrum. When white is passed through a quartz prism, the various wavelengths composing it are bent (refracted) at different angles, producing a spectrum according to Figure 4.10.

A surface that reflects all wavelengths of the visible spectrum appears white. If it absorbs all wavelengths, it appears black. If, on the other hand, a surface absorbs some wavelengths and reflects others, it has the color of the reflected wavelengths. For example, if the only wavelengths reflected are those above 610 millimicrons, the color will be red. Most simply stated, color is the result of selective reflection of the wavelengths of the incident light. Implicit in this statement is the fact that the kind of illumination influences the color. The light reflected by a particular color pigment may not conform sharply to a primary color. In the case of a green pigment, it may be a yellow green, a medium green, or a blue green.

The terms absorption and reflection indicate the results of a series of complex phenomena. In a pigmented film, incident illumination is partially reflected from the surface of the film and partially transmitted into it. The transmitted portion suffers refraction, diffraction, and absorption. Any part of the light that reaches the substrate is partially reflected from it and traces another complex path back through the film. Finally, part of it is refracted into the air.

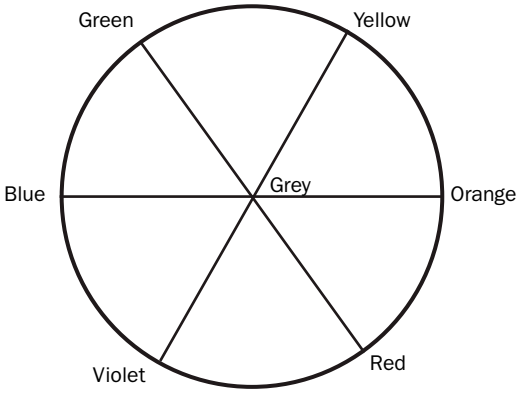


FIGURE 4.11: Color circle.

The relationship between the primary colors is made clearer by the color circle in Figure 4.11.

Colors that are opposite in the circle neutralize each other when mixed and produce neutral gray. They are said to be complementary. When any two hues that are not adjacent on the circle are mixed, there is a tendency toward grayness or lack of purity. It is a principle of decoration that complementary colors harmonize well.

Color attributes: The preceding discussion of color has been limited to hue, which is one of the three attributes of color perception. Hue is the property that differentiates the primary colors: green, yellow, orange, red, purple, and blue. There are also intermediate gradations of hue. Another attribute of color is lightness or value, the percentage reflectance of "white" light. Certain hues, notably yellow, have higher lightness than other hues such as blue, at equal chroma or purity. The lightness of any color is raised by admixture with white, lowered by admixture with black, and may be varied at will by admixture with a range of grays. The third attribute of color is chroma, also known as purity or saturation. High chroma means that the color is saturated or intense, in contrast with being diluted with gray. More definitely, chroma expresses the degree of departure from the gray of the same lightness.

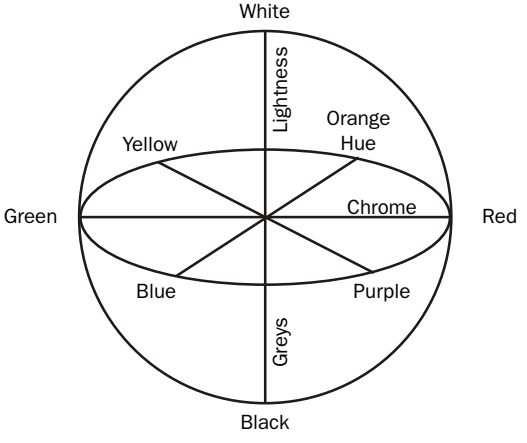


FIGURE 4.12: Color sphere.

The color sphere shown in Figure 4.12 is a device for assisting in an understanding of the attributes of color.[3]

In the use of corrosion-resistant coatings, every care must be taken in the selection of pigments to make certain that they do not reduce corrosion resistance. There are many pigments used in paint that should not be used in corrosion-resistant coatings because their incorporation would drastically reduce the resistance of the basic binder. The number of color pigments suitable for corrosion-resistant coatings is therefore limited. Fortunately, the best of the white pigments, titanium dioxide, is also inert and chemical resistant. Titanium dioxide is the whitest, brightest white available with high opacity. Not only can good white coatings be made from it, but many pastel shades as well.

Black pigments (lamp black and carbon black) are also inert and chemical-resistant. Iron oxide pigments, which are inorganic, have some very desirable chemical-resistant properties. Prior to the twentieth century, iron oxide pigments were produced from various deposits of iron oxides found in nature. Colors then covered a range of reds, purples, browns, yellows, and black. As the coatings business became more sophisticated around the turn of the century, chemical processes were developed for the manufacture of iron oxides of

TABLE 4.4: Color Pigments Useful in Corrosion-Resistant Coatings

F = Fair; G = Good; P = Poor; E = Excellent; B = Borderline

Type of Pigment			Resistant Properties			
			Exterior		Heat	
Color	Organic	Inorganic	Alkali	Acid	Durability	Resistance
Red	Toluidine Red					
	Monastral Red		P	P	G	P
		Iron Oxide Red	G	G	G	G
		Molybdenum	G	B	G	B
		Cadmium Red	B	B	G	E
Orange	Red Iron Oxide		G	G	G	G
	Molybdenum Orange		G	B	G	B
Yellow		Yellow Iron Oxide	G	G	G	G
		Chrome Yellow Zinc Chromate (Primer only)	F	F	G	P
		Nickel TiO_4 Titanate	G	G	G	G
Green		Chrome Oxide Green	G	G	G	G
		Chrome Green	F	F	G	P
	Pthalocyanine Green		E	E	E	E
Blue		Prussian Blue	P	G	G	P
	Ultramarine Blue		P	B	P	P
	Thalocyanine Blue		E	E	E	E
Black	Lamp Black		G	G	G	G
	Carbon Black		G	G	G	G
White		Titanium Dioxide	G	G	G	G
		Zinc Oxide	F	F	G	G
Metallic		Aluminum Flake	P	P	E	E
		Stainless Steel Powder	E	G	E	E
		Lead Flake	G	E	E	G

the same chemical types found in nature. These products, however, were purer in composition, richer in color, finer in particle size, and more uniform in their properties. Thus, they are the ones primarily used in corrosion-resistant coatings as we know them today.

With a few exceptions, the desirable coating properties of the iron oxide pigments are:

1. High hiding power (up to 1,000 ft^2/lb)
2. High tinting strength
3. Color fastness
4. Heat resistance (excepting yellow and black oxides)
5. Non-bleeding (insoluble in solvents)
6. Chemical resistance (unaffected by alkalies and weak acids)
7. Ease of dispersion in all vehicles (oils, resins, and water)
8. Many grades have very fine particle size, permitting dispersion in impeller and sand and bead mills.
9. High infrared reflectance (for camouflage paints)
10. High ultraviolet absorption
11. Low price[3]

Due to their favorable chemical and physical properties, iron oxide pigments are desirable for corrosion-resistant coatings when the proper color can be obtained from them. They are used not only as mass colors or individual colors, but are also used in connection with titanium dioxide to form the pastel colors.

The color of iron oxide pigments generally is not as clean as some of the organic reds, yellows, greens, and blues. However, their resistance characteristics for corrosion-resistant coatings outweigh this disadvantage. Table 4.4 shows a number of color pigments used in corrosion-resistant coatings. Depending on the coatings intended use the properties shown for the various pigments indicate the influence that the pigment will have on the effectiveness of the coating. Only those that are indicated as good or excellent should be used where severe corrosion conditions exist. Table 4.5 indicates the chemical composition of pigments that are common to corrosion-resistant coatings.

Reinforcing Pigments

Reinforcing pigments, often called extender pigments, are usually considered of minor importance as fillers or bulking materials, which are used primarily to lower cost. Reinforcing pigments, however, actually have a profound effect on the performance of most pigmented coatings and, in most cases, are far more important from a corrosion-resistant standpoint than the color pigments. Most of

TABLE 4.5: Chemical Composition of Common Pigments

Pigment	Gloss[A]	Color	Approximate Composition
WHITE HIDING PIGMENTS			
Antimony Oxide	Inert	White	90% Sb_2O_3
Basic Carbonate White Lead	Slight	White	65-75% $PbCO_2$ 35-15% Lead Hydroxide
Basic Sulfate White Lead	Slight	White	15-28% PbO
Zinc Oxide	Slight	White	98.5% ZnO (min)
Titanium Dioxide, Rutile	Inert	White	98% TiO_2
Titanium Dioxide, Anatase	Inert	White	98% TiO_2
Titanium Calcium, Rutile	Inert	White	30% TiO_2 70% $CaSO_4$
Titanium Calcium, Anatase	Inert	White	30% TiO_2 70% $CaSO_4$
Lithopone	Inert	White	30% ZnS 70% $CaSO_4$
Zinc Sulfide, Barium Sulfate	Inert	White	50% ZnS 50% $BaSO_4$
Zinc Sulfide	Inert	White	98% ZnS
EXTENDERS			
Barium Sulfate (Barytes)	Inert	——	99% $BaSO_4$
Barium Sulfate (Blanc Fixe)	Inert	——	97% $BaSO_4$
Cadmium Carbonate (Natural)	Reactive	——	98% CaCO
Cadmium Carbonate (Precipitated)	Reactive	——	98.7% CaCO
Magnesium Silicate (Talc)	Inert	——	
China Clay	Inert	——	
Mica	Inert	——	
COLORED, HIDING AND/OR INHIBITIVE PIGMENTS			
Iron Oxide, Synthetic	Inert	Red	98% Fe_2O_3
Iron Oxide, Natural	Inert	Red	70% Fe_2O_3
Yellow Iron Oxide	Inert	Yellow	99%Fe_2O_2: H_2O
Chrome Orange	Inhib.	Orange	65% $PbCrO_4$, 35% PbO
Chrome Yellow	Inhib.	Yellow	70% $PbCrO_4$, 30% $PbSO_4$
Zinc Yellow	Inhib.	Yellow	38% ZnO, 7% H_2O, 43.5% CrO_2
Chrome Green C.P.	Reactive	Green	55% $BaSO_4$, 25% China Clay 20% Color
Chrome Oxide	Inert	Green	98.5% Cr_2O_2
Iron Blue	Reactive	Blue	
Lamp Black	Stimul.	Black	98% Carbon, 3% Moisture
Carbon Black	Stimul.	Black	92% Fixed Carbon
Black Iron Oxide	Inert	Black	97.75% Iron Oxides
Red Lead	Inhib.	Orange-Red	96% Pb_2O_4, 4% PbO
Litharge	Inhib.		99% PbO
Blue Lead	Inhib.	Blue-Gray	
Aluminum Paste	Reactive	Aluminum	65% Aluminum, 35% Solvent
Aluminum Powder	Reactive	Aluminum	
Zinc Dust	Inhib.	Gray	96% Zn
Metallic Lead Paste	Inert.	Gray	90% Metallic Lead, 1% Stearic Acid, 9% Mineral Spirits

[A]Class—classified as rust inhibitive, slightly inhibitive, inert, rust stimulative, or reactive
Source: *Steel Structures Painting Manual,* Vol. 1 (Pittsburgh, PA : SSPC, 1966), p. 82, 1966.

these pigments are inorganic and, for the most part, are relatively inert materials, which can therefore be used in corrosion-resistant coatings. The carbonate pigments, which are generally not used in corrosion-resistant coatings, constitute the one exception.

Several types of reinforcing pigments are given in Table 4.6. Although there are many others that are not listed, these are considered representative. Most of them, except for the carbonate pigments, are commonly used in corrosion-resistant coatings.

Reinforcing pigments are available in many different particle sizes and in many shapes, including spheroids, needles, fibers, and plates. The particle shape is most useful in developing film density, flexibility, and film strength. Particle size and shape also influence such characteristics as opacity, viscosity, film porosity, and gloss.

Table 4.6—Types and Sources of Extenders or Reinforcing Pigments			
Chemical Type	Natural Ores	Source Synthetic (Mfg.)	Common Name
CARBONATE			
Calcium	x	x	Whiting
Magnesium	x	x	--
OXIDE			
Silicon	x (Amorphous)	x (Hydrogel)	Silica
Silicon	x (Crystalline)	x (Aerogel)	Silica
Silicon	x (Diatomaceous)	x (Pyrogenic)	Silica
		x (Arc)	Silica
		x (Precipitated)	Silica
SILICATE			
Aluminum hydrate	x (Many types)	--	Clay
Calcium	x (Wollastonite)	x	--
Magnesium	x (Fibrous)	--	Talc
Magnesium	x (Platy)	--	--
Magnesium	x (Granular)	--	--
	x (Acicular)	--	--
K, Na, Al, Fe, Li	x (Many minerals)	--	Mica
SULFATE			
Barium	x	x	Barytes, blanc fixe
Calcium	x	x	Anhydride
Calcium hydrate	x	--	Gypsum

Source: W.R. Madison, *Federation Series on Coating Technology, Unit 7, "White Hiding and Extender Pigments:* (Philadelphia, PA: Federation of Societies for Coating Technology, 1967).

TABLE 4.7: Reinforcing Pigments Used in Corrosion-Resistant Coatings

F—Fair; G—Good; P—Poor; E—Excellent; B—Borderline

		Resistant Characteristics				
Generic Type	Common Name	Alkali	Acid	Water	Weather	Physical Characteristics
Magnesium Silicate	Talc; Asbestine Asbestos	F	G	E	E	Fibrous-plate like Fibrous
Barium Sulphate	Barytes	G	G	G	G	Cubical, heavy
Silica	Diatomite; Silica Flour	P	E	E	E	Porous, hard, sharp crystals
Aluminum Silicate	Clay	F	G	F	G	Plate like
Potassium-Aluminum Silicate	Mica	G	G	G	G	Plate like, used to reduce moisture vapor transfer

The film is strengthened by various means, such as:

1. Interlocking of pigment particles;
2. Pigment-relieving stresses developed in the binder;
3. Lowering of the thermal coefficient of expansion;
4. Conducting heat away from the localized heat sites; and
5. Forming a barrier to ultraviolet radiation.

The ratio of reinforcing pigment to binder is very important. It is important for the reinforcing pigment to be sufficiently covered and wetted by the binder. As indicated previously, the wetting of the pigment by the binder is a major step in the production of maintenance or corrosion-resistant coatings. The completeness of the dispersion, and therefore the wetting, has a very important bearing on the durability, gloss, and application characteristics of the coating. Table 4.7 lists some of the properties of the principal reinforcing pigments used in corrosion-resistant coatings.

Inhibitive Pigments

Inhibitive pigments are principally used in primers or first coats and in coatings that use the concept of inhibition rather than impermeability. These are pigments that react with the moisture absorbed by the coating to form sufficient ions, which then react with the underlying metal surface to passivate it and make it more corrosion-resistant. These pigments are used primarily as atmospheric

TABLE 4.8: Inhibitive Pigments Used in Some Primers for Corrosion-Resistant Coatings	
Pigment	Solubility in 1 L H_2O at Equilibrium, g of CrO_3
Zinc Chromate	1.1
Strontium Chromate	0.6
Basic Zinc Chromate	0.02
Barium Chromate	0.001
Lead Chromate	0.0005
Lead Silica Chromate	0.0005
Red Lead	essentially insoluble
Zinc Powder	provides cathodic protection to substrate

Source: Source: C.G. Munger, C.K. Othmer: Encyclopedia of Chemical Technology, "Coatings, Resistant," 3rd Ed., Vol. 6 (New York, NY:John Wiley & Sons, 1979), pp. 456–578.)

TABLE 4.9: Metallic Pigments Used for Corrosion Resistance

Generic Type	Common Name	Alkali	Acid	Water	Weather	Physical Characteristics
Aluminum	Aluminum Flake	NR	NR	E	E	Creates shingle effect, protects binder, increases moisture upon transfer resistance.
Stainless	Stainless Flake	E	E	E	G	Does not leaf as well as aluminum flakes. Reinforces binder without reducing chemical resistance.
Lead	Lead Flake	E	E	E	E	Does not leaf as well as aluminum flakes. Excellent chemical and water resistance.
Copper	Copper Flake	NR	NR	G	F-G	Leafs well, good copper color, chemical resistance only fair. Has a good anti-flaking property.
Zinc	Zinc Flake	NR	NR	E	E	Provides some cathodic protection to steel. Reinforces some organic binders. May be used with zinc powder for reinforcing purposes.

coatings and not for immersion or constantly wet conditions, since some are so soluble that osmosis could draw water into the coating, creating blisters. This has been one of the difficulties with the use of inhibitive pigments. They are, however, effective in reducing under-film corrosion in many atmospheric conditions when used properly. Table 4.8 lists a few of the inhibitive pigments found in primers for corrosion-resistant coatings. This table also gives the solubility of the various materials; the ones with the lower solubility being the ones preferred for corrosion resistance.

Metallic Pigments

Metallic pigments are categorized separately because of their unique properties. They are metals that, except for zinc dust, are generally in the form of flakes or flat platelets. This is true not only for aluminum and stainless steel pigment, but also for the various colors of bronze, which are primarily metallic copper flake. The flat plate-like structure is important in that it tends to reinforce the binder. In leafing pigments, it creates a shingle effect that prevents actinic (ultraviolet) rays of the sun and light from penetrating into the binder. The flat, plate-like structure often improves the adhesion of the coating as well.

The most common of the metallic pigments is produced through a wet ball milling process, which uses steel balls as the grinding media. The aluminum metal is in the form of an atomized powder and is charged into the ball mill in addition to stearic acid and mineral spirits. It is then milled long enough to produce flakes of the desired fineness. The stearic acid aids in the production of the flat plates, and it also imparts the ability to float on the surface of the coating vehicle. This same general procedure is used for the other plate pigments such as stainless steel, lead, and copper.

Aluminum pigment is divided into two classes: leafing pigments, which float to the surface of the coating film and impart the metallic color; and non-leafing aluminum pigment, which remains uniformly distributed through the film and gives the natural gray color of aluminum without the metallic luster. From a corrosion-resistance standpoint, the leafing aluminum type pigment is the most important. The force that causes the leafing pigments to concentrate on the surface is the convection currents caused by evaporation of the solvent in the coating. Once the flakes reach the surface of the coating prior to drying, they are held in place by interfacial tension, and as the solvent continues to dry, the viscosity of the coating increases and prevents further movement of the aluminum pigment.

Aluminum coatings have characteristic qualities almost irrespective of the binder. The hiding power of the coatings is excellent, as one coat will completely hide the underlying surface. This does not mean that in corrosive situations only one coat should be used. As with any coating, the thickness is important both to the durability and the effectiveness of the coating. The flake of the aluminum or other metal is completely opaque to light and the shingle effect of the flakes assures a continuous film. The binder is thus completely shaded from the effect of actinic rays and other forces that can damage the binder. As mentioned previously, the shingle effect of the leafed flakes materially reduces the moisture vapor transfer rate through the coating. Any moisture or other gas must travel a long distance around each individual flake in order to reach the substrate. Since sunlight and moisture are the principal factors in film deterioration, aluminum paints have outstanding durability as exterior topcoats.

The use of aluminum pigment is not limited to thin vehicles alone, but has been incorporated into heavy mastic coatings, and even very heavy roof coatings, which still provide a bright metallic surface to reflect the sun's energy. The principal way in which aluminum

coatings protect iron from corrosion is in eliminating the access of air and moisture to the substrate. The aluminum metal itself does not have any cathodic effect, as do zinc-rich coatings. So for best results, they must be applied over a good anti-corrosive primer of some of the best zinc-rich materials. Some excellent corrosion-resistant coatings have been developed through the use of IOZ-rich primers followed by aluminum-pigmented topcoats using vinyl, epoxy, asphalt, or other binders.

Leafing aluminum pigments are outstanding in heat resistance and have been used effectively for coating stacks at 800 to 1,000 °F. Silicone alkyds have been used as the binder; however, the most effective for high temperature is a pure silicone binder with aluminum leafing pigments.

The other leafing metallic pigments, such as stainless steel, lead, and copper, act in much the same way as the aluminum. Lead flake is preferred over the other materials from the standpoint of chemical resistance. Aluminum flake is affected by both acid and alkali, while the lead flake has excellent resistance to both. The same is true of the stainless steel powder.

Zinc is a metallic pigment that is usually used as a dust, although some zinc has been formed into flakes. It is principally used in anticorrosive coatings, which use the CP effect of the zinc metal. Nano-sized particles of zinc pigments have been used by some manufacturers beginning in the decade after 2000 with very promising results in thicker film formation without mud cracking. Dispersion methods are different and cost of the pigments is substantially higher than commonly available zinc powders. (A more detailed discussion of zinc-rich coatings is contained in Chapter 6.) Table 4.9 summarizes the general properties of the metallic pigments.

Solvents

Most painters do not realize the importance of solvents, or thinners, in the formation of the coating and in the development of the most effective coating film. Although solvents do not remain in the coating, they can affect the coating in many different ways (i.e., by creating porosity, discoloration, poor gloss, floating of pigment, fish-eyeing, poor coating strength, and lack of adhesion). All of these things can happen if the proper solvent or solvent combination is not used in a protective coating. The proper use of solvents will create a smooth, clear resin film with a good gloss, and the coating film will have the inherent strength and other properties of the basic resin.

Most coatings are made with multiple solvents; in fact, there are very few that use a single solvent alone. As in most cases, particularly with the synthetic resin binders, the combination of the solvents will provide a better film than where one solvent is used alone.

The choice of solvents influences viscosity, flow properties, drying speed, spraying or brushing characteristics, and gloss. Each type of binder will have its own specific combination of solvents that will provide the best film. There is no universal solvent for protective coatings; a best solvent for one may not be practical with another. Asphalt, for instance, is readily dissolved by hydrocarbon solvents such as mineral spirits or toluene; on the other hand, it would not be dissolved by alcohol. Shellac and some epoxy resins are readily dissolved by alcohol, but would not be readily dissolved by aliphatic hydrocarbons. Vinyl resins are readily soluble in ketone solvents, but are precipitated out of solution by alcohols or aliphatic hydrocarbons.

It is important to emphasize solvents and the fact that they are specific for individual binders because, not realizing this, many painters add any solvent that happens to be available. This, more often than not, causes coating problems after a period of time, if not immediately. A painter, for instance, may add mineral spirits to a vinyl coating as a thinner. Vinyl coatings will tolerate a small amount of mineral spirits without precipitation; however, because it is a slow drying material and the active solvents in the vinyl solution are more rapid, it remains in the coating until the last of the active solvents has evaporated. At this time, it is squeezed out both underneath and on top of the film. The resulting coating has no adhesion whatsoever.

Solvent Types

Active Solvents

The primary solvents for a particular binder are known as active solvents. In the case of vinyl resins, the active solvent would be the ketones. In the case of chlorinated rubber, it would be aromatic hydrocarbons. Active solvents are the ones that completely dissolve the resin and form a true solution of it.

Latent Solvents

Latent solvents are not good solvents for the binder and may only swell the binder at room temperature. At somewhat elevated temperatures, they may become sufficiently active so as to form a solution. On cooling, however, it is likely that the solution would turn to a gel. Latent solvents are used in coatings with active solvents to regulate the solvent evaporation and in some cases, improve film properties.

Diluents

Diluents are materials that are not true solvents for the resin, but which, when combined with active solvents and/or latent solvents, can be used to dilute the solution. Diluents are used for a number of purposes. One is to improve the film properties, such as flexibility of epoxies. A combination of an active solvent and a diluent, however, may provide a smoother, stronger film than when the film is cast from the active solvent alone. In many cases, they are also used to reduce cost. Both nonreactive and reactive diluents are commonly used as a means of meeting the VOC requirements that would otherwise be impossible with some resin systems using only active or latent solvents. Examples of reactive diluents are mono- and difunctional glycidyl ethers (for epoxy systems) and certain oxazolidine-based materials for urethanes.

Solvent Combination Characteristics

Compatibility

More often than not, two or more resins are combined in the formulation of one coating. The solvent combination is often used to improve the compatibility of the various resins, one with another. This is very important. If all of the resins are not fully compatible, a poor film oftentimes results. On the other hand, with a proper solvent combination, the compatibility of the resins may be maintained and a good film cast from the solvent combination. All three of the above solvent types (active, latent, and diluent) can have an effect on the compatibility of the solution.

TABLE 4.10: Aliphatic Hydrocarbon Solvents

Solvents	Evaporation Rate N. Butyl Acetate=1	Distillation Range °C	FlashPoint C losed Cup °C	Pounds/Gal.
Lacquer Diluent	4.0	96-105	6	6.1 – 6.3
V M & P Naptha	1.5	114–126	13	6.2 – 6.4
Mineral Spirits (odorless)	0.10	180 -185	55	6.3 – 6.5

Source: *Federation Series on Coating Technology, Unit 6, Solvents,* Federation of Societies for Coating Technology, Philadelphia, PA, p. 46, 1967.

TABLE 4.11: Aromatic Hydrocarbon Solvents

Solvent	Evaporation Rate N. Butyl Acetate = 1	Distillation Range °C	Flash Point Closed Cup °C	Pounds/Gal.	Sp. Gr.
Benzol	5	79–80	−12	7.34	0.885
Toluol	2	110–111	5	7.25	0.870
Xylol	0.6	139–141	28	7.25	0.869
High Flash Naptha	—	170	38	7.25	0.870

Source: *Federation Series on Coating Technology, Unit 6, Solvents,* Federation of Societies for Coating Technology, Philadelphia, PA, p. 46, 1967.

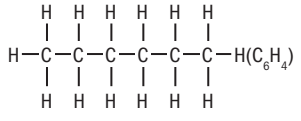
Solvent Retention

Another important characteristic of the solvent combination is solvent retention. We know that the resin dissolves in the solvent and that the solvent is used to put the resin in a state that provides proper application. On the other hand, the solvents can also dissolve into the resin, causing high solvent retention in the coating. In many cases, solvent retention is not a positive characteristic in that it can reduce adhesion and the water and chemical resistance of the coating. The retention of a slow evaporating solvent in a film can reduce the water resistance and result in blistering of the film and loss of adhesion over a period of time.

Common Solvent Groups

Aliphatic Hydrocarbons

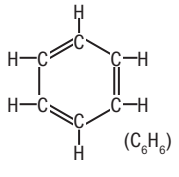
Aliphatic hydrocarbons may also be called paraffins. Chemically, they are open-chain hydrocarbons, which are sometimes called straight-chain hydrocarbons, although this can be somewhat of a misnomer. Their schematic chemical diagram is:



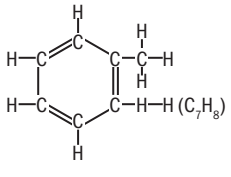
The most common of these are mineral spirits or V M & P naphtha. Mineral spirits is often called painter's naphtha. It is a relatively high boiling petroleum product used for dissolving asphalts, oils, and alkyds. Table 4.10 lists the common aliphatic hydrocarbons and their properties

Aromatic Hydrocarbons

Aromatic hydrocarbons are chemicals that have a closed-chain six-carbon group as a principal part of the molecule. The simplest chemical of the family is benzene. This chemical family includes toluene, xylene, and some of the higher boiling homologs. They are major solvents for chlorinated rubber, coal tar, and certain alkyds, and are used as diluents in combination with solvents for vinyl, epoxies, and polyurethane materials. A chemical diagram for the aromatic hydrocarbons is:



Benzene



Toulene

Table 4.11 gives the properties of the principal aromatic solvents used in protective coatings.

Ketones

Oxygenated hydrocarbons of the acetone family are ketones, which include methyl ethyl ketone and methyl isobutyl ketone. They are the most effective solvents for vinyls and are often used in epoxies and other resin formulations. The chemical formula for acetone is:

TABLE 4.12: Ketones

Solvent	Evaporation Rate N. Butyl Acetate = 1	Distillation Range °C	Flash Point Closed Cup °C	Pounds/Gal.	Sp. Gr.
Acetone	9	57–58	−10	6.59	0.792
MEK (Methyl Ethyl Ketone)	4	79–81	−4	6.71	0.806
MIBK (Methyl Iso Butyl Ketone)	1.6	114–117	22	6.68	0.802
MIAK (Methyl Iso Amyl Ketone)	0.5	140–148	40	6.77	0.814
Cyclo Hexanone	0.2	154–161	54	7.88	0.945
Diacetone Alcohol (Tech.)	0.2	60–170	15	7.64	0.909
Diisobutyl Ketone	0.2	163–173	49	6.72	0.808
Isophorone	0.03	205–220	96	7.68	0.923

Source: *Federation Series on Coating Technology, Unit 6, Solvents,* Federation of Societies for Coating Technology, Philadelphia, PA, p. 46, 1967.

TABLE 4.13: Esters

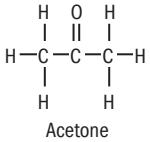
Solvent	Evaporation Rate N. Butyl Acetate = 1	Distillation Range °C	Flash Point Closed Cup °C	Pounds/Gal.	Sp. Gr.
Ethyl Acetate (95%)	4.1	75–80	13	7.47	0.897
N. Propyl Acetate	2.3	88–103	18	7.35	0.885
N. Butyl Acetate	1.0	118–128	38	7.34	0.883
Amyl Acetate (95%)	0.4	135–150	41	7.29	0.876

Source: *Federation Series on Coating Technology, Unit 6, Solvents,* Federation of Societies for Coating Technology, Philadelphia, PA, p. 46, 1967.

TABLE 4.14: Alcohols

Solvent	Evaporation Rate N. Butyl Acetate = 1	Distillation Range °C	Flash Point Closed Cup °C	Pounds/Gal.	Sp. Gr
Methyl Alcohol	6.0	65	16	6.6	0.793
Ethyl Alcohol	2.3	70-80	24	6.76	0.812
Propyl Alcohol	1.0	96-99	31	6.70	0.806
Iso Propyl Alcohol (91%)		79-84			
Butyl Alcohol	0.5	116-119	46	6.75	0.811
Cyclo-Hexanol	0.1	160-162	68	7.91	0.948

Source: *Federation Series on Coating Technology, Unit 6, Solvents,* Federation of Societies for Coating Technology, Philadelphia, PA, p. 46, 1967.

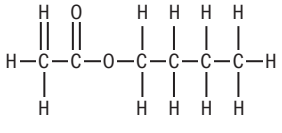


Acetone

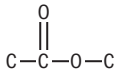
Table 4.12 gives some of the properties of the principal ketones used for coatings.

Esters

Esters are also oxygenated hydrocarbons. They usually have a very distinctive and, for the most part, pleas- ant odor. (It is usually a fruity one since banana oil is one of the esters.) They can be used as latent solvents for vinyls and are commonly used in epoxy and polyurethane formulations. Recently, the acetate esters have been used in blends with newer esters, such as ethyl 3-ethoxypropionate and butyl and pentyl propionate, to meet the needs of higher solids and/or electrostatically sprayed coatings. These help the formulator meet the more stringent VOC emission restrictions. The chemical formula for one of the ester family is:



Butyl Acetate



Ester Group of the Molecule

Alcohols

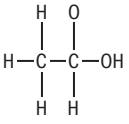
Alcohols are oxygenated hydrocarbons and are good solvents for highly polar binders such as phenolics. Some alcohols are also used in connection with epoxies. Methanol is the lowest homolog in the alcohol series. The chemical formula for ethyl alcohol, the most

TABLE 4.15: Ethers–Alcohols

Solvent	Evaporation Rate N. Butyl Acetate = 1	Distillation Range °C	Flash Point Closed Cup °C	Pounds/Gal.	Sp. Gr.
Ethylene Glycol Mono Methyl Ether (Methyl Cellosolve)	0.5	124–126	46	8.03	0.966
Ethylene Glycol Mono Butyl Ether (Butyhl Cellosolve)	0.3	132–137	54	7.74	0.931
Ethylene Glycol	0.06	166–173	74	7.51	0.902

Source: *Federation Series on Coating Technology,* Unit 6, Solvents, (Pittsburgh, PA: Federation of Societies for Coating Technology, 1967), p.46.

common of the alcohol family, is:



Ethyl Alcohol

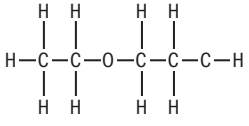


Alcohol Group of the Molecule

The properties of a series of alcohols used in protective coatings are given in Table 4.14.

Ethers

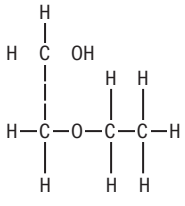
Ethers[6] are not often employed as a solvent by the coating industry because of their flammability. However, the glycol ethers are very common. They possess excellent solvency for a very wide range of resins by virtue of the presence of both ether and alcohol groups. They are especially good solvents for epoxies and also serve well in polyester resins, acrylics, and cellulosics, including nitrocellulose. They are excellent coupling solvents oil blends with poorly miscible solvent systems. Their water miscibility has led to their use as co-solvents and coalescents in a wide range of waterborne systems. Glycol ethers, such as ethylene glycol monohexyl ether and diethylene glycol monohexyl ether, are proving to be ideal solvents for VOC reduction. It is used as a thinner for latex and emulsion coatings since, in this case, the resins are dispersed rather than dissolved in the water. On the other hand, water is used for several of the IOZ silicate materials, and in that case, acts as a true solvent. There are also some resins currently available that likewise are truly dissolved in water. While these have not been used as extensively as solvent-borne resins for corrosion-resistant coatings, water-dissolved corrosion-resistant resins have improved substantially since 2000 so their use is growing, particularly in areas with extremely low VOC emission limits.



Ethyl Ether



Ether Group of the Molecule



Ethylene Glycol Mono-Ethyl Ether (Cellosolve)

Table 4.15 gives properties of some of the common glycol ethers.

Water

Water cannot be ruled out as a volatile solvent since it is the most general solvent of any existing material.

Miscellaneous Solvents

Thetrahydrofuran is a cyclic ether with very strong solvent characteristics for a wide variety of resinous materials such as acrylates, styrene, PVC, rubbers, and epoxies. It is even a solvent for high molecular weight homopolymers. The nitroparaffins are also good solvents for many synthetic resins. The principal member of the group is 2-nitropropane, which has relatively low toxicity and evaporates at about the same rate as butyl acetate. It is a solvent for nitrocellulose, acrylics, epoxies, and when mixed with toluol, is a very good solvent for vinyl chloride acetate resins. Table 4.16 indicates the properties of these solvents.

Plasticizers

Plasticizers are important in many coatings since many of the coating resins are too hard or too brittle in their original state to form a good permanent coating. A good example of this is chlorinated rubber, which in its original state is a very horny-textured substance

TABLE 4.16: Miscellaneous Solvents

Solvent	Evaporation Rate N. Butyl Acetate = 1	Distillation Range °C	Flash Point Closed Cup °C	Pounds/Gal.	Sp. Gr.
Tetra Hydro Furan	6.0	65–68	−15	7.39	0.888
2 Nitro Propane	1.1	118–122	38	8.24	0.992
Trichlorethylene	4.5	86–88	——	12.23	1.466

Source: *Federation Series on Coating Technology,* Unit 6, Solvents, (Pittsburgh, PA: Federation of Societies for Coating Technology, 1967), p.46.

TABLE 4.17: Water Permeability of Plasticized PVC Films

$P \times 10^8$ [(g/hr)(cm)^2 (mmHg)/(cm))]

	Mole % of Plasticizer					
Plasticizer	0	4	6	8	10	12
Tricresyl Phosphate	0.50	0.55	0.65	0.92	1.74	2.06
Dibutyl Phosphate	0.50	0.60	0.94	1.33	2.46	44.02
Dioctyl Phthalate	0.50	0.64	1.16	1.98	3.05	4.97
Dibutyl Adipate	0.50	0.96	1.72	2.67	4.08	5.89
Dioctyl Adipate	0.50	1.45	3.00	4.02	6.81	10.95
Dibutyl Sebacate	0.50	1.09	2.13	3.30	5.00	8.64
Dioctyl Sebacate	0.50	1.64	3.20	5.32	8.03	12.05

Note: For comparison of mole %. DOP concentration in PHR (parts/hundred of resin) are: 0 26 40 54 69 86.

Source: K. Sears, *Federation Series on Coating Technology,* Unit 22, Plasticizers. (Philadelphia, PA: Federation of Societies for Coating Technology, 1974).

that does not form a good coating because it is too brittle and gradually cracks up. On the other hand, chlorinated rubber is a very chemical-resistant material and does have film-forming properties. In order to become useable as a coating, it is necessary to add other materials to chlorinated rubber that will soften it, provide some extensibility, and decrease its brittle characteristics. To form highly corrosion-resistant coatings, softer resinous materials, such as chlorinated paraffin, are added to it to act as a plasticizer. Where some oil characteristics are practical, alkyd resins can be used as a plasticizer for the coating. Thus, materials that are not practical coatings in themselves (e.g., chlorinated rubber) can be formed into good useable coating materials by the use of modifying resins.

There are a number of theories concerning how plasticizers work. The easiest and most understandable is that the plasticizers are permanent solvents for the resin. As with any solvent, they tend to separate the large molecules so that they then become more plastic, less brittle, more extensible, and pliable. Plasticizers, as such, can be almost any material, depending again on the material that is to be plasticized (e.g., water acts as a plasticizer for clay, resins can act as plasticizers for chlorinated rubber, and high molecular weight or high boiling point oxygenated solvents act as plasticizers for polyvinyl chloride materials). Almost all PVC materials are plasticized in one way or another, and all of the vinyl sheets are made with a substantial amount of plasticizer for handling and workability.

It is essential that coatings utilize the plasticizer principle in order to obtain materials with practical properties from an application, corrosion resistance, and film standpoint. Proper plasticizers add flexibility to the coating, help prevent cracking and checking upon aging, and add compatibility to the resin system. This is particularly true where two or more resins are mixed in order to obtain desired coating characteristics. A plasticizer as a permanent solvent for both resins; it aids in maintaining a mixed resin in a compatible state.

Plastisols are a good example of the use of plasticizers in a coating. In this case, there are no other solvents involved. The resins and the plasticizer are mixed, and, as long as they are cold, there is little activity of the plasticizer on the resin. In other words, the resin is not soluble in the plasticizer in a cold state. On the other hand, when the mixture is heated, the plasticizer becomes an active solvent and the resin and plasticizer become liquid. On cooling, they then form a continuous coating.

There are both internal and external plasticizers for coatings. Internal plasticizers are those where a large molecule is copolymerized into the resin molecule in such a way that the polymerized resin becomes permanently flexible, and extendable to a greater degree than the original material without copolymerization. The use of vinyl acetate as a copolymer for vinyl chloride is an example of this. The combination of the two is a softer, more flexible, and extendable material. The advantage of an internal plasticizer is that it is permanent and a part of the molecule that does not leech out, or is extracted by water or other solvents. Other characteristics of the original resin, however, may be lost in this process so that internal plasticization is not without its drawbacks.

External plasticization is the use of a second material as a permanent solvent in order to accomplish the plasticizing action. It can generally be said that as the external plasticizer content of a coating is increased, the water permeability also increases (Table 4.17). Also, with the same molar concentration of plasticizer, the more efficient plasticizers give higher permeability. Tricresyl phosphate, for example, being a poorer plasticizer than some of the others, shows lower permeability to moisture. All factors being equal, the lower permeability would indicate increased corrosion resistance.

There are exceptions, however. In tests on plasticized PVC film exposed to 12 environments ranging from distilled water to various acids, bases, and salts, the phthalates were the least attacked. The next in order were the phosphates, and then the adipates and polymerics. Polyvinyl chloride maintenance paints, plasticized with a low concentration of tricresyl phosphate and chlorinated biphenols, have withstood weather, seawater, and chemical plant atmospheres for up to 20 years with little degradation of the paint film and no corrosion of steel or concrete substrates.

Some plasticizers can improve the exterior weather and light resistance of polymers particularly PVC. Plasticizers containing epoxy groups, such as low molecular weight epoxy resin, can help the stability of plasticized PVC formulations where temperatures are rather high, as in southern desert areas. Weather resistance is enhanced since the epoxy compounds improve heat stability.

Organic phosphates as a sole plasticizer in PVC are not good. 2-ethyl hexyl diphenyl phosphate is perhaps the best. In blends with dioctyl phthalate (DOP) and similar plasticizers, however, they can add significantly to outdoor durability. This is true of both pigmented films and thin, clear films. Unit 22 of the Federation Series on Coatings states that a 4-mil film with no UV screener, plasticized with ethyl hexyl diphenyl phosphate, will last one year in Miami, Florida. Plasticized with DOP, it will last 1 ½ years.4 If 10% of the DOP is replaced with 2-ethyl hexyl diphenyl phosphate, however, the film will last about 2 1/2 years.5

Other coating resins can also use plasticizers. Acrylics are primarily internally plasticized for use as surface coatings. This is done by copolymerization with other compatible monomers. Actually, a wide variety of external plasticizers are compatible with acrylics. These include the phosphates, phthalates, adipates, and some epoxidized oils. One of the materials, which has been most widely used, is butyl benzol phthalate, which served as the standard for acrylic lacquers for comparison to plasticizers. Lacquers of this type are used for such things as automobiles and aircraft. Chlorinated rubbers have been previously discussed. For highly corrosion-resistant coatings, polymeric plasticizers, such as chlorinated biphenyls and terphenyls, have been used. Since these are no longer available, chlorinated paraffins and aromatic phthalates are used. Very corrosion- and chemical-resistant coatings can be obtained from these combinations. Without the plasticizers, the excellent resistant properties of chlorinated rubber could not be utilized.

Epoxy resins may be modified with common plasticizers, which will reduce the original viscosity of the epoxy and lead to easier handling and application. On curing, however, the final resin or coating is softer, has poorer impact resistance, and less resistance to extraction by water and solvents. Epoxy resins used for coatings are, for the most part, internally plasticized. The materials most used are the various polyamide resins, which react with the epoxy resin in almost any concentration. The coatings derived can vary from a very hard to a very soft coating with considerable elongation. Polyamide acts both as a reactive internal plasticizer and a cross-linking and curing agent for the epoxy. Good corrosion-, chemical-, and water-resistant coatings are obtained from the epoxy polyamide combination.

Plasticizers thus have a significant use in the formation of corrosion-resistant protective coatings. They add flexibility, increase compatibility, and prevent cracking and checking of the film, but the actual resistance of the films to the environment can be increased as well.

Miscellaneous Components

There are many coating components that are included in various formulations for many different reasons. They are usually in small quantities, with the level of use seldom exceeding 1 to 2% of the entire formulation. Nevertheless, they contribute to ease in manufacture, package stability, ease of application, appearance, and quality of resistance. Only one of these components, listed as follows, actually has an effect on corrosion resistance.

Biologic Inhibitors

The growth of fungus on a coating surface gives it a very dirty, objectionable appearance. No surface is free of mildew growth since even a very thin film of dirt and moisture can prove to be a nutrient for the organisms. The effect of mildew will be more pronounced, however, if the coating contains ingredients that are also nutrients for the specific fungi. If these nutrients are present, the entire coating can be destroyed (Figure 4.13). A polyamide epoxy, for example, was rapidly destroyed in a sewer because of the nutrient value of the polyamide. An amine-cured epoxy, however, showed no sign of decomposition under the same conditions.

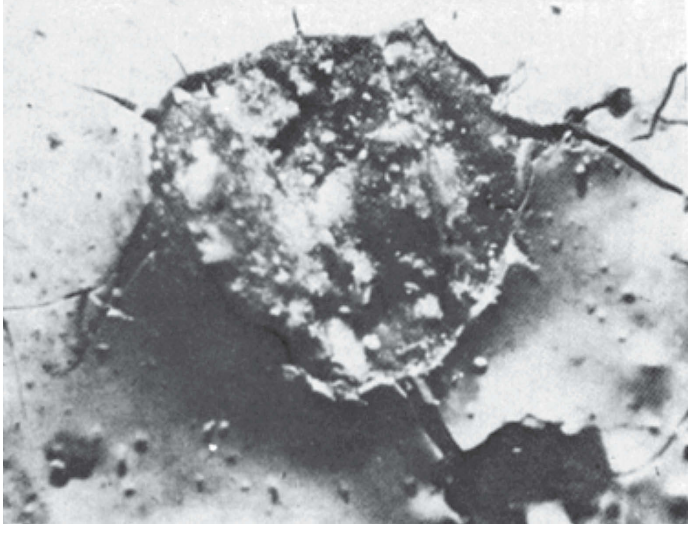


FIGURE 4.13: A photomicrograph of mildew erupting through the coating surface. In this case, the mildew is living on the coating ingredients and so is not just on the surface. Source: W.J. Stewart, *Federation Series on Coating Technology*, Unit 11, "Driers and Additives," (Philadelphia, PA: Federation of Societies for Paint Technology, 1969).

Vehicles vary greatly in their resistance to biologic growth. Common oils, such as linseed oil, are most susceptible. Reaction products of oils and other resins, such as alkyds, epoxies, and urethane esters, increase in resistance, while a high polymer, such as a vinyl chloride acetate resin, is highly resistant. Most other polymers, such as epoxies, chlorinated rubber, urethane, and so on, are also highly resistant unless they are modified with a nutrient resin.

The most foolproof way of combating fungus or bacterial attack is to formulate with nonnutritive materials, starting with the basic resin and continuing through the pigments, plasticizers, and so forth. Even if biologic growth inhibitors are necessary, a highly resistant formulation will allow maximum advantage to be contributed by the biocides. Mercury and copper compounds have proven most successful in preventing objectionable fungus growths. Phenyl mercury compounds provide the best protection. Their use, however, is objectionable and even prohibited under many conditions. Two organic phtalamide fungicides have been found effective at low concentrations while at the same time having a low toxicity.

Algae is one of the serious fouling problems aboard ships, particularly the very large cargo carriers, because of the depth of the boot-topping (area between the light and heavy load lines). Algae and weed growth and crustaceans reduce the cruising speed of a ship, increase the use of fuels, and add to emissions into the ozone layer of the atmosphere. Copper, copper oxide, and tributyl tin com-

pounds have been used to prevent this problem. Coal tar, vinyl, epoxy, and IOZ coatings containing either copper or tin compounds, or both, have been effective.

The International Convention on the Control of Harmful Anti-fouling Systems on Ships (AFS) (2001) banned the use of tin-containing anti-fouling coatings. Manufacturers have turned to sophisticated systems containing copper in various forms along with co-biocides as a means of obtaining equivalent dry-docking intervals previously obtained by the use of tin compounds. This is discussed in greater detail in Chapter 12, "Coatings for Marine Vessels."

The finished coating is the sum of all its individual parts. The resins, pigments, plasticizers, solvents, and possible special additives all contribute to the effectiveness of the coating and its life under corrosive conditions. While all of these ingredients can be combined and sealed in their container, the liquid coating is still of no value until it is applied to the substrate, formed, and cured in place. It is not a coating and it is not at all effective until this last step is taken. Time, or its life after formation, will determine the true effectiveness of the material.

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5 Corrosion-Resistant Organic Coatings

Corrosion-resistant organic coatings are the high-performance materials that give long-term protection to industrial, marine, chemical, and petroleum structures from serious corrosion conditions caused by marine atmospheres, chemicals, and industrial processing. They are, for the most part, specialty products designed to resist many different corrosive conditions as linings or coatings. They are not only resistant to corrosion, but are used to prevent contamination of liquids as well (e.g., refined oil, iron-sensitive chemicals, and food products). Whatever the problem (protection against corrosion or contamination), the corrosion-resistant coating is the key material that separates two reactive materials.

Corrosion-resistant coatings are also known as maintenance coatings, as compared to industrial product finishes. The former are, for the most part, applied in the field to either existing or new structures and are subject to all of the difficulties of field application and field curing. The latter, however, are applied under very carefully controlled conditions of both application and cure. The actual coating materials could generically be quite similar and yet, because of the differing methods of application, the two types of products may be quite different in their basic formulation.

There is an important distinction to be made between these two approaches to protective coatings because there is an overlap in the materials used and because many pieces of equipment (e.g., motors, pumps, etc.) are coated at the time of manufacture (in-plant). Because of such controlled application conditions, it could be assumed that these plant-applied coatings are superior to the field-applied ones. This may be a poor assumption, since an epoxy product finish can be a very different coating from a corrosion-resistant epoxy applied in the field.

The product finish, for instance, may consist of two coats of an epoxy ester machinery enamel compared to a 10 to 12 mils (250 to 300μm) high-build, field-applied epoxy coating. The life expectancy of these two epoxy materials would be quite different under the same actual operating conditions. This often becomes obvious in the field when a manufacturer supplies pre-painted equipment, and the new structure is coated by the general contractor or an on-the-job painting contractor. Once the unit is in operation, the manufactured item, even though it is supposedly coated with a similar generic coating, often fails a considerable amount of time before the field-applied material. This chapter will consider only the corrosion-resistant, field-applied organic coatings.

Protective coatings can be divided into several classes according to the basic chemical reactions involved in film formation. These classifications are given in Table 5.1, together with the principal generic coating materials in each class. Some of these generic materials can be further classified according to the individual materials, which also may be significant from a protective coating standpoint. Examples of this are epoxy coatings, which can be broken down into epoxy amine coatings and epoxy polyamide coatings, or urethane materials, which can be broken down into aromatic isocyanate-cured urethanes, aliphatic isocyanate-cured urethanes, and moisture-cured urethanes. Each of the subdivisions has its own properties.

Natural Air-Oxidizing Coatings

The classification of natural air-oxidizing coatings is included here not because of its overall importance in the corrosion-resistant coating field, but mainly because the corrosion engineer may encounter areas where such materials can do an effective job. Today, oil-type coatings are commonly used for wood structures, since it is difficult to improve on the penetrating characteristics of an oil as compared with the much higher molecular weight synthetic resin materials that tend to remain on the surface of wood. Because of their highly penetrating characteristics, there may be areas and conditions where a drying oil coating could prove to be more effective than some of the more sophisticated generic materials. Oils are also combined with many other resins to form drying oil varnishes. One of these materials, which appears to be worthy of comment, is Tung oil phenolic varnish. Tung oil is a fast-drying material, since it has three conjugated double bonds, and, when combined with phenolic resins, provides an air-drying film of maximum film hardness, excellent water resistance, and good flexibility and toughness.

Prior to the development of resins such as vinyls or epoxies, the Tung oil phenolic varnish, when properly formulated, made a very corrosion-resistant coating. For example, two coats of a red lead Tung oil phenolic primer and two coats of black Tung oil phenolic topcoat were applied to floats carrying a dredging pipe from a large seagoing dredge. The coating, which was applied over an abrasive-blasted surface, was a good, even coating. Even after several years in this severe service, the coating maintained the pontoons in essentially a corrosion-free condition. Chemically, natural oils are triglcerides (i.e., a combination of one molecule of glycerine [glycerol] and three molecules of long-chain fatty acids). These are combined through an ester linkage to form the oil.

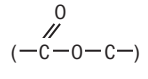
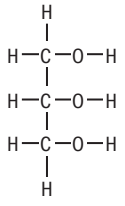


TABLE 5.1: Protective Coating Classifications

Basic Coating Formation	Generic Coating Material
Natural Air-Oxidizing Coatings	Drying Oil Tung Oil Phenolic Varnish
Synthetic Air-Oxidizing Coatings	Alkyds Vinyl Alkyds Epoxy Esters Silicone Alkyds Uralkyds
Solvent Dry Lacquers	Nitrocellulose Polyvinylchloride-Acetate Copolymers Acrylic Polymers Chlorinated Rubber Coal Tar Cutback Asphalt Cutback
Co-reactive Coatings	Epoxy Coal Tar Epoxy Polyurethane Polyaspartics Polyesters & Vinyl Esters Polysiloxane Silicone
Emulsion-Type (Coalescent) Coatings	Vinyl Acetate Vinyl Acrylic Waterborne Acrylic Acrylic Epoxy
Heat-Condensing Coatings	Pure Phenolic Epoxy Phenolic Epoxy Novolacs
100% Solid Coatings	Coal Tar Enamel Asphalt Polyesters Epoxy Powder Coatings Vinyl Powder Coatings Plastisols Furan Materials

Oils are generally liquids, while fats, which are also triglycerides, are solid at room temperature. Lard is the most common example of a fat. The difference between fats and oils is that fats are triglycerides formed with saturated fatty acids (no double bonds) and oils are formed with unsaturated fatty acids (one or more double bonds). Glycerine is a trihydric alcohol, chemically designated with the formula:



(5.1)

The formula for linolenic acid, which has a triple double bond, is shown in Figure 5.1. The numbers in parentheses indicate the carbon atom that is unsaturated in the 18-carbon chain molecule.

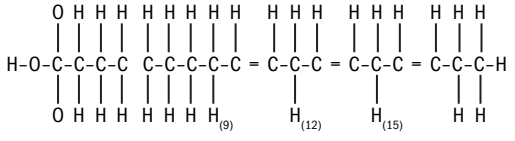
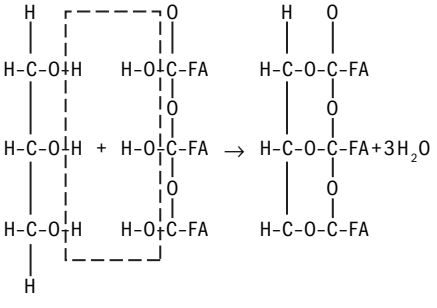


FIGURE 5.1: Chemical formula for linolenic acid.

When the glycerine and the fatty acid are combined into an oil, the chemical formula shown in Figure 5.2 results.



1 Glycerol + 3 Fatty Acid → Triglyceride (Oil) + 3 Water

FIGURE 5.2: The chemical combination of glycerine and fatty acid results in an oil: FA = fatty acid molecule..

A description of the drying oil reaction is provided in the *Federation Series on Coatings Technology, Unit II,* as follows:

> The shortest possible description of the drying of oil is that it is a conversion from a liquid to a solid. When a drying oil is exposed to the air in a thin film, there is a variable induction period during which oxygen absorption is negligible and there is no polymerization, which would be evidenced by thickening. The explanation is that the oil contains natural antioxidants and they must be destroyed by oxygen before normal oxidation can commence. Following the induction period the oil absorbs oxygen from the air. In the case of thin linseed oil the total amount of oxygen taken up is 10 to 12% by weight. Concurrently, there is a buildup in the oil of unstable peroxide and hydroperoxide compounds. They increase to a maximum and then decrease, even while oxygen absorption is continuing. Polymerization starts with the development of the peroxides and is most rapid at the time when the peroxides are disappearing the fastest, indicating that decomposition of the oil peroxide compounds introduces cross-linkage of the oil. Since the fatty acid chains that are cross-linked are in different planes, the resulting polymers are three-dimensional. The dried films contain ether linkages (—O—). The polymerization is accompanied by evolution of water, hydrogen peroxide, and carbon dioxides (CO_2).
>
> There is wide overlapping of the various stages. When the oil polymers reach a certain stage in size and number, they join in a structure or framework throughout the film. It is now "set-to-touch." More technically, it is a gel. The film is very soft because it consists of liquid material, within a framework of solid material. Naturally, the reactions are more rapid at the surface of the film where there is contact with the most oxygen. The continued conversion from liquid to solid results in a stage when the surface of the film is all solid material—it is "surface dry." The process extends slowly downward through the films until finally it becomes "through dry." Even then the film contains a small amount of liquid material, which plasticizes or flexibilizes the film. Complete conversion to solid material is greatly retarded by poor accessibility to oxygen and, perhaps, by the non-drying stearic and oleic components. Fully recognizing that the stages of drying overlap, it may clarify the process to think of it as oxidation, polymerization, gelation, and consolidation.

An understanding of this oil reaction is important since it is peculiar to wherever the unsaturated oil molecules are found. The air oxidation of linseed oil, alkyds, epoxy esters, urethane oils, and so forth, all follow this process through the unsaturated oil attached to the resin molecule.

TABLE 5.2: Natural Air-Oxidizing Materials

Property	Linseed Oil Paint	Tung Oil Phenolic Pigmented Coating
Physical Properties	Soft-Flexible, excellent for wood	Hard-Tough
Water Resistance	Fair High M.V.T. Rate	Good
Acid Resistance	Poor	Fair
Alkali Resistance	Poor	Poor
Salt Resistance	Poor-Fair	Fair
Solvent Resistance	Poor	Fair
Weather Resistance	Good	Good
Age Resistance	Gradually Hardens and Brittles over Several Years	Good, better than oils alone
Temperature Resistance	——	——
Recoatability	Good	Fair-Good
Best Characteristic	Penetration of Wood	Moisture and Weather Resistance
Poorest Characteristic Brittle on Aging	Alkali Resistance	
Primary Coating Use	Paint for wood	Mild Corrosion Resistance

Natural Drying Oils

Driers

Metallic driers are common in the use of all oil-type paints. Oils dry slowly without the use of metallic driers, thus it is conventional to use them to achieve practical drying times. Dryers, which catalyze the action of oxygen with the drying oil, are the metallic salts of metals such as lead, manganese, cobalt, and others. The salts are usually the lead, manganese, or cobalt napthanates, and many formulations use both cobalt napthanates for the rapid surface dry, and lead napthanate in order to create a through dry. Cobalt alone creates a rapid surface reaction, which often can cause wrinkling. The use of lead driers has been severely restricted by government regulations regarding toxic substances and hazardous waste.

Oil Coating Advantages

Drying oils and oil-modified coatings have a number of advantages. Their number one advantage is probably ease of application. These materials are generally brush-applied; they brush easily and smoothly over both metal and wood surfaces, with the oil acting as a lubricant. They may also be applied by air spray. The oil-modified film allows controlled moisture penetration and helps to control the expansion and contraction of wood. Oil-based materials are sufficiently flexible, except after very long aging, to expand and contract with the summer and winter grain of the wood without cracking and chipping. Eventually, however, cracking and chipping does take place, although well formulated oil coatings will withstand the summer wood expansion much better than most more sophisticated coatings such as vinyls and epoxies. Oil-modified materials tend to wet metal surfaces very well. They have an affinity for metal surfaces and are able to penetrate hand tool cleaned rusty surfaces to a much greater degree than many other coating materials. Oil coatings generally have good weather durability and will provide protection for a number of years, until the resinified oil becomes sufficiently brittle to check and crack.

Oil Coating Disadvantages

Oil paints or coatings have a number of disadvantages. They are not highly corrosion-resistant. This is due to the relatively high moisture vapor transfer rate, the transfer of ions through the coating, and the fact that they are not sufficiently alkali-resistant to withstand the alkali buildup at the cathode. The lack of resistance to alkali is one of the major drying oil deficiencies. Even mild alkalies tend to react with the oil part of the molecule, causing disintegration of the coating. Since they are not alkali-resistant, they are not satisfactory for application to concrete or other alkaline surfaces. Most oil-based films become brittle with aging, at which time they have a greater tendency to allow moisture vapor transfer as well as ionic transfer. Eventually, they tend to crack, craze, and then chip from the surface. Table 5.2 lists their general properties.

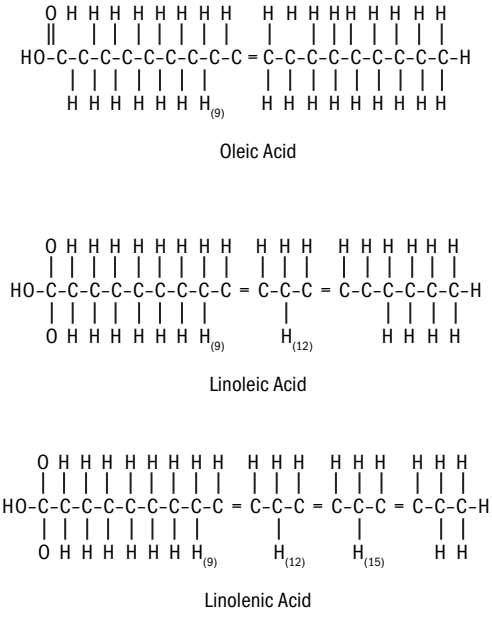


FIGURE 5.3: Comparison of some unsaturated C^{18} fatty acids. The C==C bonds are chemical groups that react with oxygen and change the liquid oil to a solid.

Synthetic Oxidizing Coatings

While drying oils may be used without other resin additives for oil-base house paints, there are a number of other uses of oils, such as incorporation into varnishes, alkyd resins, epoxy ester resins, oil-modified urethane resins, and other similar materials. This diversity of utility shows that the oils still maintain a prominent and essential position as coating components. They are more widely used as a portion of a binder in organic coatings than any other product of natural origin. For industrial use, they are gradually being replaced by acrylic esters, vinyl copolymers, epoxies,

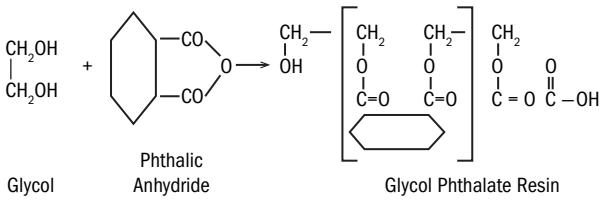


FIGURE 5.4: Typical polyester reaction.

urethanes, and synthetic materials.

From a chemical standpoint, all of the oil-modified resins are based on unsaturated fatty acids. Figure 5.3 shows the structural formulas for three of the acids, which are incorporated into alkyds, epoxy esters, oil-modified urethanes, and varnishes.

Alkyd Resin Formation

There are other oils used in the paint industry in addition to the preceding three. Some of these are safflower oil, soya, tall oil acids extracted from waste materials in paper processing, Tung oil, oiticica oil, castor oil, styrenated oils, and various fish oils.

Figure 5.4 shows the simplest reaction of two materials to form a polyester resin. This is an example of the basic reaction that takes place in the formation of alkyd-type resins, although other materials may be used. The reaction of glycol and phthalic anhydride actually produces a hard, brittle resin, which is heat-convertible or thermoplastic.

To form an air-drying alkyd resin, a drying oil fatty acid, such as one of those shown in Figure 5.3, is added to materials such as phthalic anhydride and glycerine. In this case, the phthalic anhydride and the glycerine react to form a resin similar to the one shown in Figure 5.4. However, since the glycerine has an additional hydroxyl group, the drying oil fatty acid reacts with it and is incorporated into the resulting resin. A simplified indication of this reaction is shown in Figure 5.5.

This same reaction can be shown using letters as symbols of the chemical molecules: G =glycerol, PA = phthalic anhydride, and FA = fatty acid, similar to those shown in Figure 5.3.

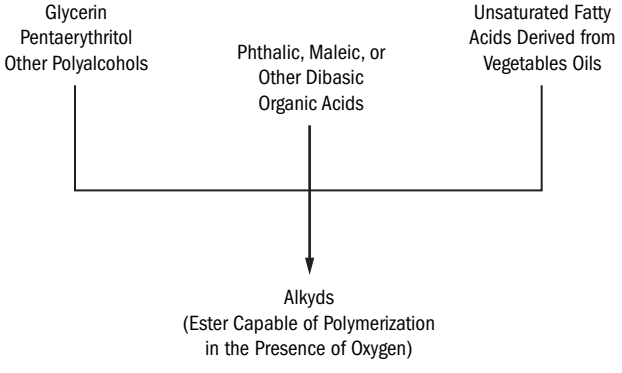


FIGURE 5.5: Formation of an air-drying alkyd resin..

In this case, an essentially linear resin is formed with the long-chain fatty acid, providing solubility and flexibility. If the glycerine were changed to a four-hydroxyl molecule (pentaerythritol), as is often done, an even more complex resin structure would result. The fatty acid molecules attached to the alkyd resin can then react with other similar FA groups (in the same way that an oil reacts with oxygen, in that it polymerizes, gels, and hardens). All of the various oxygen-convertible resins, including the alkyds, epoxy esters, and urethane oils, react to form a film through the drying oil fatty acid group and follow the same chemical reaction pattern.

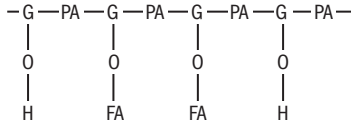
Alkyds

Any resin that is a polymer of ester-type monomers is a polyester resin. Alkyd resins, in general, can be considered polyesters. However, the term alkyd generally applies to polyesters that are modified with triglyceride oil or fatty acids. Alkyd resins, then, generally mean the reaction product of a polybasic acid, polyhydric alcohol, and a monobasic fatty acid or oil, as has been previously shown. The name alkyd comes from the "al" of alcohol and the "cid" (≈kyd) of acid.

Alkyds are undoubtedly the most common of all of the oil-modified materials, as they have the broadest usage. Alkyds generally surpass all other present types of coatings in versatility and volume, providing a broad spectrum of performance with general economy. Alkyds have been the "work horses" of the coating industry. They derive their versatility from the numerous variations in raw materials from which they can be made. Alkyds are made from three basic materials (i.e., polybasic acid, a polyhydric alcohol, and a fatty acid), each of which have an almost infinite number of variables, making the combinations available to form alkyds almost endless.

Alkyds can be classified in a number of different ways, the most common of which is according to the oil length. This, in general, means the percentage of oil in the alkyd, based on the total nonvolatile components. They are designated as short, medium, long, and very long oil alkyds. The longer the oil length of the alkyd, the more oil is present. Long oil alkyds generally have an oil content of 60% or more, while short oil alkyds have oil levels below 40%. Table 5.3 shows the properties and the classification of alkyds by oil length.

The alkyds that have been described so far are pure alkyds, as differentiated from modified (e.g., vinyl) alkyds. In the pure alkyds, the oil length influences all properties and is the primary factor in determining solubility, viscosity, flexibility, and hardness.



(5.1)

The alkyds that are most important from the standpoint of corrosion protection are the medium oil alkyds. They have a wide range of properties and are common for most of the applications familiar to corrosion engineers. As far as alkyds go, they are not as easy to apply as the longer oil materials. On the other hand, because of the reduced oil content and higher amount of the polyester resins, they are more corrosion-resistant. Figure 5.6 shows a typical use for an industrial-type alkyd, showing both the color and the gloss characteristics. Exterior equipment enamels of this type are common throughout the world.

Figure 5.7 shows the installation of an alkyd red lead primer to the deck and deck structures of a small coastal tanker. This was a typical marine use of alkyd coatings. There is a growing trend toward more corrosion-resistant chemical conversion types of protective coatings in this service.

Short oil alkyds are primarily used for baking finishes and are therefore particularly well suited as product finishes. They also have fair corrosion resistance.

TABLE 5.3: Classification and Properties of Alkyds by Oil Length

	Short	Short Medium	Medium Medium	Long Medium	Long	Very Long
Oil (% TNV)	35–43[A]	43–	48–	53–59	59–74	74–85
Fatty Acids	39–	40–	45–	50–55	55–70	70–80
Phthalic Anhydride	50–	38–	36–	33–30	30–20	20–10
Solvent Type	Aromatic Hydrocarbon	Aromatic	Aliphatic Semi-Aromatic	Aliphatic	Aliphatic	Aliphatic
Usual Solvents	Xylol, Toluol	Xylol	Mineral Spirits VM&P Naptha Aromatic Naptha	Mineral Spirits	Mineral Spirits	Mineral Spirits
Normal Solid of Solution	45–50	45-50	50–60	50-60	60–70	70–100
Normal Cure	Bake	Bake, force air dry	Force or air dry	Air dry	Air dry	Air dry
Normal Application	Spray or Dip	Spray or Dip	Spray Dip Brush	Dip Brush	Brush or Roll	Brush or Roll

[A]Formulas modified with non-fatty monobasic acid may have an oil length as low as 25%.
Source: J.R. Blegen, *Federation Series on Coating Technology,* Unit 5, "Alkyd Resins" (Philadelphia, PA: Federation of Societies for Paint Technology, 1969), p. 9.

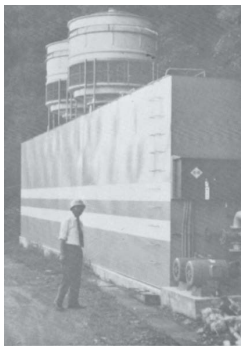


FIGURE 5.6: Alkyd-coated air cooler. Source: LaQue, F.L., *Marine Corrosion: Causes and Prevention,* Chapter 16. John Wiley & Sons, New York, NY, pp. 189–190, 1975.



FIGURE 5.7: Alkyd red lead primer applied to hand-cleaned steel in a marine atmosphere.

TABLE 5.4: Modifiers for Alkyd Resins

Alkyds+	Nitrocellulose
	Urea-Formaldehyde Resins
	Melamine-Formaldehyde Resins
	Phenolic Resins
	Chlorinated Rubber
	Epoxy Resins
	Polyisocyanates
	Silicones
	Reactive Monomers (Styrene)
	Cellulose Acetobutyrate
	Phenolic Varnishes
	Polyamides
	Natural Resins

Source: H.J. Lawson, "Chemistry and Technology of Alkyd Resins," *Applied Polymer Science,* Chapter 37, J.K. Craver and Roy W. Tess, eds. (Washington, DC: Organic Coatings and Plastic Chemistry Division of the American Chemical Society, 1975), pp. 543, 545.

The long oil alkyds, however, have been very popular materials used in architectural paints, both interior and exterior. While they have some use from an industrial standpoint, they are primarily used as coatings for exterior wood structures and as exterior trim enamels. These materials are much closer to oil paints than they are to the alkyds used for corrosion-resistant purposes.

Modified Alkyds

Alkyds are modified with a large number of other resinous materials, and this is one of their distinct advantages. Each of the other resins provides some of its properties to the alkyds and, in doing so, makes for a versatile series of coating materials. The primary materials that can be combined with alkyds are listed in Table 5.4. Some, but not all, of these combinations are of interest to the corrosion engineer. Most of these materials are actually reacted into the basic alkyd resins and are considered copolymers. They usually have increased corrosion resistance when compared with a pure alkyd, depending on the modifying resin. The following alkyd modifications will be taken up individually.

Vinyl Alkyd

Alkyd resins can be combined with hydroxyl-modified vinyl chloride-vinyl acetate resins to form a combination that adds some of the vinyl properties to the alkyds. The vinyl alkyd, as compared with an unmodified alkyd, has decreased drying time, improved adhesion, very good water resistance, and very good exterior weather durability. Usage of vinyl modifications has decreased due to their inability to meet volatile organic compound (VOC) restrictions based on volume solids content. Acrylics can be used to modify alkyds. The method of preparing the vinyl and acrylic alkyds is generally quite similar and consists of three steps.

1. The blending of vinyl or acrylic solutions with that of the alkyd.
2. A copolymerization method, which involves the unsaturation of the fatty acids.
3. The chemical combination of the polymers by other functional groups such as the hydroxyls, usually forming an ester linkage between the two resins.

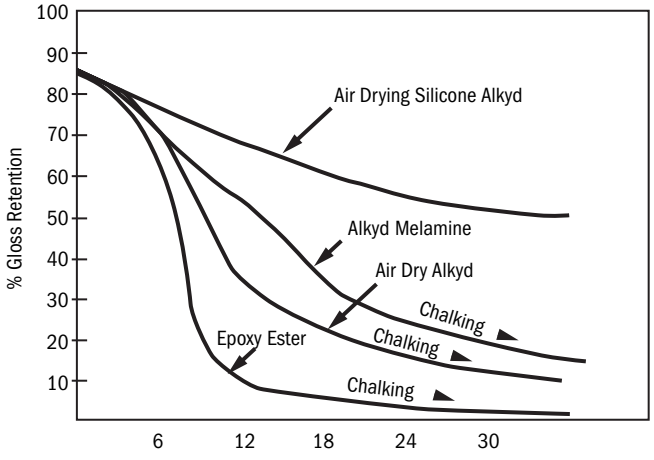


FIGURE 5.8: Performance comparison of silicone alkyds and standard air-drying alkyds and epoxy. Source: K.J. Craver, R.T. Ross, *Applied Polymer Science,* Chapter 37, "Chemistry and Technology of Alkyd Resins" (Washington, DC: Organic Coatings and Plastics Chemistry Div. of Amer. Chem. Soc., 1975), pp. 543, 545.

The vinyl alkyds, with their good water resistance and durable weather properties, have been used extensively by the U.S. Navy for application to its ships. These materials are listed under a government standard specification for this purpose.

Silicone Alkyds

Like the vinyl alkyds, the silicone alkyds are a definite step above the pure alkyds in their resistance to general weathering conditions and particularly to resistance to high temperatures. In this case, the reactive hydroxyl group on the long oil air-dry alkyd resins reacts with the hydroxyl group on the silicone intermediates to give a copolymer structure that chemically combines the alkyds and the silicone. Performance characteristics are directly proportional to the percentage of silicone resin vs. alkyd resin in the formula. This creates quite a different molecule, even though it still retains a high percentage of unsaturated fatty acids. It therefore combines the workability of the alkyds with the durability, gloss retention, general weather resistance, and heat resistance of the silicones. The silicone alkyds are increasingly used as maintenance and marine finishes because of these improved properties. Silicone alkyds also are used rather extensively for stack coatings and for similar areas where moderately high temperatures are involved. The improved weather resistance and durability of the silicone alkyds is shown in Figure 5.8, comparing the silicone- modified product with standard air-drying alkyds and epoxy.

Silicone intermediates are also reacted with hydroxylated polyesters. The simplest of these is the glycol phthalate resin, as shown in Figure 5.4. This resin has two terminal hydroxyl groups, which readily react with the silicone intermediates to give silicone polyester copolymers. These have outstanding gloss retention and weather resistance. Silicone-modified polyesters such as these are extensively used in strip coating for steel and aluminum building panels where the maximum exterior durability is a requirement.

Uralkyds

Uralkyds or urethane oils are materials that again utilize the reactive hydroxyl groups on the basic resin's molecule. In this case, they are reacted with toluene diisocyanate or other isocyanates, to upgrade the properties of the alkyd or oil-base coating. Commercial products contain 15 to 30% by weight isocyanate. The alkyd molecules still retain the oxidizing oil fatty acid group, so that the curing of these materials is primarily through the oil oxidation reaction. A reaction of the isocyanate with alkyds greatly improves the abrasion resistance of the final product, and these materials are often used for wooden floor coatings to withstand excessive abrasion. The isocyanate component also increases the alkali resistance compared to conventional alkyds. Abrasion resistance appears to be their outstanding property. Hydroxylated polyesters are also used in connection with isocyanate materials to provide high-quality maintenance finishes. These, however, are more appropriately classed under the urethane label and will be discussed later.

High Solids Alkyds

Government regulations restricting the amount of volatile compounds that can be released into the atmosphere have given resin manufacturers the economic incentive to create high-solids alkyds, waterborne alkyds, waterborne uralkyds, and epoxy esters. Long oil alkyds formulated at 90% solids by weight, resulting in VOC levels of 250 to 300 g/L (2.1 to 2.5 lb/gal) have gradually replaced alkyds formulated at 70% solids by weight with VOC levels of 350 to 450 g/L (2.9 to 3.75 lb/gal). Similar reductions are occurring in medium oil alkyds. Formulation variables with the newer high-solids alkyd resins require very careful blending, balancing of components, and selection of driers. Reactive aluminum and zirconium driers have replaced some traditional cobalt and lead alkyd driers.

Waterborne Alkyds

Waterborne alkyds are also available; however, they contain water-miscible co-solvents such as glycol ethers or alcohols, which limits their use as corrosion-resistant materials. The selection of driers must be done carefully as they have to be hydrolytically stable. Selection and amounts of the co-solvent is very important as it controls the release of solvents, which in turn controls the drying and curing rates of the applied film.

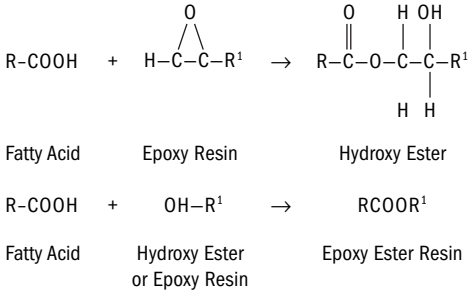


FIGURE 5.9: Reactions which form the epoxy ester: R = remainder of unsaturated oil molecule, R1 = epoxy resin molecule.

Polyamide Modified Alkyds

Alkyds may be modified with small quantities (usually less than 5%) of polyamide resins and other thixotropes to produce a controlled level of thixotropy into the alkyd coating. Greater film build is achieved; however, the film tends to yellow more and become lower in gloss. Usage is relatively small and largely confined to decorative "dripless" alkyds.

Epoxy Esters

Epoxy esters are a type of alkyd in that a high molecular weight epoxy resin is reacted with one of the alkyd resins. This reaction is an important one because of the rather extensive use of epoxy ester coatings. The reaction that takes place is usually between solid grade epoxy resins and drying oil fatty acids. This reaction requires elevated temperatures to form the epoxy ester; therefore, this reaction does not take place except

TABLE 5.5: Alkyds: General Properties

Property	Medium Oil Alkyd	Vinyl Alkyd	Silicone Alkyd	Uralkyd	Epoxy Ester
Physical Properties	Flexible	Tough	Tough	Hard Abrasion Resistant	Hard
Water Resistance	Fair	Good	Good	Fair	Good
Acid Resistance	Fair	Best of group	Fair	Fair	Fair-Good
Alkali Resistance	Poor	Poor	Poor	Poor	Fair
Salt Resistance	Fair	Good	Good	Fair	Good
Solvent Resistance	Poor-Fair	Fair	Fair	Fair-Good	Fair-Good
Weather Resistance	Good	Very Good	Very Good Excellent gloss retention	Fair	Poor
Temperature Resistance	Good	Fair-Good	Excellent	Fair-Good	Good
Age Resistance	Good	Very Good	Very Good	Good	Good
Best Characteristic	Application	Weather Resistance	Weather & Heat Resistance	Abrasion Resistance	Alkali Resistance
Poorest Characteristic	Chemical Resistance	Alkali Resistance	Alkali Resistance	Chemical Resistance	Weathering
Recoatability	Excellent	Difficult	Fair	Difficult	Fair
Primary Coating Use	Weather Resistant Coating	Corrosion-Resistant Coating	Corrosion-Resistant Coating	Abrasion-Resistant Coating	Machinery Enamel

under manufacturing plant conditions. The end product, the epoxy ester, can then be used to make the air-drying epoxy ester coatings. The reactions to form the epoxy ester are given in Figure 5.9.

While the epoxy resin becomes a chemical part of the epoxy ester molecule, the drying or curing of the coating results from the oxidizing reactions of the unsaturated fatty acid part of the resin. It therefore dries like an oil-based enamel. Such a combination improves the chemical resistance of the basic polyester or alkyd resin and makes them a step above the ordinary alkyd resin for chemical resistance, particularly under alkaline conditions. Epoxy esters provide a very hard coating and make a good machinery finish or similar type product, primarily for interior use. They are not satisfactory for exterior weathering conditions, however, as they tend to chalk rapidly and excessively.

In a consideration of all of the various alkyds and alkyd modifications for corrosion-resistant coatings, it is necessary to keep in mind that all of them are based on unsaturated fatty acids, and that this is the reactive part of the molecule that provides the curing mechanism for the coating. The alkyds are a step above linseed oil paint from the standpoint of corrosion resistance, and the various alkyd modifications are again a step above the plain oil-based alkyds. Nevertheless, the words vinyl alkyds, acrylic alkyds, silicone alkyds, and so on do not include the durability that is indicated by the generic names of vinyls, epoxies, and urethanes. These are strictly modifications of the basic alkyd coating, improving its general resistance while maintaining its essentially easy application. The oil-based part of the alkyds is the critical part from the standpoint of corrosion resistance, and these materials should not be compared to other coating materials that are used for severe corrosion resistance.

The alkyds are generally used for atmospheric coatings in areas not considered severely corrosive. They provide interior coatings for houses, shops, factories, and offices, as well as exterior coatings for tanks, silos, buildings, structural steel, railroad equipment, bridges, and topside marine surfaces. The general properties of the various alkyd resins are shown in Table 5.5.

Lacquers

Lacquers are materials that form a coating by evaporation of solvents. The resins, which have been discussed, are permanently soluble and, for the most part, thermoplastic. They are higher polymers that are inert and do not react to cure in the environment, and they are permanently soluble in their own solvents.

Nitrocellulose

As was described in Chapter 1, nitrocellulose is the oldest of the synthetic lacquer-type materials, and its growth paralleled that of the automobile industry inasmuch as it provided a high production finish for automobiles. Nitrocellulose is developed from natural cellulose, primarily from wood fibers and cotton linters. In its normal state, cellulose is an insoluble material. However, the molecule does contain a number of hydroxyl groups and can therefore be esterified. Through esterification, it can be made soluble and thus into a useable product.

The manufacture of nitrocellulose consists of reacting refined cellulose from either wood or cotton with a combination of nitric and sulfuric acid (H_2SO_4), so that all or most of the hydroxyl groups on the cellulose molecule are nitrated. With this reaction, the insoluble cellulose molecule becomes soluble in oxygenated organic solvents and is capable of making a good, solid, continuous film when the solvents evaporate from the nitrocellulose solution. Nitrocellulose is still used today in a variety of product finishes, particularly for furniture. It is not, however, used as a corrosion-resistant coating.

The chemical reaction that takes place to form nitrocellulose is shown in Figure 5.10. Cellulose also may be reacted in quite a different way to form ethycellulose, which is a cellulose ether. Ethycellulose and hydroxyl ethycellulose are specialty film-forming resins. They are not particularly used in the corrosion-resistant coating field, but they are of considerable importance to the ink, paper coating, pharmaceutical, and other miscellaneous industries.

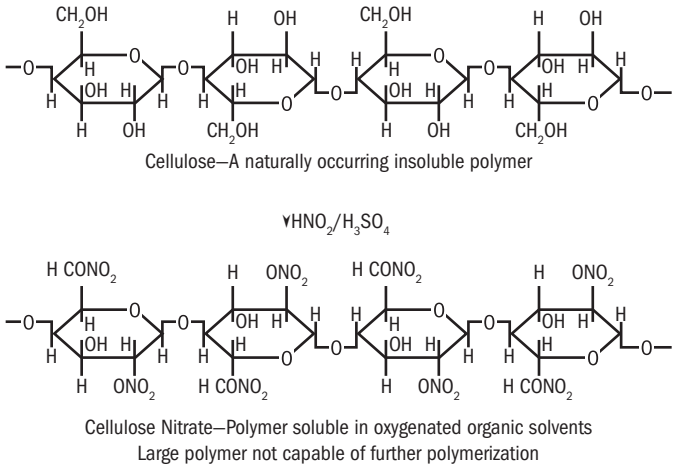


FIGURE 5.10: Chemical formation of nitrocellulose.

Vinyl Coatings

Vinyl resins and vinyl resin coatings are one of the specialty coatings that will perform for years where other materials have failed. They have a broad and useful range of properties. Polyvinyl chloride (PVC) is nearly 150 years old. The copolymerization of vinyl chloride and vinyl acetate in the United States began in about 1928. The actual development of practical coatings from the vinyl resins, however, did not take place for several more years.

In 1936, the Union Carbide Corporation began its first commercial production of its vinyl chloride copolymer resins, which was the beginning of serious coatings development work in vinyls. From a corrosion-resistant coating standpoint, the vinyl copolymer containing 86% vinyl chloride and 14% vinyl acetate, or this ratio combined with a small amount of maleic acid, is the basis for almost all of the corrosion-resistant vinyl coatings as they are known today. Unfortunately, vinyl resins are basically low in volume solids and cannot meet the current VOC restrictions in the United States and many countries in the European Continent. Polyvinyl acetate is widely used for decorative wall coatings, but is of no particular interest to corrosion engineers.[1]

Theoretically, a vinyl resin is any material composed of a basic vinyl molecule that is a carbon-double-bond-carbon group. The most well-known basic material in this class is a PVC resin. It is not, however, used as a maintenance coating, as the PVC is relatively insoluble.

Soluble resins have been made by copolymerizing various vinyl molecules to form excellent coating materials. Examples are vinyl chloride copolymerized with vinyl acetate, vinylidene chloride, vinyl cyanide (acrylonitrile), or acrylates. These vinyl copolymers have properties that lend themselves particularly to surface coating applications.

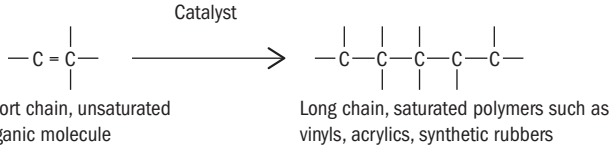


FIGURE 5.11: Short-chain molecules, reacted with the proper catalyst, form long-chain polymers in the double bond polymerization process.

Double Bond or Addition Polymerization

Some of the most important polymers used in the coating industry are those formed by double bond or addition polymerization. Materials that use this mechanism primarily contain the vinyl group $CH_2 = CH_2$. Chemically speaking, vinyl resins include a number of other materials, such as polyethylene, polystyrene, polyacrylates, and methacrylates, in addition to PVC, polyvinyl acetate, and their copolymers. All of the above contain the basic vinyl group, and all of the monomers containing this group, when combined with the proper catalyst, react together to form long-chain polymers.

This reaction is schematically shown in Figure 5.11. In this case, the double bond in one molecule breaks, reacting with similar molecules to form a saturated, very high molecular weight polymer. The formation of polymer by the double bond process does not sacrifice or give off any part of the molecule, as is the case during polymerization by condensation. The molecular weight of the polymer is a multiple of that of the monomer.

Vinyl chloride, one of the simplest of the unsaturated monomers, can be made to react with other vinyl chloride monomers to form a linear straight-chain polymer, as represented in Figure 5.12.

When the vinyl acetate monomer and the vinyl chloride monomer are reacted together, they also form a long-chain linear polymer. As mentioned previously, commercial PVC-acetate resin contains about 86% vinyl chloride and 14% vinyl acetate. The two materials are mixed in this proportion prior to the polymerization reaction, and the finished polymer results with the same composition. The copolymer is formed as shown in Figure 5.13. These polymers can be made up from hundreds or thousands of the single monomer units, and molecular weights from 25,000 to 100,000 are not uncommon. This type of polymerization is interesting since no byproducts (e.g., water) are formed during the reaction. None of the atoms that make up the original monomer molecule are lost during the process. The chemical bonding between the two monomers after polymerization is a carbon-carbon bond, which makes a very stable and resistant polymer. This is the primary reason for the vinyl polymer's excellent chemical and age resistance.

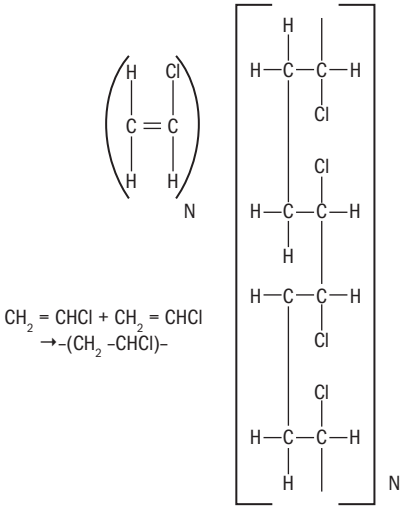


FIGURE 5.12: Reaction of vinyl chloride monomers can form a linear short-chain polymer.

As mentioned previously, all of the materials that contain the vinyl double bond grouping could technically be called vinyl materials. On the other hand, it has become customary in industry to limit the term vinyl resin to vinyl acetate, vinyl chloride-vinyl acetate copolymers, and other similar copolymers. The acrylate and methacrylates are generally called acrylics, and polyethylene and polystyrene are referred to by these respective names.

The long-chain carbon molecules of vinyl resins make them thermoplastic, which therefore makes it possible to produce solution-type coatings from them. These long, saturated carbon chains also make them physically strong and resistant to a wide range of chemical reactions, such as those involving acids, alkalies, and many salts. These vinyl resins have a broad chemical resistance when compared with the more common coating polymers.

The outstanding properties of vinyl coatings (PVC acetate type) are as follows.

Film Formation

The ability to form a homogeneous, tight film over a surface is a basic property. The film formed by the vinyl resins is different from many other coating materials in common use because it is pre-reacted or polymerized and because it goes through no oxidation, chemical reaction, or other change in the formation of the film or in aging. This is important, since these coatings do not rely on temperature, humidity, solar radiation, or moisture vapor in order to cure in place. As long as the solvents will evaporate from the film, the finished coating will be formed, having all of the properties inherent in the basic resin. This dense, homogeneous, continuous film accounts for much of the long life of vinyl coatings.

Chemical Resistance

A vinyl coating is basically inert to almost all inorganic substances (e.g., acids, alkalies, and salts), as well as to water, oil, grease, alcohols, and similar materials. Because of its polymeric structure and its independence of other materials such as catalysts to develop its basic resistance, vinyl coatings are inherently chemical resistant. There are only a few materials, its own solvents or similar products, which will destroy its film integrity. There are few other coatings that will resist both strong acids and alkalies, and strong oxidizing chemicals as well. Vinyl coatings, for example, have been used as a coating for the belly-band on sulfuric and nitric acid tank cars where concentrated acid spills are common. A more recent development for this exterior service features a vinyl modified waterborne latex that works quite well and meets the most stringent VOC regulations. It is used extensively for interior and exterior of boxcars and car carriers. It also has been used as a lining for caustic storage tanks and tank cars holding 50% or greater concentration of sodium hydroxide (NaOH). Vinyl coatings also have been used to line perchloric acid fume ducts, where any other organic material would have caused an instant fire or explosion. These extremes indicate the versatile chemical resistance of these coatings.

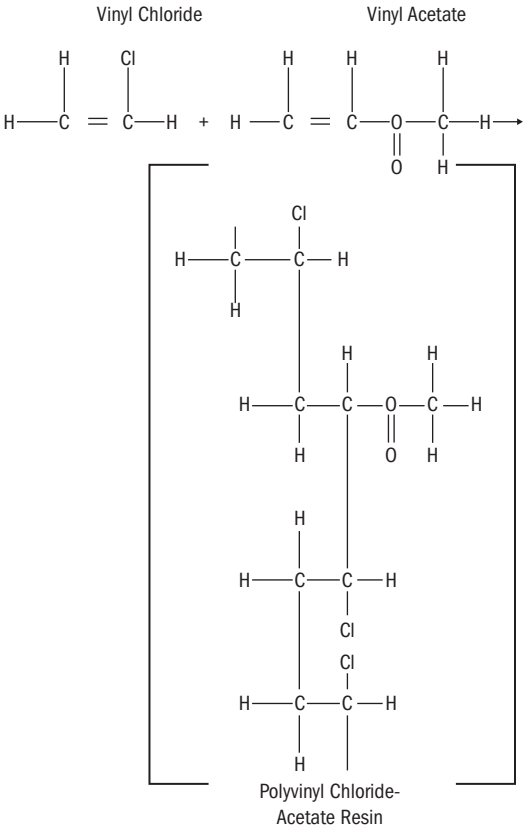


FIGURE 5.13: Formation of a long-chain linear polymer from the vinyl acetate and vinyl chloride monomers.

Water Resistance

Vinyl coatings are generally unaffected by continuous water exposure. Some of the oldest vinyl coatings in existence are on the interior of water storage tanks or penstocks. Fifteen or more years without any maintenance or coating breakdown has been the common experience. Two coatings, Bureau of Reclamation specifications VR-3[2] and VR-6[3], were standard products for use on penstocks, dam gates, and similar structures for many years, with actual use experience ranging over 15 to 20 years with little or no maintenance. The Corps of Engineers enjoys a special dispensation from VOC restrictions for the use of vinyl coatings on dams.

Age Resistance

Continuous use in various water installations is an indication of the age resistance of vinyl coatings. There is no other coating, with the exception of hot-applied coal tar enamel, that has the long-term exposure of vinyl coatings in water. Another similar exposure is the vinyl lining in sewer pipe and structures. The oldest installation was in 1948 and it is still in service, performing well for over 50 years. It is anticipated that the vinyl lining will last the life of the sewer, which is 100 years or more.

A related report was made by A.K. Doolittle at the annual NACE meeting in March, 1963, where he reported on the oldest fully

TABLE 5.6: Nine Year Plus Exposures

Number of Exposures	Number of Years	Substrate	Surface Preparation	System
1	19	Steel	White Metal Blast	Vinyl
1	18	Concrete	Acid Etch	Vinyl
1	15	Steel	White Metal Blast	Vinyl
1	15	Steel	Commercial Blast	Vinyl
1	14	Concrete	None	Vinyl
1	12	Steel	White Metal Blast	Vinyl
1	11	Steel	White Metal Blast	Vinyl
2	10	Steel	White Metal Blast	Vinyl
1	9	Concrete	None	Vinyl
1	9	Steel	Commercial Blast	Inorganic Zinc
3	9	Steel	White Metal Blast	Vinyl
14				

TABLE 5.7: Categories of Chlorinated Rubber-Based Coatings				
Category	1	2	3	4
Chlorinated Rubber, %	50–60	45–60	20–23	5–50
Nonreactable Resin and Plasticizer, %	40–50	0–25	––	––
Alkyd or varnish selected for job in hand), %	––	20–30	65–80	0-25
Other Polymers, Resins, and Plasticizers, %	––	––	––	0–95
Chemical Resistance	Excellent	Good	Fair (much higher than conventional enamels)	––
Outdoor Weathering	Good	Very GGood	Excellent	––
Adhesion to Metal	Fair	Good	Excellent	––
Typical Applications	Paints and mastics for indoor, extremely corrosive environments; unusually severe outdoor environments; extreme non-flammability.	Paint for typically tough corrosive environments outdoors; water and chemical-resistant enamels; for masonry, railroad, marine, swimming pool pool, food processing, buildings; excellent non-flammability.	Product finishes for fast dry with excellent water and chemical resistance; traffic paints; Navy flame-retardant paint.	Embraces a host of specialty finishes from chlorinated rubber to acrylics with excellent chemical resistance and durability, to marginal varnishes fortified with a little Parlon to make them salable.

documented coating installation in the United States that could be inspected at that time. Table 5.6 shows the exposures of nine years and older, which he inspected. It is important to note that out of all of the oldest exposures, only one was not a vinyl coating. These long-time exposures were not mild ones either, but were considered extremely severe conditions for any coating to withstand. These included equipment coated for protection against 15% to 18% caustic soda, viscose storage tanks, and filter presses exposed to caustic, carbon disulfide, hydrogen sulfide (H_2S), and so forth. There were also potable water tanks, dam gates, pipe racks in chemical plants, atomic energy installations, and a phosphoric acid plant included in the inspection.

Vinyl Organisols and Plastisols

Vinyl chloride polymers of high molecular weight may also be applied as organosols and plastisols. These coatings, based on very high molecular weight resins of vinyl chloride (produced by emulsion polymerization followed by spray drying) with or without co-monomers, are applied as fine particles of polymer dispersed in volatile non-solvents (organosols) or in plasticizers (plastisols) and applied as dispersions. After application (by spraying, dip coating, reverse roll coating, knife coating, etc.), the coatings are baked at a high enough temperature to fuse the individual particles of resin together.

Vinyl dispersion resins are widely used in fabric coatings, synthetic leathers, floor coverings, overshoes, gloves, wire goods, tool handles, racks, and other applications.

Vinyl Powder Coatings

Organosols may contain as little as 5% volatile material, plastisols even less. They are low VOC products. Zero VOC vinyls are possible with powder coating technology, in which somewhat similar resins are used as binders for coatings. In this case, the liquid continuous phase is essentially replaced by air. The coatings are applied with either electrostatic spray followed by fusing, or with a fluidized bed process in which the heated articles to be coated are passed through a field of powder suspended in air, which melts onto the articles and are then baked to final cure.

Vinyl powder coatings are largely used for metal furniture and cabinets, gas distribution pipelines, tools, electrical motors and transformers, bottles, racks, and small metal parts of all kinds.

Chlorinated Rubber Coatings

Chlorinated rubber coatings consist of natural rubber reacted with chlorine. This forms a very hard, horny-textured resin lacking in the elastic and resilient characteristics of rubber products. The coating has a specific gravity of 1.64, which is almost twice that of pure rubber. It is odorless, tasteless, and nontoxic, and will not support combustion or burn.

The chlorinated rubber coating also is stable to heat for considerable periods up to 125 °C. At higher temperatures, there is a tendency toward chemical decomposition with the evolution of hydrochloric acid (HCl). At about 130 °C, the chemical breakdown becomes significant. Boiling water or steam is destructive to chlorinated rubber and is not recommended for coating applications that require durability under these conditions. In spite of this, chlorinated rubber has low water absorption.

In the absence of sunlight, aging has very little effect on chlorinated rubber. Pigmented compositions are durable in the sunlight; however, sunlight causes both discoloration and embrittlement in clear, unstabilized films.

The electrical properties of chlorinated rubber are excellent, as might be expected from a chlorinated polymer. Dielectric constant at 25 °C is 2,200 V/mil. It has excellent abrasion and shock resistance if properly compounded with other materials.

Coatings made with chlorinated rubber, particularly those that are modified with chlorinated resins, have very good chemical resistance, particularly to inorganic chemicals. Chlorinated rubber by itself, however, is not practical and must be modified in order to be usable. It is essentially modified in two ways. One way is to use chlorinated resins as the modifiers and another is to use alkyd resins.

Acrylic resins are also used to enhance the gloss characteristics of chlorinated rubber finish coats.

There are actually about four categories in which chlorinated rubbers can be placed. The first category consists of formulations containing high proportions of chlorinated rubber modified with nonreactive resins and plasticizers. These nonreactive materials are most often highly chlorinated materials (e.g., chlorinated paraffin), and this category is often called an all-chlorinated system. These materials are used in situations requiring maximum chemical or flame resistance.

The second category differs from the first in that part of the nonreactive resin or plasticizer is replaced with an alkyd or an oleoresinous varnish. The chlorinated rubber contents still remain high; however, some of the excellent chemical resistance that is available in the first category is sacrificed. Corrosion resistance is still good, however, and the coating gains in adhesion, weatherability, and ease of application.

In category three, the alkyd resin becomes a major ingredient, and chlorinated rubber is, in essence, fortifying the alkyd. Coatings in this category are often called chlorinated rubber-fortified alkyds. They have good weatherability, adhesion, gloss, and brushability, plus some improved chemical and water resistance over the alkyd alone.

Category four is intended for alkyd or oleoresinous materials, which require some upgrading, particularly in their speed of drying. Table 5.7 shows the categories of chlorinated rubber-based coatings and some of their properties.

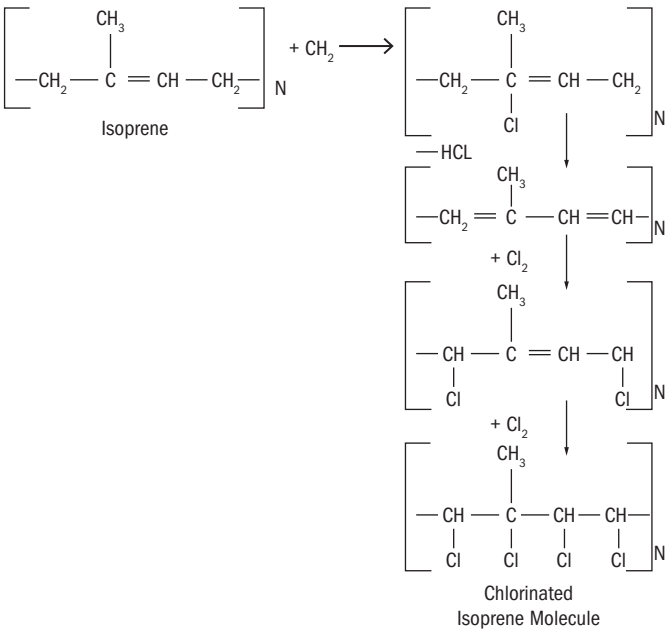


FIGURE 5.14: Formation of chlorinated rubber.

The properties of chlorinated rubber are better understood in light of its chemical makeup. In the chlorination process, rubber reacts with chlorine in an amount sufficient to yield a product of approximately 64 to 65% chlorine. Rubber is made up of isoprene units. These undergo a complex chlorination reaction with both addition and substitution of chlorine. The chlorination process is brought to an end when the double bonds have disappeared and the chlorine content is high enough to ensure optimum stability, compatibility, and resistance to fire. The chlorine atoms are probably scattered along the available carbon atoms with little tendency for more chlorine atoms to be on a single carbon atom. Generally, there is less than the theoretical chlorine content for the chlorine substituted isoprene unit, $C_5H_6C_{14}$. The isoprene–chlorine reaction is illustrated in Figure 5.14.

Chlorine-containing organic chemicals generally have very good chemical-resistant properties. As can be seen from the formula for chlorinated rubber or chlorinated isoprene, the amount of chlorine in the molecule is substantial. It is this, as well as the saturated carbon bonds, that give it good chemical resistance.

One of the positive properties of chlorinated rubber is that is has the ability to fast through dry so that rapid application is possible. It increases the drying speed of alkyds substantially and, when used as a chlorinated rubber lacquer, dries rapidly and hard. These coatings (i.e., the fully chlorinated coatings) are primarily used in the chemical and marine industries, although one of its major uses is in coating concrete swimming pools. As chlorinated rubber topcoats, they provide a very good maintenance coating. They are hard, tough, and chemical resistant; they have good resistance to extended weathering; and they can be readily repaired and recoated. They remain popular outside of the United States, where their low volume solids do not meet VOC regulations.

Acrylic Polymers

Acrylic resins are primarily polymeric derivatives of acrylic and methacrylic acid. More important resins are polymers of methyl and ethyl esters of these acids or copolymers of mixtures of these monomers. Propyl, butyl, and isobutyl esters are also used, as well as acrylamides, acrylonitriles, and other similar materials. These monomers may be blended in any number of different proportions and then polymerized into finished resins. Because of the variation in esterification and the copolymerization of the various esterified acrylic monomers, there is almost an untold number of combinations that can be used. The polymers can vary from very hard, brittle materials to very soft, flexible plastics.

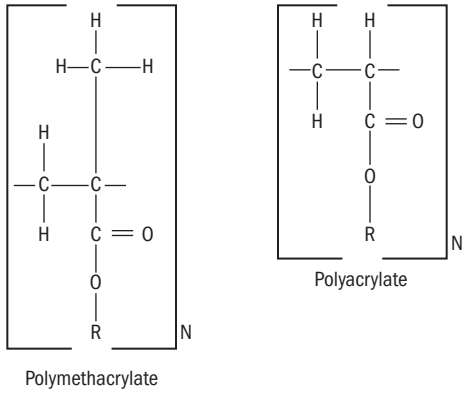


FIGURE 5.15: Chemical formulation of the acrylic polymers, polymethacrylate, and polyacrylate.

The solution and film properties of the various acrylic polymers, when they are made into coatings, are regulated by the molecular weight, the nature of the polymer solution, and the composition of the polymer or copolymer chemical structure. The effect of molecular weight is rather obvious. Film formation of any solution coating depends either on the formation of the primary chemical bonds or upon the entanglement of the polymer chains by secondary chemical interaction. In the case of thermoplastic coatings, the longer the polymer chain, the more thoroughly the chains will be mixed and the tougher and more coherent the film will be. This is not completely beneficial, even though the high polymers have better properties, since the viscosity of the coating solutions increases exponentially with the molecular weight. The molecular weight of the acrylics, therefore, must be kept down to a reasonable level at which a workable viscosity can be obtained with the polymer in solution.

The acrylic polymers used in coatings are primarily those of the polymethacrylates and polyacrylates. The chemical structure is shown in Figure 5.15.

TABLE 5.8: Effect of Various Monomers on Film Properties

Film Property	Contributing Monomers
Exterior Durability	Methacrylates and Acrylates
Hardness	Methyl Methacrylate Styrene Methacrylic and Acrylic Acid
Flexibility	Ethyl Acrylate Butyl Acrylate 2-Ethylhexyl Acrylate
Stain Resistance	Short-Chain Methacrylates
Water Resistance	Methyl Methacrylate Styrene Long-Chain Methacrylates and Acrylates
Mar Resistance	Acrylonitrile
Solvent and	Acrylonitrile Methacrylamide Methacrylic Acid
Adhesion to Metals	Methacrylic/Acrylic Acid

Source: W.H. Brendley, G.V. Calder, L.A. Wetzel, "Chemistry and Technology of Acrylic Resins for Coatings," *Applied Polymer Science,* Chapter 55, J.K. Craver and W.T. Gess, eds., (Washington, DC: Organic Coatings and Plastics Chemistry Division of the American Chemical Society, 1957) pp. 863, 865.

TABLE 5.9: General Durability Characteristics of Acrylic Homopolymers

	Methacrylate	Acrylate
Methyl	Very Good	Poor
Ethyl	Excellent	Fair
Iso-Butyl	Excellent	Good
N-Butyl	Excellent	Excellent

Source: W.H. Brendley, G.V. Calder, and L.A.Wetzel, "Chemistry and Technology of Acrylic Resins for Coatings," *Applied Polymer Science*, Chapter 55, K. J. Craver and Roy W. Tess, Eds., Organic Coatings and Plastics Chemistry Division of the American Chemical Society, Washington, DC, pp. 862, 865, 1975.

The properties of the polymers are dependent on three different items: (1) the presence of the CH_3 or hydrogen on the alpha carbon; (2) the length of the ester side chain indicated by "R"; and (3) the functionality in the ester side chain.

Commercial acrylic polymers are almost always copolymers of several monomers so that a wide range of hardness, strength, and flexibility can be achieved. Table 5.8 shows the effect of various monomers on coating film properties.

Acrylic resins are characterized primarily by their water-white color, resistance to change in color as they age, and their perfect transparency. Acrylics generally have excellent durability properties due to the chemical nature of the polymer itself. The main polymer chain is comprised entirely of carbon-to-carbon single bonds (which, as previously discussed, are relatively inert), and not as susceptible to chemical change as are the ester, ether, and amide linkages. The ester side chain can be hydrolyzed; however, such change does not necessarily result in a breakdown of the polymer carbon chain. The general durability characteristics of some of the esters of methacrylates and acrylates are shown in Table 5.9.

The acrylates increase in flexibility, durability, and water resistance as the ester chain link increases. Most of the acrylic materials with which corrosion engineers will be involved are those acrylics that are co-reacted with other resins (e.g., epoxies, vinyls, and isocyanate modifications). The use of the acrylic in these combinations is to increase the exterior durability and weather resistance and to retain the appearance of the coatings over long periods of time.

Many of the acrylics also are applied as emulsions and water dispersions. Historically, these were applied as decorative coatings rather than for corrosion resistance. Improvements in the manufacturing of waterborne acrylics have resulted in "industrial grade" acrylic coating systems with very good corrosion-resistant properties along with enhanced color and gloss retention properties. Except for the these newer resins and modifications of the other corrosion-resistant coating resins, the acrylics are primarily used as product finishes on automobiles, refrigerators, and similar products, which require excellent durability in the long-lasting, factory-applied coating.

Coal Tar Coatings

There are a number of coal tar coatings made by dissolving processed coal tar pitch, or a blend of these pitches, in suitable solvents. They dry entirely by evaporation of the solvents and their properties depend to a great extent on the type of coal tar raw materials and the blending of these materials. Generally, they are all quite similar. The outstanding property of coal tar coatings is their extremely low permeability to moisture and their high dielectric resistance, both of which contribute to their corrosion resistance.

Coal tar coatings are made in different consistencies; those without any inert fillers, and those that contain inert materials in order to build film thickness. Coal tar coatings, in general, are not affected by mineral oil, but can be dissolved by a vegetable or animal oil, grease, and detergents. They have good resistance to weak acids, alkalies, salts, sea- water, and other aggressive atmospheres. They derive their corrosion-resistant properties from an impermeable film concept; as such, they provide protection by exclusion of moisture and air from the underlying surface. They are alkali resistant and can be applied to concrete as well as to steel.

One of the problems with coal tar coatings is their tendency to alligator when exposed to direct sunlight. This is brought about by

the hardening of the upper layer of the coal tar film because of the exposure to the sun's ultraviolet rays. The upper layer of the film contracts and slips over the softer under layer, causing alligator marks. Coal tar cutback coatings should be protected from the sun in order to retain their corrosion-resistant properties. The coal tar cutback coatings can be considered true solvent dry lacquers.

Asphalt

Asphalt cutbacks are also extensively used as corrosion- resistant coatings. They not only are made with distilled asphalt from petroleum, but also are made from natural asphalt, or gilsonite. It is a very hard, asphaltic material and is mined in the same way that coal is mined. It has excellent chemical resistance and good weather resistance. Most of the better grades of asphaltic coatings will contain a proportion of gilsonite in order to upgrade the petroleum-derived asphalt. In general, the higher the proportion of gilsonite, the more resistant the coating will be.

Asphalt coatings are more weather resistant than the corresponding coal tar coatings since they do not tend to alligator. On the other hand, they are inferior in water resistance to the coal tar products.

Solvents used in asphalt coatings are very mild. Since they do not impart taste to water, many asphaltic coatings have been used for painting steel water tanks and concrete reservoirs for storing drinking water.

Asphaltic coatings also are combined with higher polymer petroleum resins, which increase the strength and provide more flexibility to the asphalt gilsonite coatings. Asphaltic coatings are also made with inert fillers, which add to the thickness of the coating and, in many cases, to its impervious characteristics. Some of these asphaltic type coatings have excellent resistance to industrial fumes, water, moisture, condensation, and exterior weather exposure. They do tend to lose gloss and chalk when exposed to the weather. On the other hand, this apparently does not detract from their other good characteristics or reduce their overall weather resistance.

Both asphalt and coal tar coatings have the disadvantage of being black, and while some very dark iron oxide colors can be obtained from the bituminous-type coatings, they must generally be used where a black coating with generally poor appearance is adequate. Bituminous coatings can be pigmented with leafing aluminum and provide a bright aluminum color in this manner. This, however, is the limit to which bituminous coatings can be pigmented for decorative purposes.

Advantages of Solvent-Evaporating Films

There are a number of very distinct advantages in the use of solvent-evaporating films. The advantages are general for the whole group of resins that are in this thermoplastic category. One of the first important characteristics is fast film formation. As has been described, the thermoplastic resins only require the evaporation of the solvent to form their final film so that film formation is in a simple stage, as compared with conversion coatings where two or more stages are required in order to properly form the film. This fast film formation, and the fact that the resin is completely reacted prior to its going into solution, enables one coat to follow another in rather rapid succession. This is important in many chemical areas where chemical fallout may be a problem. It is also true in marine areas where chloride-containing mist or spray may precipitate on the coating. In this case, one coat of the coating may follow another as soon as the major amount of solvent has evaporated, laying down the completed coating of one or more coats in a relatively short period of time and thus eliminating the intercoat contamination.

Where necessary, most lacquer-type coatings may be handled quickly without the necessity of going through additional stages of cure before they become hard enough to handle. There is no critical reaction time or critical reaction conditions necessary for most solvent evaporating coatings. They may be applied in subfreezing conditions as long as the solvents will evaporate from the film. They also may be applied under rather warm or hot conditions as long as the solvents are formulated to evaporate somewhat more slowly. Again, they do not have to go through the other stages of cure, which can be very critical, depending on the temperature, humidity, and air circulation. Being permanently soluble in their own solvents, repair and maintenance of lacquer-type coatings is generally easier than with thermosetting or conversion coatings. From the corrosion engineer's standpoint, these favorable factors may more than outweigh the advantages of some of the other coating types.

Disadvantages of Solvent-Evaporating Films

Solvent dry coatings also have a number of disadvantages. As mentioned previously, if the solvent formulation is too fast, it will tend to overspray, causing a rough film that may not be continuous and which may allow rapid corrosion. Improper solvent formulation may also cause the film to blush. Under high humidity conditions, a solvent combination may be such that the liquid coating dries sufficiently fast so that the surface cools and moisture precipitates on the surface before the coating is dry. This is called blushing. When this happens, the surface of the film becomes milky and white, many times causing the resin to precipitate on the surface, leaving a non-continuous film and one that is not satisfactory for corrosion resistance. Solvent retention also has been mentioned. Where there is a solvent in the formulation that does not release readily, a measurable percentage remains in the film. This can cause poor water or chemical resistance.

Often with solvent-evaporating coatings or lacquers, there is somewhat more difficulty in the application of the coating than there is in conversion coatings. This, again, is primarily due to the solvent formulation. During the application, however, it must be realized that a considerable amount of solvent is lost between the atomization point at the gun and the impact point on the surface. Gun distance must be properly controlled and a continuous wet film applied. If this is not done, then a non-continuous film will result.

The application by brush of many lacquer-type coatings also is difficult. This is particularly true when they are formulated with fast-drying solvents. They pull on the brush, leave brush marks, and may not provide a smooth, even film. Vinyls and chlorinated rubber coatings are more susceptible to this than are the bituminous cutbacks.

Probably the most obvious property of solvent-applied coatings that can cause difficulty is that of being permanently soluble in their own solvents. Each one of the thermoplastic resins is, of course, susceptible to any of the solvents in which it is readily dissolved. Resins that require oxygenated solvents to dissolve (e.g., alcohols, esters, ketones, or ethers) usually have good resistance to aliphatic hydrocarbon solvents. On the other hand, resins that are easily dissolved in hydrocarbon solvents generally have poor resistance to the oxygenated solvents as well. As an example, vinyl resins are excellent materials for use in gasoline, diesel oil, and many of the other aliphatic hydrocarbon solvents. On the other hand, they are not practical for use with aromatic solvents, such as toluene or xylene. These are the diluent materials used in making the solvent formulations.

TABLE 5.10: Solvent Dry Lacquer Coatings: General Properties

	Vinyl Chloride	Vinyl	Chlorinated Rubber Properties				
	Acetate Copolymer	Acrylic Copolymer	Resin Modified	Alkyd Modified	Acrylic Lacquers	Coal Tar	Asphalt
Physical Property	Tough Strong	Tough	Hard	Tough	Hard- Flexible	Soft Adherent	Soft Adherent
Water Resistance	Excellent	Good	Very Good	Good	Good	Very Good	Good
Acid Resistance	Excellent	Very Good	Very Good	Fair	Good	Very Good	Very Good
Alkali Resistance	Excellent	Fair-Good	Very Good	Poor-Fair	Fair	Good	Good
Salt Resistance	Excellent	Very Good	Very Good	Good	Good	Very Good	Very Good
Solvent (Hydrocarbon) Aromatic	Poor	Poor	Poor	Poor	Poor	Poor	Poor
Aliphatic	Good	Good	Okay	Okay	Okay	Fair	Poor
Oxygenated	Poor	Poor	Poor	Poor	Poor	Poor	Poor
Temperature Resistance	Fair 65 °C (150 °F)	Fair 65 °C (150 °F)	Fair	Fair 60 °C (140 F)	Fair	Depends on Softening Point	Depends on Softening Point
Weather Resistance	Very Good	Excellent	Good	Very Good	Excellent	Poor	Good
Age Resistance	Excellent	Excellent	Very Good	Good	Very Good	Good	Good
Best Characteristic	Broad Chemical Resistance	Weather Resistance	Water Resistance	Drying Speed	Clear Color Retention, Gloss Retention	Easy Application	Easy Application
Poorest Characteristic	Critical Application	Critical Application	Spray Application	Chemical Resistance	Solvent Resistance	Black Color	Black Color
Recoatability	Easy	Easy	Easy	Easy	Easy	Easy	Easy
Primary Coating Use	Chemical-Resistant Coatings	Exterior Chemical-Resistant Coatings	Maintenance Coatings	Weather-Resistant Coatings	Weather-Resistant Coatings	Water-Resistant Coatings	Chemical-Resistant Coatings

Coal tar and asphalt coatings also create difficulty where they are to be overcoated with other coatings, even oil-based paints. In both cases, the bituminous resins dissolve sufficiently to bleed and cause discoloration of the overcoating material. Even the newer water-borne acrylics will discolor when applied over coal tar and asphalt coatings. Harder coatings applied over the bituminous materials may also tend to shrink and alligator on drying. The general properties of solvent dry lacquers are shown in Table 5.10.

Co-Reactive Coatings

As previously noted in Chapter 4, co-reactive coatings are considerably different from the coatings that dry by solvent evaporation. The co-reactive coatings discussed in this chapter are those that react at room temperature to form corrosion-resistant coatings on large, new, or existing structures. Some of the advantages of these materials are that they are usually relatively low in molecular weight during application and then, due to cross-linking with added materials or from moisture in the air, cross-link in place to form high molecular weight thermoset coatings on the surface.

The process of cross-linkage is the key to the formation of co-reactive coatings and it is also the key to their general resistance. The cross-linkage increases the size of the molecule, which generally can increase the corrosion resistance and definitely does increase the resistance to various solvents. Many of these co-reactive materials, then, not only have a relatively broad resistance to chemicals in general, but also to solvents, which in the case of solvent deposited coatings would destroy the coating in short order.

Of the number of co-reactive coatings available, the epoxies are undoubtedly the most important from a corrosion engineer's standpoint. They are not only important because of their properties, but also because of the numerous reactions that take place with the various curing agents for the epoxy resins. These many different curing agents create a multitude of epoxy coatings, all of which have some good and different properties from a corrosion resistance standpoint. Some of the most important properties will be considered in the discussion of epoxy resins.

Epoxy Resins

The principal types of epoxy resins that are used for corrosion-resistant coatings are those based on the condensation of bisphenol A and epichlorohydrin. In this case, the polyhydroxy bisphenol A is reacted in the presence of alkali with epichlorohydrin to form the basic epoxy resin. This is shown in Figure 5.16, which depicts two epoxy groups at the terminal ends of the polymer. Epoxy resins made with bisphenol F can have higher chemical resistance when formulated with proper curing agents. Multifunctional epoxy resins such as novolacs (a reaction product of phenol with formaldehyde) have more reactive groups on the backbone chain, resulting in higher cross-linking density in the film, thus providing greater chemical resistance. While some formulations involving novolacs are ambient

cured, greater resistance is achieved at higher curing temperatures. Specialty resins with epoxy groups attached to other polymeric species provide epoxy-functional resins for specialty applications. Examples are the epoxy ester, monofunctional and difunctional diluents, epoxy-functional silanes, and others.

The success of the epoxy coatings has been the result of the chemical reaction of curing agents through the secondary hydroxyl groups on the body of the epoxy resins and the terminal epoxide groups, both of which are shown in Figure 5.16. These reactive groups on the basic epoxy resin react separately, for the most part, so that the hydroxyl groups may be reacted with one type of curing agent while the epoxy terminal oxirane groups can react with other, quite different curing materials. The most common co-reactants are the aliphatic and aromatic amines, clycloaliphatic amines, polyisocyanates, the epoxy adducts, the low molecular weight polyamides/amidoamines, acid and anhydrides, polysulfides, isocyanates, latent curing agents, and phenolformaldehyde resins. The curing mechanism of these materials can involve either the epoxide or the hydroxyl groups on the resin molecule or a combination of both.

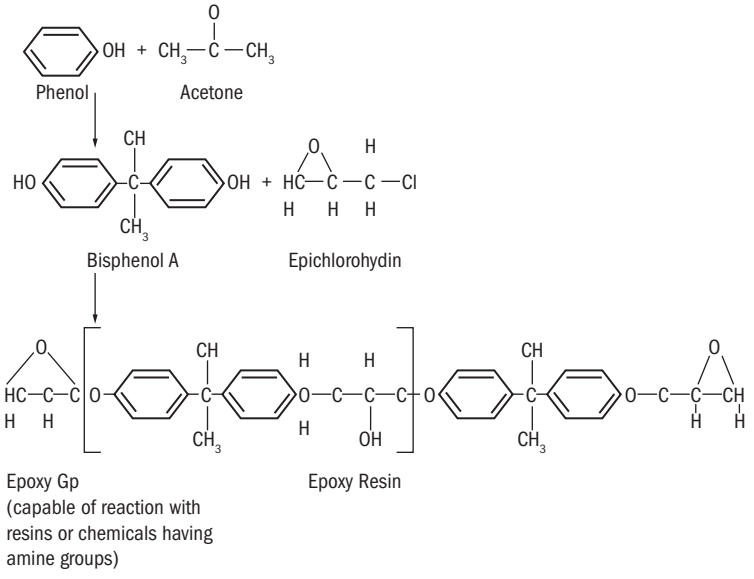


FIGURE 5.16: Epoxy groups form at terminal ends of the polymer.

The basic epoxy resins may be in the form of relatively low viscosity liquid resins or they may be solid resins of increasing hardness, depending on the size of the molecule. Both the liquid and the solid resins may be used to form corrosion-resistant coatings, or a combination of both the liquid and solid epoxy resins can be mixed into a coating in order to develop the reactivity necessary for the particular material desired. With the number of curing agents outlined earlier and the various combinations of epoxy resins that are available or that can be combined, the epoxies in general are a very versatile type of material from which to develop corrosion-resistant coatings.

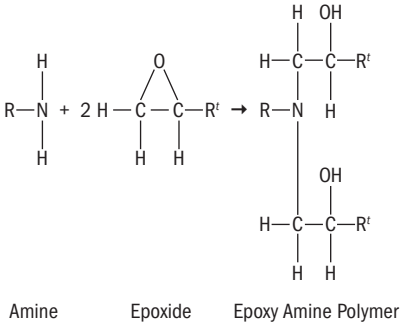


FIGURE 5.17: Amine epoxy reaction: R = aliphatic part of amine molecule, R^t = epoxy resin molecule.

Aliphatic Amine-Cured Epoxies

The principal corrosion-resistant epoxy coatings are formed by the use of the amine-epoxide reaction. In this case, the terminal epoxy groups on the basic resin react with the active hydrogen groups on the primary and secondary amines, as shown in Figure 5.17. This reaction takes place readily at room temperature. Depending on the amine, the reaction can be almost explosive or it can be quite slow. These reactions are temperature sensitive so that at low ambient temperatures the reaction takes place rather slowly or, in some cases, not at all. At higher ambient temperatures, the reaction takes place much faster.

Cycloaliphatic Amine-Cured Epoxies

Today, the cycloaliphatic amines are among the most common curing agents used in epoxy coatings.[4] They are well-suited for low VOC coatings. Unlike aromatic amines, they are liquid at room temperature. Modifications such as with acid accelerators or Mannich-base formation are necessary to achieve complete room temperature cure with epoxies.

Mannich Bases

Amines may be modified with methylol phenol to produce a Mannich base, which has a better compatibility with epoxy resins than unmodified amines. They can produce blush-resistant epoxy systems that cure at temperatures of 30 to 35 °F (–1 to 2 °C). These systems may be applied under cold or damp conditions with good to excellent chemical resistance and excellent adhesion. Phenol contents must be limited for toxicity reasons (1% maximum in Europe).

Diethylene triamine (DETA) is a common tri-functional amine used to cure epoxy resins and to form the cross-linked coating. This is shown in Figure 5.18, which indicates a tri-functional amine reacting with the epoxide resin to tie the resin molecule together in a typical cross-link pattern. Note the number of hydroxyl groups that form due to the amine–epoxide reaction.

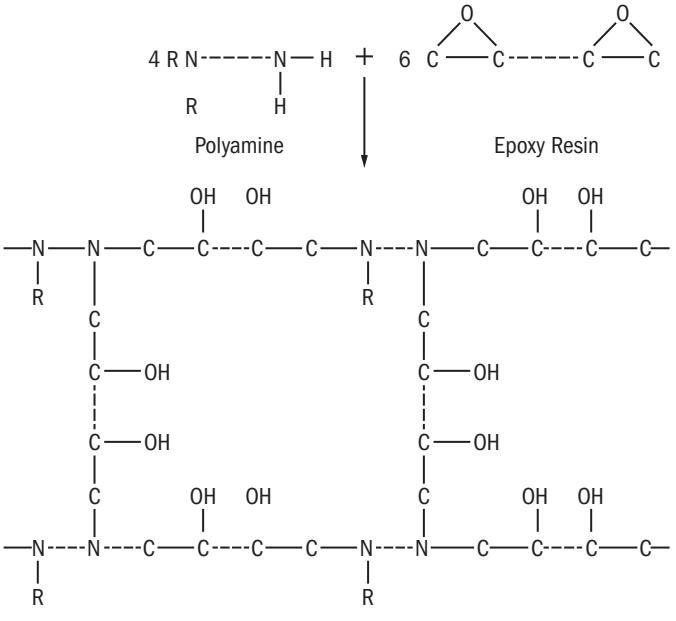


FIGURE 5.18: The reaction of a diethylene triamine and an epoxy resin forms a typical cross-link pattern.

As might be expected from the reaction shown, it is necessary for such an epoxy coating to be marketed in a two-package system, the

ingredients of the two packages being mixed just prior to application. Various amines react at different rates so that the pot life of the mixed system can be regulated to react within just a few minutes or after several hours or even days. The usual pot life of such a system for corrosion-resistant coatings is in the neighborhood of four to eight hours. The reaction actually continues over a number of days, with the coating becoming harder and more resistant.

The aliphatic amine-cured epoxies present certain handling hazards. The amines are moderately toxic and are skin irritants, which may cause allergic reactions. Care should thus be taken during the application of an amine-cured epoxy to prevent contact with the skin and to avoid inhalation of the vapors containing the amine.

The aliphatic amine-cured epoxy systems form very hard, adherent coating systems, which have very good chemical and corrosion-resistant properties. They are tightly cross-linked and therefore have good solvent resistance. They have excellent alkali and salt resistance and good water resistance. This being the case, they are used as protective coatings under many highly corrosive conditions. Their weather resistance is not the best since they tend to chalk rather readily.

Polyamide Epoxy

The reaction of the basic epoxy resin with the polyamide curing resins forms the basis for probably the most widely used corrosion-resistant epoxy coatings at the present time. While the polyamides might seem to be a type of curing compound, the polyamides are actually resinous materials that have amine groups attached, and it is these amine groups that react with the epoxide group on the epoxy resins. The reaction is the same as described with the aliphatic amine, with the much larger polyamide resin acting as the cross-linking mechanism.

There are a number of different viscosities and molecular weights of polyamide resins, and they can be used in different quantities with different epoxy basic resins. Again, there are a number of coating characteristics that can be changed in this manner. However, the polyamide epoxy coatings are generally considerably softer and more resilient and flexible than the amine-cured epoxy coatings.

They also differ in other properties. Polyamides have excellent alkali resistance but their acid resistance is not as satisfactory as the amine-cured epoxy coatings. The weather resistance of the polyamide epoxy coatings is considerably better than that of the amine-cured type. Thus, the former materials are primarily used for exterior atmospheric corrosion resistance, while the latter are used to a greater extent as tank linings and interior coatings for acidic corrosion conditions. The polyamides have lesser solvent resistance than the amines. The polyamide epoxy coatings cure readily at room temperature and, as usually formulated, have good pot lives for easy application. The polyamide resins, being rather large molecules, form a more bulky curing agent than the amines, so that, for the most part, they are packaged in two containers on an almost equivalent volume basis for the epoxy resin solution and the polyamide resin curing agent. This also makes for easy handling in the field during application.

Amine Adducts

Polyamine adducts are made by reacting epoxy resins of relatively low molecular weight with an excess of typical polyamines, such as diethylene triamine. Amine terminated epoxy resin is the resulting product, which can then react with the basic epoxy resin in the usual amine reaction. The resulting product is similar to the amine-cured epoxy; however, it has the advantage of lowering the volatility and the safety hazards of the low molecular weight amine. The amine adduct, which has very little free monomeric amine included in it, has a much lesser tendency to blush or for the monomeric amine to migrate to the surface of the coating. This is a distinct advantage. Also, the greatly increased combining weight of the adduct, as compared to the monomeric amine, makes for a much larger volume and therefore a less critical curing agent: basic resin mixture. Again, in this case, the curing agent can be in an almost equivalent volume to the base resin to facilitate mixing in the field.

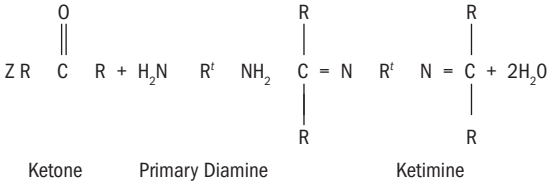


FIGURE 5.19: Ketimine curing agent prepared by reacting a primary amine with a ketone.

Ketimine Epoxy Coatings

Another approach used to form corrosion-resistant coatings is the ketimine curing agent. In this case, the amine curing agent is a so-called "blocked" amine curing agent. This is prepared by reacting a primary amine with a ketone, as shown in Figure 5.19. The active hydrogens on the primary diamine have been removed in forming the ketimine and, in this form, the curing agent is not active and is therefore referred to as blocked. The ketimine does not become active until water from the air acts with it, regenerating the original amine and the ketone. The amine then proceeds to react in the same manner as any primary amine, as shown in Figure 5.18. The ketone merely evaporates so that is no longer enters into any of the coating reaction.

This type of curing agent has its advantage in high-solid epoxy coatings where amine curing agents would react so rapidly that the formation of the coating could not be controlled. It is also used in high-build, solventless coatings. The ketimine approach prevents the highly exothermic amine reaction from occurring until the amine is gradually released by moisture from the air, thus making for a coating that is reasonable from an application standpoint. The use of ketimine epoxy coatings has decreased due to its reliance on proper combinations of available moisture and temperature for optimum curing reactions and more importantly, its purported toxicity to human organs.

Cardonal-Based Epoxies

Coating systems based on cardonal (a major constituent cashew nut shell liquid [CNSL]) have increased the use of epoxy coating systems over marginally prepared surfaces. These low viscosity products have good penetrating properties into less than perfectly cleaned corroded substrates and provide flexibility, toughness, adhesion, and impact resistance, even at low temperatures. When first introduced, coatings based on this epoxy system had poor ultraviolet resistance, thus were better suited to primer and intermediate coat applications. Improvements in the resin systems in the decade beginning in 2000 have significantly improved their chalking resistance. Specially formulated epoxies using cardonal have the characteristic of reducing sterical hindrance during the curing process, thus allowing the epoxy film to achieve greater levels of cure at both low and high temperatures. This natural alkyl phenolic material

has an aromatic ring that provides a strong chemical resistant backbone while the hydroxyl group gives strong adhesion and good reactivity for fast and low temperature cure. A long aliphatic side chain provides good flexibility, low viscosity, extended pot life, and high hydrophobicity for excellent water resistance and corrosion protection. In addition to high bio content, the combination of low viscosity, fast cure, and workable pot life of CNSL-based products can lower volatile organic emissions of the final coating by allowing high solids or solvent-free formulations.

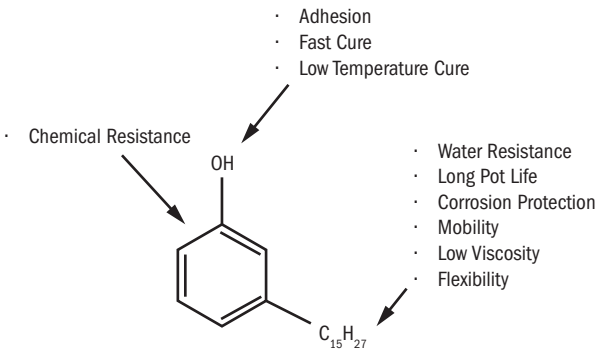


FIGURE 5.20: Phenalkamine curing agents. Source: Cardolite Corporation.

Phenalkamine Curing Agents

The Mannich reaction of cardanol, formaldehyde, and certain amines is called a phenalkamine. Phenalkamines share some similar advantages to other Mannich base curing agents, such as extremely fast cure, low temperature cure (even below 0 °C), good chemical resistance, good surface appearance, good moisture tolerance, and non-blushing properties. However, due to the long aliphatic side chain of cardanol, phenalkamines also have very good pot life, good flexibility, surface tolerance, and excellent water and salt water resistance.

Bisphenol F Epoxy Coatings

Low molecular weight bisphenol F epoxy resins offer some particularly advantageous properties, particularly for aggressive corrosion conditions. They give more highly cross-linked polymeric matrices than do the bisphenol A systems of similar molecular weight, thus yielding a coating with somewhat better solvent, heat, and chemical resistance. Low VOC coatings below the threshold limits of 2.1 lb/gal (250 g/L) are possible.

Epoxy Novolac Coatings

The increasing purity and aggressiveness of solvents and chemicals has produced a need for even higher cross-link densities than possible with traditional epoxy coatings. A popular answer to this problem is the use of epoxy phenol novolac resins. Aliphatic amine cured resins of this type are highly resistant to most solvents (including ketones, chlorinated hydrocarbons, and lower alkyl alcohols). They resist mineral acids such as hydrochloric, hydrofluoric, and sulfuric acid, and alkalis such as liquid ammonia. Some cross-linked systems are even resistant to methanol (especially when post-cured). Although many of these systems will ambient cure, all of them benefit from post-curing with heat.

Solventless (Solvent Free) Epoxies

The high-build solventless epoxies are becoming more and more popular due to the problems involved with the use of solvents and air pollution. There are a number of materials presently on the market that are referred to as high-solid solventless epoxy coatings. These are made with a sufficient amount of reactive diluent to reduce the viscosity so they can be applied by normal spray units in the field. Actually, they are not always 100% solids epoxy coatings, since they can contain a very small amount of solvent in addition to the reactive diluent. Most of these materials react to form a coating according to the amine-type reaction, and may use the ketamine blocked amine type of approach.

There are a number of advantages to the solventless (solvent free) epoxy coatings. Some can be applied by ordinary paint spray equipment, particularly the coatings with somewhat less than 100% solids. They build a heavy film and react in place to form a very good corrosion-resistant coating. Truly 100% solids epoxy coatings, for the most part, use a two-part spray gun in which the amine is metered into the system at or near the gun tip.

In both of these cases, although to a greater extent with 100% solids coatings, care should be taken not to build thickness in excess of the manufacturer's recommendations. Each coating has its own inherent stress level and overbuilding the coating may cause cracking, particularly at stress points in the steel. The high-solids materials often are also applied as a hot mix coating. If such a hot resin mixture is applied to a cold substrate, poor wetting can result with very poor adhesion of the coating, particularly if it is applied as a very heavy film. These problems should be taken into consideration during application where high solids epoxies are involved.

Newer epoxy resin modifications have resulted in less thixotropic formulations of 100% solids epoxy coatings with longer reaction times, greater film flexibility, and, most importantly, greater penetrating properties. Of particular importance to the maintenance of existing structures are the newer non-pigmented epoxy sealers, which have sufficient flexibility to reduce the stress imparted to existing coating systems while still maintaining a proper substrate for the rest of the coating system. The curing reactions are generally slow enough to allow more time between coats without the worry over intercoat delamination. Non-pigmented epoxy sealers should always be overcoated, particularly in exterior exposures. They do not have very good resistance to ultra-violet (actinic) rays of the sun and will deteriorate quickly.

Aromatic Amine Curing Agents

Here again, we are dealing with the amine-basic epoxy resin reaction. In the case of the aromatic amines, the curing is much slower, and, under some conditions, must be stimulated by an increased temperature of around 300 °F in order to properly cure. Aromatic amines are primarily used for structural plastics; on the other hand, there are a few corrosion-resistant coatings that use aromatic amines and which are considered to be air curing. In these cases, the aromatic amine is dissolved in a strong solvent for both the basic epoxy resin and the amine, which allows intimate contact of the amine group on the aromatic molecule with the epoxide groups on the epoxy molecule. A reaction does take place at ambient temperatures. It is, however, generally slower than the reaction with most aliphatic amines. This process is included here because the aromatic amine cures of the epoxy provide the maximum chemical and solvent resistance available with an air-cured epoxy. These materials have excellent corrosion resistance and, where they can be used as linings or coatings subject to strong chemical atmospheres, perform well.

High-Build Epoxy Coatings

High-build epoxy coatings should be differentiated from high-solids or 100% solids epoxy coatings in that they are usually coatings of the amine or polyamide type to which are added inert pigments, such as silica, mica, talc, titanium dioxide, and similar pigments to the maximum pigment volume, which provides complete wetting of the pigment and the surface over which it is applied. These high-build materials are generally very inert and are designed on the impervious coating concept (i.e., there are no inhibitive pigments included and the resistance of the coating is due to its completely inert characteristics). These coatings are usually quite flat, have a semi-gloss or no gloss, and are generally used under severe corrosion conditions. Many have been used as linings. They may be used alone, in one or more coats over a substrate, applied over IOZ primers, or as either a base coat or an intermediate coat over which lower solids epoxies with a higher gloss are applied. These are practical materials and are used where the corrosive conditions indicate the need for added coating thickness.

Silicone-Modified Epoxy Resin

A silicone modification of the epoxy is accomplished by reacting the methoxy groups of a methoxy polysilicone intermediate with the secondary hydroxyl groups on the solid basic epoxy resin. In this case, the OH group on the epoxy resin is being used rather than the epoxide group. The silicone modification is a plant reaction and cannot take place in the field inasmuch as the two reacting materials must be at elevated temperatures in order to provide the new molecule. About 10 to 20% of the silicone intermediate is incorporated with the basic epoxy resin. The epoxide groups on the molecule are not affected, and the resulting silicone-modified epoxy resin is cured in the field by the use of an amine curing agent. These materials have improved water resistance, acid and chemical resistance, and weather resistance. The reaction with the silicone intermediate and the basic epoxy resin is shown in Figure 5.20.

Epoxy-Phenolic Coatings

The epoxy phenolic coating is another instance where the hydroxyl group on the epoxy resin is a primary area of activity. The phenolic resin may be any number of reactive phenolic resins. The specific chemistry of this is given later in this chapter under "Heat-Condensing Coatings;" however, the essential reaction is shown as follows:

$$R{-}OH + HO{-}CH_2{-}R^1 \rightarrow R{-}O{-}CH_2{-}R^1 + H_2O$$

where R = epoxy resin and R^1 = phenolformaldehyde resin. (5.3)

As the molecular weight of the epoxy resin is increased, chemical and solvent resistance is increased and the flexibility and impact resistance is improved. Increasing the level of the phenolic resin improves the general chemical and solvent resistance of the epoxy phenolic coating at the expense of some of the flexibility and resistance to alkalies. Many of the epoxy phenolic coatings are baking coatings requiring several hundred degrees of temperature to properly cure. These are discussed later in this chapter.

There are also epoxy phenolic coatings available that will cure at substantially lower temperatures. They are very slow to cure at ambient temperatures; however, at approximately 60 °C (140 °F), they do cure to a chemical resistant coating with very nearly the equivalent resistance to those of the high bake. Many of these coatings are used for solvents, saltwater, and particularly for the lining of tank cars or barges transporting concentrated NaOH solution. These epoxy phenolic coatings or linings provide excellent chemical and corrosion resistance.

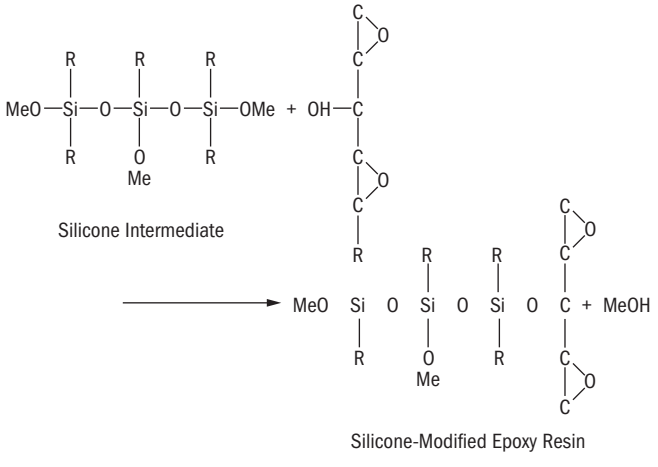


FIGURE 5.21: Formation of a silicone-modified epoxy resin.

Epoxy-Urethane Coatings

Basic epoxy resins also can be cross-linked at room temperature with polyisocyanate compounds. The isocyanate reacts primarily with the hydroxyl groups from the higher molecular weight solid epoxy resins (Figure 5.21).

The reaction of the isocyanate with the hydroxyl does not interfere with the epoxide groups on the epoxy resin molecule; thus, some excellent corrosion-resistant coatings have been developed using this reaction. In this case, the isocyanate is used to react with as many of the hydroxyl groups on the epoxy resins as possible, increasing the size of the epoxy resin molecule and eliminating the hydroxyl group, which reduces water and chemical resistance. The isocyanate reacted epoxy resin is then cured in place as a coating through use of the amine reaction between the terminal epoxide groups on the epoxy resins. The resulting material, cured at room temperature, has a very high degree of solvent, acid, and corrosion resistance. Federal government restrictions on free isocyanates have reduced the use of this type of epoxy coating.

Coal Tar Epoxies

Coal tar epoxies are a combination of the basic epoxy resin with coal tar. The coal tar is in the form of a semi-liquid pitch and is blended with the basic epoxy resin and solvent. The curing mechanism for the coal tar epoxy is the amine reaction with the terminal epoxide groups on the epoxy resin. It is not known whether a reaction, if any, takes place between the coal tar and the epoxy resin. It appears possible that some of the hydroxyl or methylol groups on the phenolic compounds within coal tar may react with some of the hydroxyl groups on the epoxy, causing some cross-linking between the two materials. This, however, is merely a supposition. On the other hand, there is some evidence that this might take place because of a reduction in the solubility of the coal tar when combined with the epoxy. Some reaction also may be indicated because of the fact that some coal tars, even those in the same softening range, will produce better and more effective coal tar epoxy coatings than others. There is a distinct difference in effectiveness between many

TABLE 5.11: Co-Reactive Coatings: Epoxy

						Coal Tar Epoxy		
	Aliphatic Amine Cure	Polyamide Cure	Aromatic Amine Cure	Phenolic Epoxy	Silicone Epoxy	Amine Cure	Polyamide Cure	Water Based Epoxy
Physical Property	Hard	Tough	Hard	Hard	Medium-Hard	Hard (brittle)	Tough	Tough
Water Resistance	Good	Very Good	Very Good	Excellent	Good-Excellent	Excellent	Excellent	Fair-Good
Acid Resistance	Good	Fair	Very Good	Excellent	Good	Good	Good	Fair
Alkali Resistance	Good	Very Good	Very Good	Excellent	Good	Good	Very Good	Fair
Salt Resistance	Very Good	Very Good	Very Good	Excellent	Very Good	Very Good	Very Good	Fair-Good
Solvent Resistance (Hydrocarbon) Aromatic	Very Good	Fair	Very Good	Very Good	Good	Poor	Poor	Poor-Fair
Aliphatic	Very Good	Good	Very Good	Very Good	Very Good	Good	Good	Good
Oxygenated	Fair	Poor	Good	Very Good	Fair	Poor	Poor	Poor
Temperature Resistance Weather Resistance	95 °C Fair, Chalks	95 °C Good, Chalks	120 °C Good	120 °C Fair	120 °C Very Good, Chalks Resistant	95 °C Fair	95 °C Fair	95 °C Good
Age Resistance	Very Good	Very Good	Very Good	Very Good	Very Good	Very Good	Very Good	Good
Best Characteristics	Strong Corrosion Resistance	Water and Alkali Resistance	Chemical Resistance	Chemical Resistance	Water and Weather Resistance	Water Resistance	Water Resistance	Ease of Application
Poorest Characteristics	Recoatability	Recoatability	Slow Cure	Very Slow Air Cure	Recoatability	Black Color Recoatability	Poor Recoatability Black Color	Proper Coalescence
Recoatability	Difficult	Difficult	Difficult	Difficult	Difficult	Difficult	Difficult	Difficult
Primary Coating Use	Chemical Resistance	Water Immersion	Chemical Coating	Chemical Lining	Weather Resistance	Water Immersion	Water Immersion	Atmospheric Corrosion

of the coal tar epoxies produced around the world because of the source of the coal tar.

A combination of the two materials appears to combine the good properties of both the epoxy and the coal tar to form a superior water and saltwater-resistant coating. It is not often that a combination of two widely different materials such as epoxy and coal tar result in a finished material that is superior to either when used alone. This appears to be the case in the coal tar epoxy combination. The combination is resistant to a wide variety of aqueous conditions as well as to materials such as HCl, NaOH, and sour crude oil. The combination of the two materials resists sagging up to 200 °C and is less brittle and more resistant to impact than unmodified coal tar alone. As previously stated, the curing mechanism of the coal tar epoxy is by an amine-curing agent. The aliphatic amine provides a very hard, tough, adherent coating. The coal tar epoxy also may be mixed with the polyamide curing agents to form a much more resilient, somewhat softer coating, also with good adhesion. The polyamide coal tar epoxy has excellent water resistance.

The polyamide coal tar epoxy also has some serious drawbacks. It tends to delaminate between coats for any number of different reasons. Water or moisture on the surface, too long a period between coats, and even exposure to strong sunlight for even a few hours will cause delamination of the following coat. The amine-cured coal tar epoxy also will show some of this deficiency. This is something for a corrosion engineer to keep in mind when using coal tar epoxy coatings. The problem has been serious enough so that in certain instances, polyamide coal tar epoxies have not been used for exterior coating work. In order to overcome this situation, several suppliers of polyamide coal tar coatings have produced a high-solids material that can be applied in one coat at from 15 to 20 mils (375 to 500μm) thickness. The material applies well and produces a smooth, even coat. There is no problem with delamination since no additional coats are necessary.

Two areas where coal tar epoxy coatings are most effective include the sewage and marine industries. In the sewage industry they are used for both steel and concrete surfaces. In this case, the amine-cured coal tar epoxy is essential because of the bacterial attack on the polyamide-curing agent. Coal tar epoxy is not only resistant to the continued water immersion, but it also provides good protection against oxidized H_2S, which is the corrosive agent found in sewage conditions. In the marine industry, they are used as coatings for underwater ship hulls, ballast tanks, and combined cargo and ballast tanks, and for resistance to both saltwater and crude oil. Here again, there is a H_2S problem and the coal tar epoxy has excellent resistance to the sour crude.

Another property of the coal tar epoxy coating is its excellent resistance to CP currents. In the marine industry, it is used as a shield around impressed current anodes to spread the current away from the anodes and to reduce the current density (CD) in that particular area. It is one of the few materials that will withstand the strong CDs found in this area.

Because the coal tar epoxy resins have been labeled as a suspected carcinogenic, many countries have banned their use. Some manufacturers have produced alternative coatings based on hydrocarbon resins that look like, apply like, and appear to be a reasonable alternative to coal tar epoxy; however, there is considerable debate over the validity of the equality of performance. One distinct advantage of the hydrocarbon resin based coal tar epoxy is that it is not as likely to create dermatitis of the skin and it does not have the same burning sensation on the skin when applied in hot weather.

Waterborne Epoxy Coatings

Much research has been spent on waterborne epoxy resin systems as a result of the various regulations limiting the use of organic solvents in coatings. These coatings are usually two-package epoxy-polyamide systems in which the epoxy component is an emulsion based on a proprietary mixture of a liquid epoxy resin and an aliphatic epoxy monomer. The low viscosity imparted to the epoxy resin by the aliphatic diluent is desirable to ensure proper coalescence of the resin co-reactants during film formation as the water evaporates. The polyamide curing agent component is supplied in a mixture of a high-boiling aromatic solvent and a hydroxyl-free water miscible solvent such as ethylene glycol monoethylether acetate. As in the case of a conventional two-package epoxy system, the curing agent component is packaged separately. Where weather conditions permit (average humidity and temperatures near 15 °C), coatings of the water-based type have given good service, even under some reasonably severe corrosion conditions. Table 5.11 gives the characteristic properties of the various epoxy coating combinations.

Much of the early sales of waterborne epoxies were for commercial and institutional concrete structures, due to flash rusting and deficient performance on steel vs. solvent-borne epoxies. Newer resins, including water-miscible polyamides (with and without external emulsifiers of the nonylpheno ethylene oxide type) have given better performance. Patented[5-6] anti-corrosive amine-cured metal coatings are self-emulsifiable and can be used with amine adduct and amidoamine curing agents. Modifications of the same technology uses an alkyl phenol formaldehyde novolac resin to give a multifunctional epoxy dispersion, which results in a very stable resin with high performance properties for room temperature curing primers and finish coats.

Polyurethanes

Polyurethanes are a class of coatings that have found substantial growth in the corrosion protection market because they provide a unique combination of flexibility, weatherability, chemical and abrasion resistance, and corrosion resistance. This unique combination of physical/chemical properties is derived from diverse raw material selection, allowing polyurethanes to be used in many applications, from automotive to wood coatings. Furthermore, polyurethanes allow for increased productivity from reduced curing times, driving their widespread acceptance across markets.

This section will focus on corrosion protection coatings that are capable of curing at ambient conditions, and will not include discussions on urethane-modified oil-based coatings because they do not provide adequate corrosion protection for the industrial maintenance market. Since 1990 a three-coat system based on a zinc-rich primer, epoxy intermediate, and aliphatic polyurethane topcoat has become the standard in the corrosion industry for civil engineering applications across the globe.[8] The proven performance of three-coat systems has resulted in polyurethanes becoming the top-selling topcoat in the industrial maintenance market.[9] While three-coat systems are currently the industry standard, two-coat systems, where the intermediate and topcoat are replaced with a single thick topcoat, have made progress in recent years using polyaspartic coatings. Two-coat systems maximize productivity and return-to-service times in both factory and site-applied application conditions.

Isocyanates will react with any molecule containing labile hydrogen. The most common reaction is with alcohols to form urethanes, and this reaction is typically catalyzed with either a tin or amine catalyst (Figure 5.22). Isocyanate reactions with water and amines to form polyureas also have an important role in anti-corrosion coatings. Single-component polyurethane coatings (i.e., moisture cured) are based upon the above reaction with water to form a polyurea coating. Water reacts with isocyanates yielding CO_2 and producing an amine that further reacts with isocyanates. Primary and secondary amine reactions with isocyanates are typically very fast, oftentimes making them unusable with traditional coatings application equipment. Polyaspartic esters are a special class of secondary amines designed to have reduced reactivity that are suitable for coatings applications.

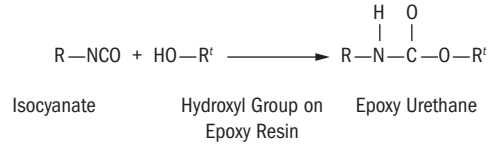


FIGURE 5.22: Formation of an epoxy urethane.

Polyurethanes are formed by reacting multifunctional isocyanates (polyisocyanates) with multifunctional alcohols (polyols), and each component has greater than two reactive groups attached per molecule (typical functionality = 2.3 - 3.5). For example, the trimer shown in Figure 5.22 is generated by reacting three HDI molecules together yielding a crosslinker with three reactive isocyanate groups. Polyols and polyisocyanates are employed in two-component polyurethane coatings to form high-performance, cross linked films.

Both polyols and polyisocyanates are carefully selected to formulate coatings for specific environments. For example, castor oil polyols provide hydrophobicity and flexibility, polyester polyols provide enhanced chemical resistance, and acrylic polyols are known to provide excellent weatherability. Hydrogen bonding between ester groups provides polyester polyols with a unique balance of flexibility and chemical resistance at the expense of higher viscosity. Acrylic polyols with styrene exhibit enhanced chemical and water resistance at a lower cost, although at the expense of weatherability. Fluorinated polyols have found application on bridges due to their outstanding weathering resistance, justifying their higher cost. Polyol combinations, usually blends of polyesters and acrylics, are used to optimize all-around performance and cost for each specific application.

Both aromatic and aliphatic isocyanates are utilized in the corrosion protection market, with aromatics mainly used in primers and aliphatics providing light stability for topcoat applications. Frequently used isocyanates are shown in Figure 5.22 and the isocyanates are often reacted with themselves to form adducts for higher functionality and reduced occupational exposure. Aromatic isocyanates are typically more reactive than aliphatic. Reactivity is also affected by steric hindrance and catalysts.

Coatings based on aromatic isocyanates are used as primers in three-coat systems and topcoats in buried pipe coatings. Prepolymers of TDI and MDI, synthesized by reacting excess MDI/TDI with a polyol, are employed in these applications and a range of physical properties can be obtained by varying the polyol selection. Typical polyurethane primers are single component moisture-curing systems formulated with anti-corrosive pigments and/or barrier forming pigments. While epoxies are typically more water resistant than aromatic urethane coatings, the isocyanate's increased reactivity allows for more reliable curing and increased productivity at low temperatures. As compared to coatings based on aliphatic isocyanates, aromatic coatings bring enhanced chemical and water resistance, however their exterior applications are limited due to ultraviolet (UV) degradation.

Light-stable polyurethane topcoats based upon aliphatic isocyanates have grown in importance in the corrosion market. Polyisocyanates based upon HDI and IPDI are the mainstay in these topcoats, and HDI trimer (Figure 5.23) is an exemplary crosslinker. Two-component

water-based coatings are capable of providing similar performance, however solvent-based coatings are preferred in anti-corrosion applications due to lower cost raw materials, application largely independent of environmental conditions, and longer pot life. Solvent-based topcoats are supplied in either one-, two-, or three-component systems, with the most common being multiple component where each component is typically comprised of:

- Component 1 - Polyols, solvents, extenders, pigments, additives, co-resins, and additives
- Component 2 – Polyisocyanates
- Component 3 - Catalysts

High-solids two-component polyurethane coatings are available, as are solvent-free two-component coatings that use specialized application equipment. One-component systems (i.e., moisture-cured) are used to some extent, and offer advantages in painting during cold and/or damp conditions. In the Northeast United States, they are used to extend the painting season into winter because they cure relatively independent of environmental conditions.

Polyurethane coatings display many unique advantages described above, and possess some disadvantages mainly revolving around their reaction with water. CO^2 evolution from the side reaction with water limits application at humidity levels greater than 95% and film builds greater than 75 µm. Furthermore, solvents must be "urethane-grade" that ensures relatively low water concentrations. Lastly, weathered polyurethanes should be sanded to provide mechanical adhesion if recoating is desired.

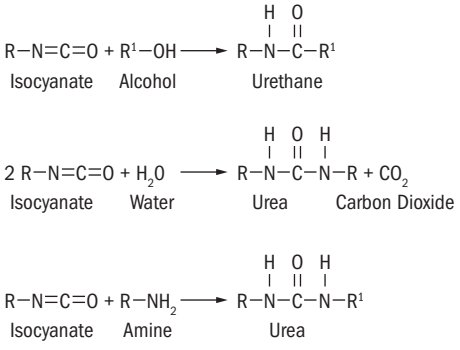


FIGURE 5.23: Reactions of isocyanates to form urethane and urea.

Beginning shortly after the year 2000, coatings based upon polyaspartic esters found increased utilization in both anti-corrosion and flooring markets mainly due to their rapid curing times. Polyaspartic esters are secondary amines designed to have lower reactivity than a typical amine and higher reactivity than polyols. The polyaspartic resin replaces the polyol component in traditional two-component polyurethane coatings, and their enhanced reactivity allows for reduced dry times while still maintaining adequate pot life for conventional spray equipment. Unlike traditional two-component polyurethane coatings, high film builds (ca. 175 µm-250 µm) (7-10 mils) are possible because the polyaspartic's enhanced reactivity does not allow the isocyanate's side reaction with water to become substantial (Figure 5.22). A high film build topcoat over a zinc-rich primer can give similar performance to a traditional three-coat system, and the two-coat system saves labor cost and increases productivity. Lastly, polyaspartics display reduced viscosities as compared to conventional polyester and acrylic polyols, allowing for lower VOCs in the final coating formulation. One disadvantage of these coatings is variable cure rates depending on humidity levels

The reaction of isocyanate with hydroxyls is the primary basis for various isocyanate or urethane coatings. As outlined by ASTM D16,10 "Standard Terminology Relating to Paint, Varnish, Lacquer and Related Products," there are six different types of urethane coatings. For historical purposes only, these are listed below.

- Type I: One Package Pre-reacted Polyurethane Oil
- Type II: One Package Moisture Cured Polyurethane
- Type III: One Package Heat Cured (Blocked) Urethane
- Type IV: Two Package Catalyst (Moisture Cure With Small Amount of Accelerator or Co-reactant)
- Type V: Two Package Polyol (Isocyanate and Polyol-Containing Reactive Hydrogen)
- Type VI: One Package, Nonreactive Lacquer Polyurethane

Non-Yellowing Urethanes

One common use of these materials is for aircraft and pleasure boats where the properties of the urethanes are used to their best advantage (i.e., any aircraft coating must be abrasion-resistant to ice, dust particles, rain, etc.). They must: (1) withstand continual exposure to weathering conditions; (2) have a good, long-lasting gloss; (3) have top-quality color retention; and (4) be resistant to hydraulic fluids, gasoline, jet fuels, and similar solvents. The general properties of the various urethane coatings are given in Table 5.12.

As can be seen from Table 5.12, the general corrosion and chemical resistance of the urethane is not as great as some of the other corrosion-resistant coatings. The outstanding urethane property is that of abrasion resistance.

There are probably no other coatings available that have the resistance to abrasion that polyurethanes do. Thus, they make excellent floor and deck coatings and withstand much more traffic and hard use than most other coatings. Their chemical and corrosion resistance is also sufficient for this type of use when combined with the excellent abrasion and impact resistance. The exceptions would be those areas where there is continuous acid or chemical spillage requiring acid-proof brick and tile floors. For example, the Tabor Abrasor values for polyurethane will have approximately one-tenth the loss of coating per 1,000 revolutions, compared to an amine catalyzed epoxy. Urethane coatings have excellent impact properties and can withstand both direct and reverse impact, which is a property that many other resistant coatings do not have. The same urethane coating can be designed to have flexibility, impact resistance, and high abrasion resistance, all combined into one coating.

New non-yellowing urethanes, in addition to the abrasion and impact characteristics, also provide a coating with an excellent depth of color, good color retention, and good gloss retention over long periods of time in weather exposure. In fact, they are equal, if not superior, to some of the acrylic coatings.

One of the areas where urethanes may have a problem is in the retention of adhesion when exposed to water, either in immersion or as moisture. It is a characteristic that must be kept in mind for corrosion-resistant applications. Generally, urethane coatings are used as topcoats and applied over good epoxy primers for best results for corrosive conditions. (The NACE Technical Practices Committee report of Task Group T6B25 on "Urethane Protective Coatings for Atmospheric Exposures" is recommended for more specific information on urethane coatings.)

Elastomeric Polyurethane/Polyurea Coatings

While these coatings have been around since well before the turn of the century, the major advancement in market share for this

TABLE 5.12: Co-Reactive Coatings-Urethanes: General Properties[A]

Properties	Type 1 Oil Modified	Type 2 Moisture Cure	Type 3 Blocked	Type 4 Prepolymer Catalyst	Type 5 Two Component	Aliphatic Isocyanate Cure (Non-Yellowing)
Physical Property	Very Tough	Very Tough, Abrasion Resistant	Tough, Abrasion Resistant	Tough, A brasion Resistant	Tough-Hard, Rubbery	Tough-Rubbery
Water Resistance[B]	Fair	Good	Good	Fair	Good	Good
Acid Resistance[B]	Poor	Fair	Fair	Poor-Fair	Fair	Fair
Alkali Resistance[B]	Poor	Fair	Fair	Poor	Fair	Fair
Salt Resistance[B]	Fair	Fair	Fair	Fair	Fair	Fair
Solvent Resistance (Hydrocarbon) Aromatic	Fair	Good	Good	Poor	Good	Good
Aliphatic	Fair	Good	Good	Fair	Good	Good
Oxygenated	Poor	Fair	Fair	Fair	Good	Fair
Temperature Resistance Weather Resistance	Good 100 °C Good, Yellows	Good 120 °C Good, Yellows	Good 120 °C Good, Yellows	Good 100 °C Good, Yellows	Good 120 °C Good, some yellowing, chalk	Good 120 °C Excellent, good color and gloss retention
Age Resistance	Good	Good	Good	Good	Good	Good
Best Characteristic	Exterior, Wood Coating	Abrasion, Impact	Abrasion, Impact	Speed of cure	Abrasion, Impact	Weather Resistance, Color and Gloss Retention
Poorest Characteristic	Oil Base Chemical Resistance	Dependent on Humidity for Cure	Heat Required for Cure	Chemical Resistance	Two package	——
Recoatability	Fair	Difficult	Difficult	Difficult	Difficult	Difficult
Primary Coating Use	Clear Wood Coating	Abrasion Resistance, Floors	Product Finish	Abrasion Resistance	Abrasion Resistance, Impact	Exterior Coatings

[A]The properties of urethanes vary over a wide range due to the many and varied basic polyols and isocyanates. The above listings are only indicative. Manufacturers must be contacted for specific properties of specific materials. Harder coatings are more resistant than softer, more rubbery types.
[B]Resistances are for non-immersion conditions.

technology has been the development of 100% volume solid polyurethane, polyurea, and hybrid polyurethane/polyurea coatings.

A pure polyurethane coating is the result of a reaction between an isocyanate component and a resin blend made with only hydroxyl-containing resins that contain no intentional urea groups. Polyurethane systems may contain catalysts, additives such as moisture scavengers, and anti-foam agents.[8]

A polyurea coating is the result of a one-step reaction between an isocyanate component and a resin blend component. The resin blend component must contain amine-terminated polymer resins, and/or amine terminated chain extenders and should not contain any intentional hydroxyl moieties.[8]

A polyurethane/polyurea hybrid coating has a composition that is a combination of the two above-mentioned coating systems. The isocyanate component can be the same as either the polyurea or the polyurethane system. The resin blend may be a blend of amine-terminated and hydroxyl-terminated polymer resins and/or chain extenders. To bring the reactivity of the hydroxyl-containing reins to the same level of reactivity as the amine-terminated resins, the addition of one or more catalysts may be necessary.[8]

Polyurea coating systems have the following advantages:[11]

- Fast cure: Polyurea can be sprayed on sloped surfaces without drip or run formation. Foot traffic can resume on coatings applied to horizontal surfaces within 30 seconds.
- Relative insensitivity to moisture and temperature during application: Little effect is encountered on adhesion or coating performance due to weather variations (e.g., high humidity, temperature, and residual moisture).
- 100% solids: Two-component, one-coat systems can be sprayed or poured at 1:1 volume ratio, which eliminated the need for multi-coat applications.
- Excellent physical properties: These include tensile strength, tear strength elongation, and thermal stability.
- Formulation flexibility: The chemistry can be adjusted to produce soft or hared elastomers. Also, pigments, fibers, and fillers can be added to further differentiate the end product.

Reference standards include SSPC-PS 28.01,[12] "Two-coat Zinc-Rich Polyurethane Primer/Aliphatic Polyurea Topcoat System," and SSPC-PA 14,[13] "Application of Thick Film Polyurea and Polyurethane Coatings to Concrete and Steel Using Plural-Component Equipment."

A combination of a proprietary 100% solids polyurethane formula applied over a rubber lining has solved a major erosion/corrosion problem in piping used to transfer oil-rich coal tar sands in Canada. The combination of heat resistance and abrasion resistance of this proprietary system has exceeded all other linings in durability for this severe service condition.

Polyaspartic Coatings

The chemistry of polyaspartic coatings was first introduced in the early 1990s. It is based on the reaction of an aliphatic polyisocyanate and a polyaspartic ester, which is an aliphatic diamine. This technology was initially used in conventional two-component polyurethane solvent-borne coating formulations because the polyaspartic esters are excellent reactive diluents for high solids polyurethane coatings.

More recent developments in polyaspartic coating technology have concentrated on achieving low or near-zero VOC coatings where the polyaspartic ester is the main component of the co-reactant for reaction with a polyisocyanate. Non-yellowing and good overall weathering are typical properties of polyaspartic topcoats.

The name polyaspartics has recently become popular among formulators in the industry due to the need to differentiate it from polyureas and polyurethanes. By definition, a polyaspartic is an aliphatic polyurea because it is the reaction of an aliphatic polyisocyanate with a polyaspartic ester, which is an aliphatic diamine. However, polyaspartic coatings are very different in both application and coating performance properties from conventional polyureas. For example, polyaspartics allow the formulator to control the rate of reaction and cure; thus, pot life of the two-component mixture can range from five minutes to two hours.

Polyaspartic technology is closer in its applications and performance characteristics to two-component aliphatic polyurethane coatings. It is often used as a topcoat due to its non-yellowing nature. But, here too, there are noteworthy differences. The polyaspartic coatings, for example, can be formulated to very high solids (70-100% solids) and applied at higher film builds (up to 15 mils wet film thickness [WFT] in a single coat) than typical two-component aliphatic polyurethanes.

Polyaspartic ester technology, a direct-to-metal coating, is widely used in railcar painting because it provides high-performance protection and exceptional color and gloss retention (Figure 5.24). Because no primer coat is needed, the efficiencies of reducing a conventional two-coat system to a one coat direct-to-metal (DTM) system are very cost effective and result in productivity benefits. Polyaspartic coatings are often used in bridge applications as a result of their ease of application and fast curing, which lead to cost savings and the ability to keep pace with the construction schedule. (Figure 5.25) A two-coat high productivity coating system can achieve the same performance advantage of a typical three-coat system.

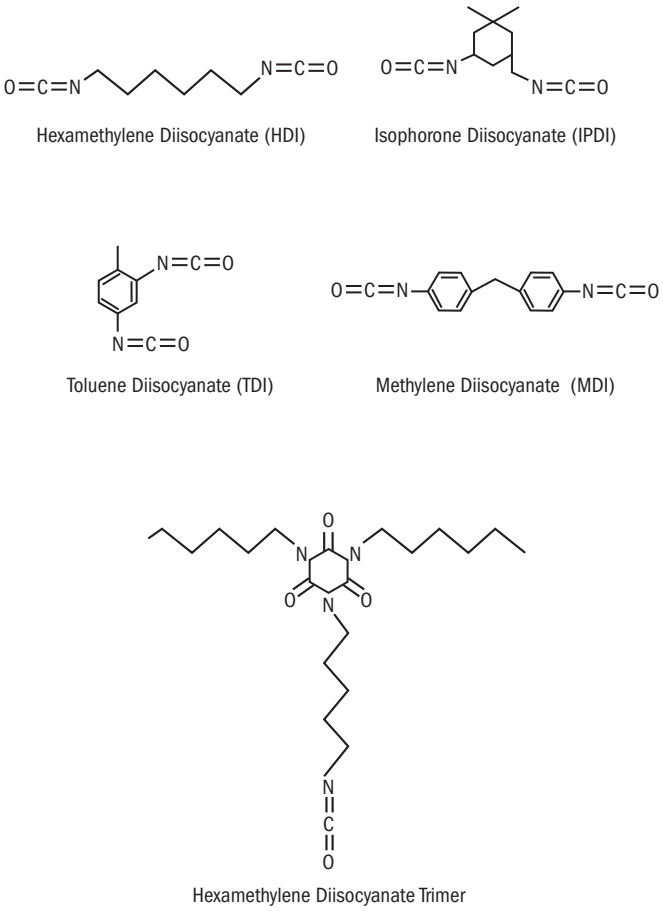


Figure 5.24: Aromatic and aliphatic diisocyanates used to synthesize higher functional polyisocyanates like the trimer shown above.

Polyester Coatings

The application of polyester coatings in the area of alkyd resins was discussed earlier. Polyesters are included in the discussion of co-reactive coatings because they have been used as linings for tanks, portions of tanks, or bottoms of tanks for many different corrosive conditions. The polyester, as used for these purposes, has excellent corrosion resistance. Polyester resins are used mostly in the reinforced plastics industry, where they are used as binders for synthetic, glass, or graphite fibers, to form a myriad of high-technology products. There are two areas where polyester resins are used particularly for coatings. The first is the so-called gel coat, which is used primarily in connection with the formation of reinforced plastics. It generally is used as the first material on the mold in order to provide a dense, glossy, weather and corrosion-resistant surface, which also has a good appearance. Another area where polyesters are effective is that of 100% solids coatings, which have good corrosion resistance properties. These materials have been used extensively for lining tank bottoms. The polyesters with which we are involved as co-reactive coatings are the unsaturated polyesters, which are linear polyester resins based on dihydric alcohols, and dibasic acids, which contain sufficient unsaturation so that they have the capability of cross-linking with vinyl type monomers to form a thermoset polyester. The unsaturation in the polyester usually comes in the unsaturated acids or anhydrides that are used to form the polyester. Cross-linking of the coating is then accomplished by use of such monomers as styrene, vinyl toluene, methyl methacrylate, and others. The formation of the coating is in place using the double bond reaction between the polyester resin and the styrene activated by a catalyst such as one of the organic peroxides (methyl ethyl ketone peroxide or cumene peroxide). The chemistry involved in this process is shown in Figure 5.26.



Figure 5.25: Source: Bayer Material Sciences, Pittsburgh, PA.

The addition of the styrene or a similar vinyl-type monomer is necessary to further polymerize the polyester resin, cross-link it, and render it insoluble. The styrene acts in two ways: (1) as a solvent for the basic polyester resin; and (2) when a catalyst is added (e.g., methyl ethyl ketone peroxide and a cobalt accelerator). A rapid reaction takes place at room temperature, cross-linking the polyester and forming a solid resin coating or lining. One of the disadvantages of the polyester-styrene copolymers has always been their tendency toward shrinkage. This is due to the internal shrinkage of the molecule when polymerization takes place. This has been improved by

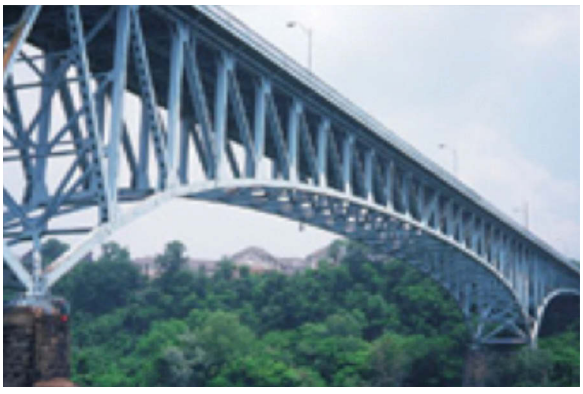


Figure 5.26: Source: Bayer Material Sciences, Pittsburgh, PA..

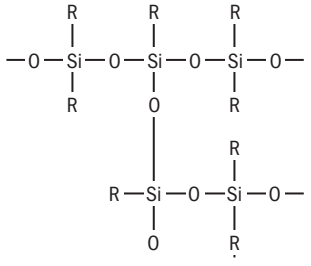
the incorporation of glass fibers or flakes and siliceous fillers. Considerable shrinkage (3 to 15% or more), however, still takes place when a large area of polyester resin and glass is applied to a tank bottom or similar structure. Thus, shrinkage must be taken into consideration during application, particularly on hot, windy days.

A polyester glass structure provides a good corrosion-resistant coating or lining. Its thickness may range from 100 to 250 mils, and its resistance to acidic water or acids is very good. It is not, however, satisfactory for alkaline solutions since both the glass and polyester tend to break down in a caustic solution. A polyester glass structure on tank bottoms, sidewalls, and similar areas is usually applied using a double-tip spray gun in which the catalyst is added to the resin at the spray gun tip. Such spray guns may include a glass chopper, which chops fiberglass roving into sections from one-half inch to four inches in length so that the glass, resin, and catalyst are all blown on the surface at the same time. Alternately, sheets of fiberglass may be laid down on top of the freshly sprayed polyester resin. In either case, the surface is then rolled in order to smooth it out prior to the final set of the resin. As an additional measure to prevent permeation of liquids into the coating, a final coat of polyester should be applied to avoid having any exposed fiberglass strands, which act as wicks for moisture into the film. Where shrinkage has been properly accounted for, a very good corrosion-resistant lining material can be obtained.

Silicones

Silicones are formed by chemical modification of quartz, sand, or silicon, and they may be thought of as hybrids of glass and organic resins. They have much the same inertness as glass but at the same time, can be incorporated into coatings in the same manner as organic polymers. They are a silicon-based polymer that has primarily silicon-oxygen-silicon linkages. The silicon atom is tetrafunctional in the same way that the carbon atom is, and one or more of the attached functional groups may be based on organic carbon.

The organic groups that have the most desirable properties combined with the silicon are the methyl and phenyl groups. High phenyl-containing resins tend to have better heat and oxidation resistance than the methyl substitutes. Most of the silicone resins used in the coating industry are a combination of the two, forming methyl phenyl silicone polymers. Properties can be varied widely, depending on the ratio of the methyl and phenyl groups. Polymers used by the coating industry, for the most part, have the following configuration.



Silicon Polymer where R = organic groups. (5.3)

A silicone polymer may have a number of different organic groups attached to the silicon atoms. As the number of organic groups on the silicone polymer increases, the resin becomes softer, more flexible, somewhat slower curing, and more thermoplastic. Most of the silicone resins are dissolved in hydrocarbon solvents. The solvents are usually included in the manufacture of the resins to improve control of the hydrolysis of the basic silicon molecule to prevent gelation. Modified silicone resins, such as those represented above, generally require curing at high temperatures to obtain their optimum characteristics. They do, however, respond to catalysts. Zinc catalysts, such as zinc napthenate, are used most often and yield good results. The cure temperatures can be reduced to 400 °F (205 °C) using zinc.

Some of the properties of silicone coatings are as follows.

Hardness

Generally, somewhat softer than many organic coatings, hardness properties can be improved if silicone resins are modified with organic coating materials.

Adhesion

Silicone adhesion is generally good to most substrates, depending, as in the case with organic materials, on the cleanliness of the surface.

Abrasion Resistance

Silicone polymers have generally poor abrasion resistance. Again, modification with organic materials can considerably improve resistance.

Chemical Resistance

In general, chemical resistance of silicones is good, including water, mild acids, alkalies, and other corrosion-resistant materials. Modified resins generally have poor solvent resistance.

High Heat Resistance

Heat resistance is one of the outstanding properties of silicone coatings. They can withstand temperatures of 540 to 640 °C (1,004 to 1,184 °F) when pigmented with aluminum or black pigments. When pigmented with ceramic frits, silicone coatings have gone as high as 760 °C (1,400 °F). A modified silicone resin based on the methyl phenyl polymers is often used to topcoat IOZ coatings for continuous use at temperatures of 360 to 540 °C (680 to 1,004 °F).

Weather Resistance

Silicone resins have the property of being transparent to ultraviolet light. Because of this, they are not generally subject to the kind of degradation and coating failure associated with organic coatings. They have excellent water resistance and resistance to thermal change, which undoubtedly contribute to their weather resistance. Unmodified silicone coatings have been exposed to weather conditions for over 12 years with no loss of gloss, color change, chalking, or other similar types of failure.

Corrosion Resistance

Silicone resins have excellent electrical properties. They are good electrical insulators. These properties, combined with their natural water repellency, make them good candidates for corrosion-resistant coatings. One of the longtime uses of the silicone resins has been on the exterior of smoke stacks, where they are not only subject to varying temperatures but to sulfur dioxide (SO_2) and other combustion products as well. They have no problem in passing U.S. government specifications requiring exposure at temperatures up to 480 °C (960 °F) and then passing a 20% salt spray test.

It has been mentioned that silicones are copolymerized with other organic polymers in order to improve the organic material's properties of heat resistance and weathering. In some cases, silicones can be co-blended with other organic materials. Generally, however, copolymers have more desirable characteristics. Copolymers are made from several silicone intermediates, which have hydroxyl or methoxy groups attached to the silicone molecule. These are the groups that can react with the organic polymers that have active hydroxyl groups. These silicone intermediates are shown in Figure 5.27.

The organic materials that form satisfactory copolymers with the silicone intermediates are alkyds, polyesters, polyols, epoxies, epoxy esters, uralkyds, acrylics, and others. Generally, the copolymers have increased heat and weather resistance over and above the organic coating material alone. The silicone organic copolymers cure into a final coating using the same mechanism as the organic part of the copolymer. This has been shown previously under alkyds, where the silicone alkyd is cured by the oxidation reaction of the oil-modified alkyds. Silicone copolymer maintenance coatings generally have good color and gloss retention, and tend to chalk at a much slower rate than the organic finish alone. Improved water and corrosion resistance are also common.

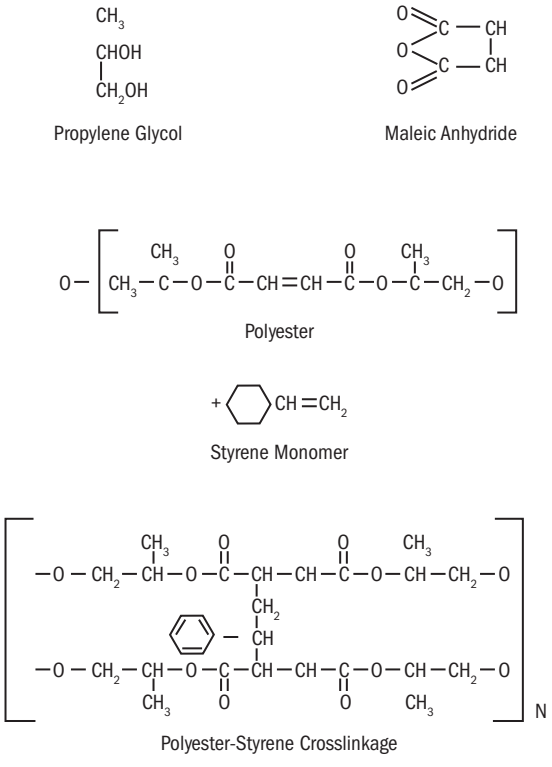


Figure 5.27: Chemical reaction between the polyester resin and the styrene when activated by a catalyst such as one of the organic peroxides.

One of the popular uses of the silicone copolymers is for coil coating. This is where strips of metal are coated in a continuous process, rolling from a coil of metal passing through the coating and baking process, and then recoiled within a matter of only a minute to a minute and a half. The temperature in this case is a high bake (600 °F). The materials used are silicone-polyester copolymers and are generally made with the linear silicone intermediates for flexibility. Such materials have been exposed in South Florida for over seven years and have been unaffected by the weather exposure with no color change or appreciable chalking.

Many of the silicone copolymers are important to the corrosion engineer and may become even more important because of their water-, weather-, and corrosion-resistant characteristics. Silicone alkyds, epoxy silicones, and similar materials have upgraded temperature, weather, and chemical resistance over the organic materials alone.

Emulsion-Type Coatings

The formation of coatings from emulsions is not new. It is, however, becoming increasingly important because of the newer and more stringent air pollution regulations. There is increasing effort and research on the development of emulsion-type coatings of the high-performance type. Water-dispersed coatings would be ideal from a solvent standpoint since there would be no solvent pollution problem if all coatings could be made in this way. Unfortunately, the water-based, high-performance coatings that are of interest to the corrosion engineer have practical drawbacks. The basic reason is the process of coalescence. The resin particles are discrete in the emulsion and must completely join together to form a continuous film. So far, this has been difficult. Even un-pigmented latex films are more porous to water and ions than are solvent-applied films of the same resin. This is aggravated by the many additives necessary to make the discrete resin particles disperse in the water, then flow together to form a continuous film. Heat of fusion of the resin particles makes for good latex coatings. This, however, is not practical for coatings applied in place.

Most of the architectural latex paints are made from thermoplastic resin types, such as styrene-butadiene, vinyl acetate, vinyl-acrylic copolymers, acrylic esters, vinyl-acetate-acrylic, styrene-acrylic, and others. In this case, the resin is suspended in water in the form of very minute spherical particles. In order to keep these particles separated, each one is coated with an extremely thin layer of emulsi-

TABLE 5.13: Necessary Emulsion Coating Ingredients

Ingredient	Function
Prime Pigment	Hiding, Color
Extender Pigment	Hardness, H_2S Resistance
Reactive Pigment	Rust Inhibition
Pigment Dispersant	Disperse Pigment
Defoamer	Prevent foaming of paint
Thickener	Provide Viscosity
Can Preservative and Mildewcide	Inhibit bacteria and mildew growth in the can

Source: A. Mercurio, Roy Flynn, "Latex Based All Surface Primers," *Journal of Coatings Technology 751*, (1979): p.654.

TABLE 5.14: Helpful Emulsion Coatings Ingredients

Ingredients	Function	Example
Surfactant	Pigment Wetting	Polyglycol
Coalescent	Film-Forming Aid	TBP
Glycol	Freeze-Thaw Stability	Ethylene Glycol
Oil Modifier	Chalk, Metal Adhesion	Alkyd + Cobalt
2nd Reactive Pigment	Addition Rust, Stain Resistance	Barium Metaborate CA-Zn, Molybdate, Zn Phoso Oxide

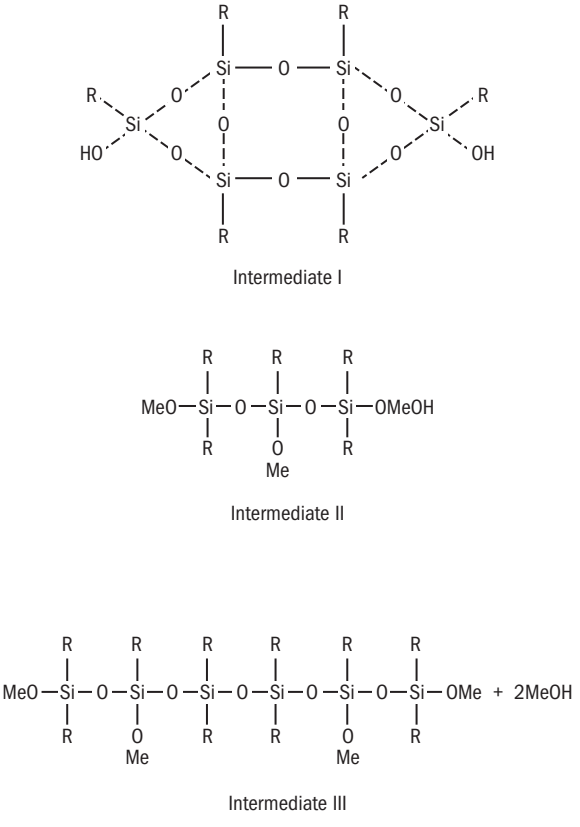


FIGURE 5.28: Silicone intermediates used to react with other organic polymers containing active hydroxyl groups. Source: Clope and Glazer, *Federation Series on Coating Technology,* Unit 14, "Silicone Resins for Organic Coatings." (Philadelphia, PA: Federation of Societies for Paint Technology, 1970) pp. 16–17.

fier, which is necessary to keep the particles apart and to keep them from flocculating.

The films of latex coatings are a complex mixture and consist of a number of materials (i.e., hiding pigment, extender pigment, pigment wetting and dispersement aids, emulsifiers, thickener and protective colloids, fusion or coalescing aids, freeze-thaw stabilizer, wet edge promoter, defoamer, fungicide, water, and the dispersed resin. Table 5.13 indicates some of the necessary emulsion coating formulation ingredients and their functions. In addition, Table 5.14 is a series of helpful materials for use in emulsion-type coatings. Most of these materials are required in the coating in order to help it to coalesce into a usable coating film. The film formation is the result of the fusion or coalescence of the resin particles, including pigment and the other materials included in the tables.

In the liquid coating, the dispersion factors are the emulsifier, thickener, and protective colloid. These predominate, otherwise the resin pigment dispersion tends to semi-coalesce and precipitate to the bottom of the container. After the coating has been applied to the surface and the water starts to evaporate, the resin particles come closer together and the coalescence must begin in order to fuse the resin particles to form a continuous film. At this point, the dispersion factors must cease to predominate and the coalescent or film forming factors take over. Figure 5.28 is a schematic representation of the resin particles as they gradually coalesce into a complete film.

The process of coalescence occurs as water evaporates from an emulsion coating. Note that a complete film is not formed until Stage 4 is reached. Stage 1 shows the dispersed resin particles as they would appear in the coating liquid. Stage 2 is after partial water evaporation. At this state, there would be poor film characteristics and lack of toughness. In Stage 3, there is some coalescence, but it is not complete. In this form, there would be a high permeability to water and atmospheric salts. Stage 4 shows the complete coalescence of the resin particles. While they never form a really smooth film, such as is possible with solvent evaporation, particles have flowed together in order to provide a continuous coating. Figure 5.29 shows a highly magnified, completely coalesced, non-pigmented film of latex, indicating the packing orientation of the resin particles as they coalesce into a film.

Ideally, when a resin emulsion is pigmented, each pigment particle in the finished coating is completely surrounded by the matrix of fused resin particles. This, however, is never entirely the case, although the results are approachable when using a coating with a low pigment volume concentration. For use as a corrosion inhibiting coating, this is the type of formulation that should be considered. With high pigmentation, such as the coatings used for flat wall paints, there would be little chance of reaching a state where the resinous phase is continuous. Even in solvent films, which are highly pigmented, this is difficult.

TABLE 5.15: Coalescent-Emulsion Type Coatings (Atmospheric Use Only)

Properties	Vinyl Acetate	Vinyl Acrylic	Acrylic	Epoxy
Physical Property Water Resistance	Scour Resistant Fair	Scour Resistant Good	Scour Resistant Good	Tough Good
Acid Resistance	NR[(A)]	NR	NR	Fair
Alkali Resistance	NR	NR	NR	Good
Salt Resistance	Fair	Fair	Fair	Good
Solvent Resistance Aliphatic hydrocarbon	Fair	Good	Fair	Good
Aromatic hydrocarbon	NR	NR	NR	Good
Oxygenated hydrocarbon	NR	NR	NR	NR
Temperature Resistance	60 °C (140 °F)	60 °C (140 °F)	60 °C (140 °F)	70 °C (158 °F)
Weather Resistance	Good	Very Good	Very Good	Fair
Age Resistance	Good	Good	Good	Good
Best Characteristic	Weather Resistant	Weather Resistant	Weather Resistant	Reasonable Corrosion Resistance
Poorest Characteristic	Porosity	Porosity	Porosity	More porous than solvent base
Recoatability	Good	Good	Good	Fair-Good
Principal Use	Decorative Topcoat	Decorative Topcoat	Decorative Topcoat	Topcoat

[(A)]NR = Not recommended.

Improvements in emulsion technology have led to anticorrosive primers and medium- to high-gloss topcoats, which have some good atmospheric and reasonable corrosion-resistant properties, particularly those that utilize newer industrial grade aqueous dispersions of acrylic resins. Epoxies, coal tar epoxies, and similar coatings have been developed using the water emulsion film forming processes. The newer corrosion-resistant emulsion-type coatings are approaching the continuous resin phase, with some, such as the waterborne epoxies, providing good films.

Emulsion-type epoxy coatings have, for the most part, been two-package epoxy polyamide systems, although newer resins are available with different functionalities. The epoxy portion is a liquid epoxy resin with some aliphatic epoxy monomer as a diluent to lower the viscosity of the epoxy resin and to help in the coalescence of the two film-forming resins during the drying periods. The polyamide part of the system, which is used as a curing agent, also has some added materials to reduce the viscosity and aid in the coalescence of the polyamide and the epoxy resins to form the finished coating. These are usually high-boiling aromatic solvents and a water miscible solvent. The two parts of the system are packaged separately and, when mixed, have a reasonable pot life. Such epoxy emulsions have been used in seamless floor base coats, as block fillers, and both as maintenance primers and maintenance finish coats. Some of the newer waterborne epoxy systems have provided good results in the field for atmospheric corrosion type conditions. Some of the resin-based systems are approved as potable water tank linings.

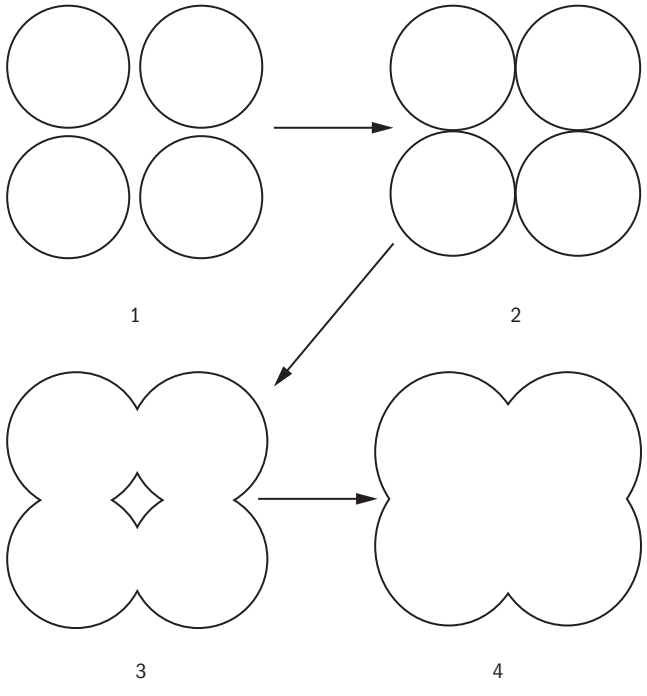


FIGURE 5.29: Degrees of coalescence.

The waterborne epoxy coatings are not yet as effective as the solvent-type epoxy coatings of the same type, despite recent improvements in the technology. This is particularly true under damp, moist, or immersion conditions. Some have been used as topcoats for IOZ base coats with good results. Under certain conditions, vinyl acrylics and acrylic water-based materials have been used as topcoats for corrosion-resistant primers, both organic and inorganic, where conditions are right and the corrosion- resistant base coat will withstand the corrosion conditions of the area. These coatings have been effective as decorative topcoats. Generally, however, they do not contribute substantially to the anticorrosive characteristics of the total coating. There is some danger in the use of these materials as topcoats over IOZ coatings when humid conditions exist. White salt reaction products from the zinc in the base coat may form underneath and penetrate through the porous water-based topcoat. (This problem is discussed in more detail in Chapter 6.)

None of the water-based emulsion-type materials will coalesce properly under cold, humid atmospheres. This factor should be taken into consideration whenever these materials are considered for coating use. Table 5.15 gives the general properties of the presently available water emulsion-type coatings that may be considered for maintenance type purposes.

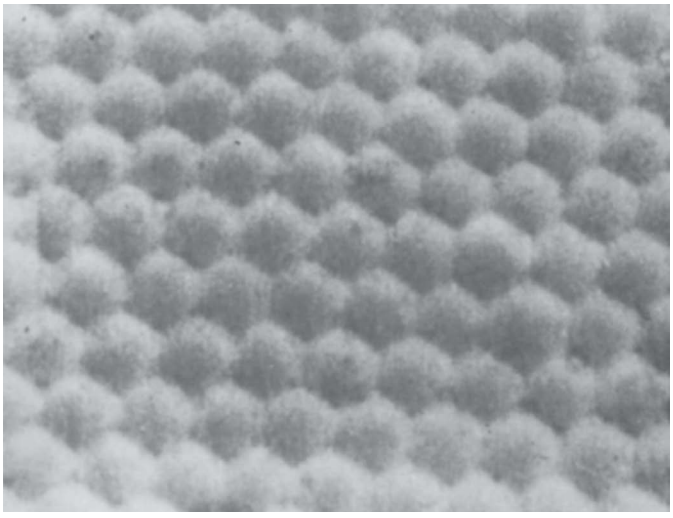


FIGURE 5.30: Coalesced un-pigmented latex, 28, original magnification 580X. Source: W.B. Fuller, *Federation Series on Coating Technology,* Unit 2, Formation and Structure of Paint Films (Philadelphia, PA: Federation of Societies for Paint Technology, 1965), p. 15.

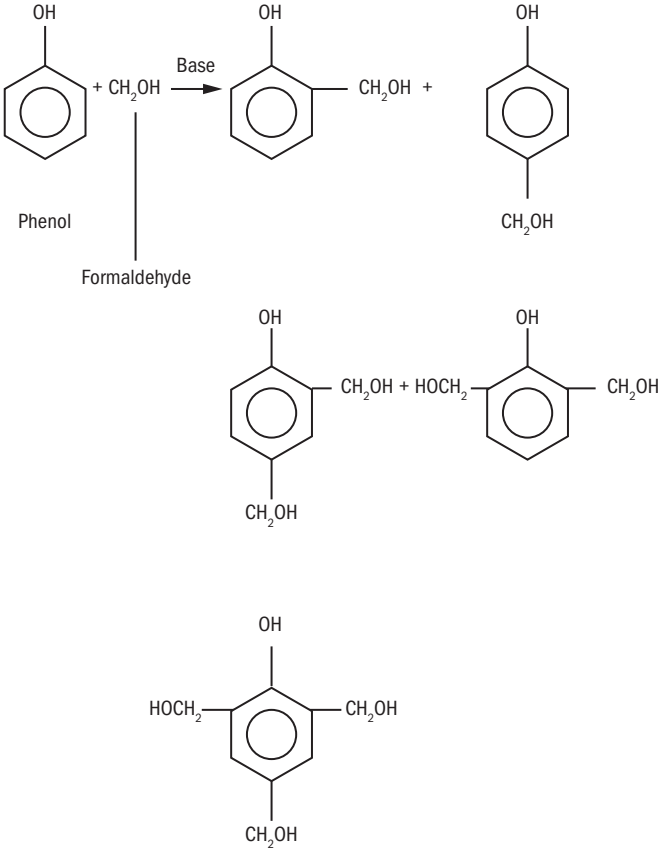


FIGURE 5.31: Chemical formulation of phenolformaldehyde.

Heat-Condensing Coatings

This group is essentially composed of two types of coatings: a so-called "pure" phenolic and the epoxy phenolic. These are two of the most corrosion and chemical resistant coatings available and are used under some very highly corrosive conditions.

Phenolic Coatings

The types of resins in which we are primarily interested are the un-substituted heat reactive resins. This is only one of a number of phenolic resins that can be used for coatings. On the other hand, these coatings are the type used for highly corrosion resistant purposes. An un-substituted phenol is one that does not have any methyl groups attached to the phenol. Phenol itself is the most important of all of the un-substituted phenols. This material is reacted with formaldehyde, which then forms a series of hydroxybenzoalcohols; these then continue to react, forming polymers of higher and higher molecular weight until it is possible to obtain a jelled cross-linked structure. After this, further heating increases the cross-link density until a completely insoluble material is obtained.

The depicted five methylol phenols are formed during the initial phenolformaldehyde reaction (Figure 5.30). The basic chemistry of the phenolformaldehyde is given in Figure 5.31. The second step is for two or more of the methylol phenols to react to form a methylene-linked polymer. This process continues with heat until a completely insoluble, highly cross-linked polymer is formed.[7]

The phenolic resin that is used in coatings of the high performance type may be very viscous or may be carried to the solid stage while it is still soluble in polar solvents such as alcohol. Un-substituted heat reactive resins are multifunctional and therefore can form a cross-linked film. They are soluble in alcohols, ketones, esters, and glycol ether. However, they are insoluble in aromatic and aliphatic hydrocarbons. Such resins are compatible with amino resins, epoxies, polyamides, and polyvinyl butyral. These phenolic resins in solution are very heat reactive and it is often necessary to store them under refrigeration. Typical alcohol solutions of the most reactive of the resins will gel in three to six months, even at ambient temperatures, and the solid resins when stored at ambient temperatures will continue to polymerize to the point of being insoluble and infusible, and therefore of no value from a coating standpoint. This is important when using heat reactive phenolic coatings since over-aged liquid coatings may be sufficiently polymerized so that the end result is poor adhesion or other application problems.

These coatings are usually applied from an alcohol solution by spray, dip, or roller. Some of the solid resins even find application as powder coatings. The application of these coatings is critical. During their condensation they release water, and it is necessary to remove this water during the curing process. The general procedure of the application is to apply the phenolic resin solution to a very clean, steel surface at a maximum thickness of about one mil. The coating is then heated to temperatures of 135 to 300 °C for a few minutes. This results in a partially cured state. Additional coats are applied using the same procedure for approximately four to six coats.

Following the last coat and the short bake as previously outlined, the coating is heated for several more hours at a temperature of approximately 230 °C. Increased cure time and higher temperatures result in increased corrosion and solvent resistance and decreased flexibility. Short, high bakes produce a more resistant film than long, low-temperature bakes. The color of the coating darkens upon baking, going from a rather golden color upon application to a very dark reddish-brown. Most of the phenolic tank linings are cured to a medium reddish-brown color during the curing period. Over-curing can result in actually charring the coating, rendering it useless. A final color that approaches black is a definite indication of over-curing.

These cured coatings are affected less by solvents than any other type of organic coating, and have remained unaffected by exposure to alcohols, ketones, esters, aromatic and aliphatic hydrocarbons, and even chlorinated solvents for a number of years. They also are odorless, tasteless, and nontoxic in the fully cured form and are therefore non-contaminating to contained material. They often are used for the storage and processing of food products such as wine, beverage alcohols, various sugar syrups, beer, alcohol fermentation, and many similar applications. They also have excellent resistance to boiling water, aqueous solutions of mild acids, and acidic and

TABLE 5.17 Heat-Condensing Coatings

Properties	Phenolic	Epoxy Phenolics
Physical Properties	Very Hard	Hard-Tough
Water Resistance	Excellent 100 °C	Excellent 100 °C
Acid Resistance	Excellent	Excellent
Alkali Resistance	Poor	Excellent
Salt Resistance	Excellent	Excellent
Solvent Resistance(Hydrocarbon)		
Aliphatic	Excellent	Excellent
Aromatic	Excellent	Excellent
Oxygenated	Very Good	Good
Temperature Resistance	120 °C (250 °F)	120 °C (250 °F)
Weather Resistance	Good(darkens)	Good
Age Resistance	Excellent	Excellent
Best Characteristic	Acid, Temperature Resistance	Alkali, Temperature Resistance
Worst Characteristic	Brittle,	Poor Recoatability
Recoatability	Poor	Poor
Principal Use	Chemical and Food Lining	Chemical Lining

neutral salts, so that their chemical resistance is quite broad. Their primary use is in tank linings, although they are extensively used as a lining for downhole petroleum tubing, which is subject to high temperatures, high-temperature water, salt solutions, H2S, and various petroleum products.

The one "Achilles heel" of these coatings is their lack of alkali resistance. They are not satisfactory for use in alkali of any concentration. While these phenolic resins constitute an older type of high-performance coating, they still continue to be used as previously mentioned because of their inert characteristics and their excellent resistance to hot water at near boiling temperatures.

Epoxy Phenolic Coatings

Epoxy phenolic coatings, which are also cured at relatively high temperatures, have exceptional chemical and solvent resistance and are used primarily as tank linings to contain chemicals of various types. The coatings rely primarily on the reaction between the methylol groups of the phenolic resin and the secondary hydroxyl groups on the epoxy resin. Epoxy resins used are those where the hydroxyl groups predominate on the molecule. These are usually the higher molecular weight epoxy resins.

The reaction of the epoxy resin with the methylol groups on the phenolic resins is an important one from the standpoint of coating technology. It occurs between the secondary hydroxyl groups of the higher molecular weight epoxy resins and the methylol group of the phenolformaldehyde resins, as shown in Figure 5.32. These coatings are usually heat cured at 180 to 200 °C (356 to 400 °F) and often have an acidic catalyst to improve the reaction between the phenolic and the epoxy resin.

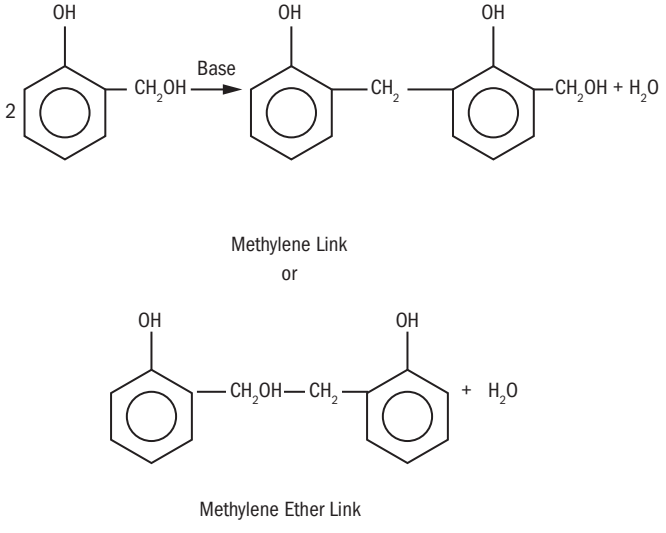


FIGURE 5.32: Five methylol phenols are formed during the initial phenol-formaldehyde reaction.

The ether linkages, as shown in Figure 5.30, are highly resistant to chemical attack. The large number of alcohol groups on the epoxy and methylol groups on the phenolic makes for the highly cross-linked structure that is obtained from the fully cured epoxy phenolic resin coatings. When the coating is cured, it is very hard, tough, and solvent- and chemical-resistant. The application of these coatings is somewhat less critical than the phenolformaldehyde coatings. These coatings are also a little less sensitive to curing conditions and may be applied in thicker coats while still obtaining a thorough cure. The procedure is nevertheless primarily the same; a coat of the resin is applied to very clean steel and baked for a few minutes at a relatively high temperature, after which another coat is applied and the same treatment follows. Once the coating is completed, the entire coating is then cured for a longer time at the same or higher temperatures for the completed coating.

These coatings, when completely cured, are also nontoxic and may be used for food containers. Heat-cured epoxy phenolic coatings are widely used as interior drum coatings and also for industrial tank linings. This is due to their high level of chemical resistance and their resistance to water and extreme temperatures. They are also used as internal linings for pipe and for coating downhole tubing.

Table 5.16 shows the broad range of chemical resistance of these coatings. One of their best properties is their alkali resistance. This type of coating has been used extensively for the lining of tank cars containing 50 and 73% caustic soda, which is transported at 110

TABLE 5.16: Chemical and Solvent Resistance of Epoxy Phenolic Baking Coatings	
A. Films unaffected by a three-month immersion in the following reagents at room temperature (all solutions are aqueous):	
Solvents	Chemicals
Ethanol	Sodium Hydroxide Cone
Isopropanol	Ammonium Hydroxide (10%)
Sec-Butanol	Acetic Acid (1%)
N-Butanol	Linseed Fatty Acids
Methyl Isobutanol	Sulfuric Acid (up to 75%)
Diacetone Alcohol	Hydrochloric Acid (up to 20%)
Hexylene Glycol	Nitric Acid (up to 10%)
Glycerine	Phosphoric (up to 85%)
Carbon Tetrachloride	Liquid Detergent (100%)
Allyl Chloride	Liquid Detergent (50%)
Methyl Isobutyl Ketone	Solid Detergent (1%)
Toluene	Sodium Methoxide (40% in methanol)
Xylene	Sodium Chlorite (25%)
Diethyl Ether	SodiumHypochlorite (5%)
Bis (B-Chloroethyl) Ether Ferric Chloride (5%) Water Salt Spray at 38 °C for 500 hrs.	Calcium Hypochlorite (5%)
B. Films unaffected by the following materials, all exposed for three weeks at 66 °C, except as noted:	
Isopropanol	Methyl Isobutyl Ketone
Sec-Butanol	Allyl Chloride
Methyl Isobutyl Carbinol	20% Sodium Hydroxide (boiling 24 hrs.)
Ethanol	73% Sodium Hydroxide (138 °C, two weeks)
Diacetone Alcohol	
Hexylene Glycole	Glycerine Glycerine (77C, six weeks) Water
C. Films soften slightly after one month at room temperature in acetone, methyl ethyl ketone, ethylene dichloride, hydrochloric acid (36%), sulfuric acid (78%), and hydrogen peroxide (15%).	

Source: R.A. Allen, *Federation Series on Coating Technology,* Unit 20, "Epoxy Resins in Coatings," (Philadelphia, PA: Federation of Societies for Paint Technology, 1972), pp. 12, 42.

to 120 °C (230 to 248 °F). The temperature-resistant characteristics of this coating are good, giving it excellent hot water resistance. In many ways, it is very comparable to the phenol-formaldehyde resin coating, having nearly the same general chemical resistance of the phenolics plus the advantage of being alkali-resistant. Table 5.17 lists the properties of heat-condensing coatings.

100% Solids Coatings

In recent years, there has been a continuing effort to develop 100% solids coatings of many different types, predominantly epoxies and polyurethanes/polyureas. There are many advantages to such coatings. There are no waste materials from the coating process such as solvents that must evaporate. The contamination to the atmosphere is generally low and, on a cost-per-mil of thickness, they are very cost effective. While application procedures may be a little complex, the film that forms is either ready for service at that point or will be as soon as the curing reactions take place. Most 100% solids coatings have the advantage of additional thickness, which helps to increase the physical properties and water and chemical resistance. Because of these very obvious advantages, there will undoubtedly be many more 100% solids protective coatings in the future. The development of nano scale pigments beginning in the decade after 2000 promises to be a boon to the development of more advanced versions of 100% volume solids coatings.

Coal Tar Enamel

Coal tar is a material derived from the coking of coal. When the coal is heated without air at about 1,100 °C (2,000 °F), it is decomposed into gases, liquids, and coal tar. The coke, or almost pure carbon, is the residue. The coal tar is further distilled and dehydrated, producing coal tar pitches of varying properties, depending on the source of the coal. The coal tar pitch is then reinforced with inert fillers to form the 100% solids coal tar enamel, which is applied to various surfaces by heating the coal tar to a liquid condition and applying it to the surface. This type of coal tar enamel is probably the oldest of all of the high-performance protective coatings since coal tar pitches have been available ever since the advent of the steel industry. It is certainly the oldest of the 100% solids coatings and has been used for the exterior of pipelines and various steel and concrete structures for many years. It also is used as an interior lining

for water pipe and has provided service without appreciable failure for 50 or more years.

The coating performance is based on the inert impervious film concept, and the outstanding properties of coal tar are very low moisture permeability, high resistance to electrical currents, and permanence when continuously immersed in various water solutions. Water resistance is its outstanding property and there are very few, if any, materials, either old or new, that have the same water-resistant characteristics. Coal tars are not affected by aliphatic oils and greases. They may, however, be softened by vegetable-type oil and certainly will be softened or completely dissolved by aromatic hydrocarbons. The resistance to all types of dilute water solutions, including acids, salts, and dilute alkalies, is very good, and their resistance to soil chemicals and soil conditions is excellent. One of the advantages of coal tar enamels is that they are applied as a thick film (100 to 150 mils (2,500 to 3,750 μm)). The coating as such is hard, tough, and sufficiently heavy to resist abrasion due to installation and soil stresses after the pipe or other structure is in the ground.

Coal tar enamels are generally supplied in three different types. Type 1, the regular enamel, is a very hard product and is designed for service from 0 to 50 °C (32 to 122 °F). This type has the highest resistance to moisture, petroleum oils, and soil stresses of any of the three grades, but it also has the least flexibility in the narrow service temperature range. Type 2 is a semi-plasticized coal tar pitch. This product has a wider service temperature range of –18 to 60 °C (0 to 140 °F). It is somewhat more flexible than Type 1. Type 3 is a fully plasticized coal tar pitch and has a service temperature range from –29 to 70 °C (–20 to 158 °F). This type is used for pipelines, which are subject to low storage and handling temperatures and where good flexibility is required.

While there are some other uses for coal tar enamel besides application to pipe, the primary use is a pipe coating and lining for soil and water service. As previously stated, the coal tar is applied as a hot-melt, and when used on the exterior of steel pipelines, may be used with or without a reinforcing wrapper. The coal tar is usually applied to the exterior of pipe by a machine, the pipe being revolved and moved forward under a pouring head where liquid coal tar is evenly distributed on the surface, usually followed by a glass or fibrous pipe wrap pulled into the liquid coal tar coating in order to force any air out of the wrap and to make a dense reinforced coal tar surface. The process is a rapid one, with the coal tar cooling quickly so that the pipe can be handled within a matter of minutes.

The over-the-ditch application of coal tar is similar to that of the plant application, except that the equipment used to distribute the molten coal tar and to apply the pipe wrap is operated on the pipe itself, making a continuous application of the coating over joints and welds as well as the pipe surface.

In some cases the hot-applied coal tar is applied by a process called daubing. This is the use of long-handled brushes dipped into the molten coal tar and spread over the surface to be protected. Many large water tank interiors have been protected by this method. This is no longer used for potable water service. Brush marks, however, are a problem during this type of application, and two or more coats are usually required in order to build up a proper film thickness and eliminate holidays. This type of application also is used for other types of steel structures where automatic applications cannot be used. The coal tar enamel is applied to the interior of steel pipe by revolving the pipe, inserting a lance in the interior, and distributing the liquid coal tar lengthwise through the pipe as the pipe revolves. A smooth, even thickness is obtained by this method because of the centrifugal force applied during the revolution of the pipe.

The application of the hot-applied coal tar to interior joints in the field is usually by daubing. Exterior joints may be daubed, but are more often poured, using a so-called diaper that allows the hot-applied coal tar to flow around the pipe and over the joints. Some of the properties of such a coal tar coating are as follows.

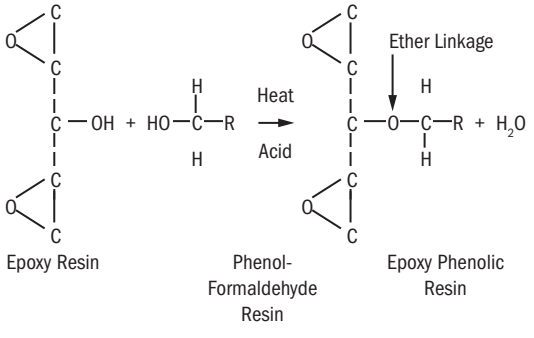


FIGURE 5.33: Formation of an epoxy phenolic resin: R = phenolformaldehyde polymer.

Water Resistance

As previously stated, the water resistance of coal tar is excellent in terms of both moisture vapor transfer rate and water absorption (Figure 5.33).

Electrical Resistance

The electrical resistance of coal tar enamel is also high, which makes it particularly suitable for both water and underground service (Figure 5.34). This is particularly true where the pipeline is under CP.

Adhesion

Coal tar enamels, when properly applied, also have good adhesion. Even though the enamel is quite thick, it is still difficult to remove from the surface, and, unless there is some surface contamination, neither water nor CP currents tend to release the adhesion. Cathodic disbonding is the process of a loss of adhesion due to moisture and cathodic currents. Properly applied coal tar enamel has excellent resistance to cathodic disbonding. The coal tar enamel is also resistant to soil bacteria and to H_2S, which may be developed by the anaerobic bacteria in the soil.

Chemical Resistance

The general chemical resistance of coal tar enamel is improved by the thickness of enamel and by its excellent water resistance. It is generally resistant to most chemicals with which it might come in contact. All in all, while coal tar enamel is an old answer to pipe and underground corrosion problems, it is also a very effective one with excellent corrosion-resistant characteristics.

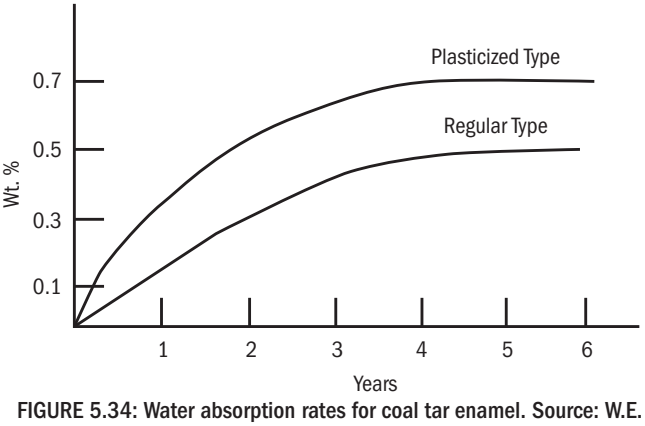


FIGURE 5.34: Water absorption rates for coal tar enamel. Source: W.E. Kemp, "Coal Tar Enamels Coatings for Underground Pipeline," *Materials Protection* 7, 9 (1970).

Asphalt

Asphalt is a naturally occurring material, which is derived either by mining (which is the method of obtaining gilsonite, a naturally occurring asphalt) or it is a residue from the distillation of asphaltic petroleum. Gilsonite is a solid material mined in much the same way as coal. It is soluble in aliphatic and aromatic solvents and has excellent chemical resistance as well as good weather resistance. Asphalts vary in their chemical and physical characteristics, depending on the distillation process and temperatures to which they are subjected. They also may be subject to steam distillation and to air blowing during the distillation process.

Unlike coal tar, asphalt has comparatively better weather resistance and does not tend to alligator in the same manner as coal tar when subjected to weather conditions. This is one of the reasons why hot-applied asphalt is applied for roof coatings where it is subject to continuing temperature changes and weather conditions. Depending on the grade of asphalt, it is usually a less brittle material than coal tar and is therefore used to a greater extent on steel structures subject to weathering and temperature changes. Asphalt has good adhesion when properly applied to steel or concrete surfaces and can be built up to the same type of thicknesses as coal tar (i.e., from 100 to 250 mils). Chemically, asphalt is a stable aliphatic hydrocarbon that has good resistance to water and most chemicals and salts. It is solvent sensitive, even to aliphatic solvents, and is softened and dissolved by vegetable oils. The water resistance of asphalt is good. It does not, however, compare with coal tar in this respect.

The application of asphalt as a 100% solids hot-melt coating is very similar to the methods used with coal tar and glass. Asbestos wrap also is used to reinforce the asphalt when applied over the exterior of pipe. Its use as a pipe coating is not nearly as extensive as coal tar. On the other hand, many steel pipes, particularly in relatively small diameters, have been dipped in asphalt and have been in service for many years with good results. This type of pipe, for example, was used throughout California as an irrigation pipe. Some of these have been recently dug up, as the ground usage has changed from agricultural to residential, with the asphalt still providing corrosion protection.

The major differences between coal tar and asphalt are the excellent water resistance of coal tar and the good weather resistance of asphalt. The asphaltic materials are used more for aboveground uses, while coal tar coatings are used underground. Many water tanks are coated with asphalt because of its nontoxic and relatively tasteless nature. Asphalt generally has good corrosion-resistant properties and it may be used wherever a decorative coating is not required. While some asphalt coatings are heavily pigmented, it is primarily a black coating, and this characteristic is difficult to change. It may effectively be applied over other coatings that have sound adhesion to a surface, although it is a very difficult material to overcoat because of its sensitivity to oils and solvents of all types.

The chemical makeup of asphalt is not complex. The various types of asphalt are primarily based on different melting point or softening point materials. They are all polymeric aliphatic hydrocarbons and their chemical properties are those that you would expect from such a material.

Polyesters

One hundred percent (100%) solids polyesters are used as tank linings or for the coating of tank bottoms. They have some very good properties, as was previously noted. The general resistance of polyester linings is good. They have good acid resistance and good resistance to oxidizing materials. They are, however, subject to hydrolysis when in contact with alkalis. They are satisfactory for acid salts and neutral salts, but strong alkaline salts are not recommended. The problem involved is the ester group, which is the part of the molecule subject to the alkaline hydrolysis, breaking the molecule at that point and causing the coating to disintegrate. Alkali resistance is affected by the glass cloth or mat reinforcing often used in connection with polyesters as tank linings.

While the weather resistance of polyester resins is satisfactory, these materials are seldom used as coatings and therefore are not often subject to weathering conditions. Some polyester materials are incorporated into cements for acid proof brick and tile, and used particularly where oxidizing products are encountered. Because of the inherent shrinkage of polyester linings (as was covered previously), they are seldom used without some type of filler or reinforcement, either of the pigment type or more often glass or synthetic fabrics or glass mats. In the case of polyester cements, they are reinforced with siliceous aggregate in order to hold down shrinkage. The polyesters have some very good properties; on the other hand, their shrinkage characteristic limits present widespread use.

Vinyl esters are similar to polyesters in many ways, including the methods of application. They provide a broader range of chemical resistance than the polyesters.

Epoxy Powder Coatings

Powder coatings are materials with which the corrosion engineer should be familiar. Although they are not practical for maintenance and field use, the corrosion engineer should be familiar with them because they are rapidly becoming one of the standard product finishes as well as pipeline coatings. They can be found on many different types of equipment that can be heated and dipped into a fluidized bed to form the coating. They may also be applied by electrostatic spray or by a flocking gun. However, the surface over which they are applied must be at fusion temperature and generally kept at that temperature for a sufficient period for the coating to fuse, flow, and cure in order to form a continuous film.

The properties of the powder coatings depend to a considerable extent on the curing agent used. Some of the curing agents, such as dicyandiamide, provide coatings with excellent chemical and corrosion resistance. The curing agents are usually friable solids.

Powder coatings can be made by two different processes: the fusion process followed by pulverization, or dry grinding of the various ingredients in a pebble mill. In the fusion technique, the powdered epoxy resin, pigment additives, and powdered curing agent are first dry blended and then passed through a specially designed extruder, which accomplishes both the fusion and mixing at temperatures that are low enough to minimize any curing that might start. The extruded material is then pulverized to the desired size. This process intimately mixes the diverse ingredients of the formulation and provides a good degree of pigment wetting and dispersion. High-gloss coatings can therefore be obtained. Such coatings are usually relatively thin (one or two mils in thickness).

Powdered coatings that need to be applied at thicknesses of 10 to 20 mils are usually made by the dry grinding process. In this case, the ingredients are all charged into a cooled pebble mill and the mill is allowed to grind for up to 24 hours to yield the completed coating formulation. The fact that the pebble mill is cooled allows a curing agent with highly reactive characteristics to be used. Most of the curing agents used in connection with these powdered coatings are ones that are heat activated so that little curing takes place at ambient temperatures.

Once the powder is ready to use by either of these processes, it is applied to the heated metal surface either by the fluidized bed technique, which lowers the heated object into the powder, or it is electrostatically sprayed on the heated metal. The object, which is above the fusion temperature, rapidly accumulates the powder and fuses it onto the surface. Some of these systems will form a coating and cure it within a matter of 30 seconds at 230 °C (446 °F). Other curing systems applied in heavier coating thicknesses can require as much as 15 to 30 minutes at 200 °C (392°F).

One common use of epoxy powder is as a coating for underground pipe. In this case, one of the heavier coatings is applied, although it is still considered a thin film coating (10 mils) in contrast to the heavy coal tar enamel-type coating. Epoxy powder coatings have excellent adhesion, impact resistance, and chemical resistance consistent with the curing agent; good thermal stability; excellent insulation properties; and resistance to corrosive soil and cathodic disbonding. These characteristics have led to their use as exterior pipe coatings. There also have been difficulties where powdered coatings are applied, particularly where fusion temperatures have gotten out of control and the surface preparation of the metal or other surface was not as satisfactory as it should have been. Powder coatings are particularly averse to application over chlorides. In these cases, the adhesion has been less than satisfactory, and blistering and loss of adhesion have resulted on pipelines. Some other uses for the epoxy powdered coating includes coatings for electrical equipment and housing finishes for office and other types of equipment, including light fixtures, handrails, automobile accessories, tubular steel furniture, cabinets, and other similar areas. Most of these are product finish utilizing blends of epoxy, polyurethane, and acrylic powders. Their uses are not necessarily of direct interest to the corrosion engineer. (See Chapter 23 for a more complete discussion of pipeline coatings of all kinds.)

Vinyl Powder Coatings

The vinyl powder coatings are in many ways much simpler than the epoxy coatings because the vinyl is a thermoplastic material, which does not require curing in order to fuse and obtain adhesion. The vinyl powders are mixed with pigments, milled to a stable consistency, and, in the case of a fusion milling technique, reground. As they do not contain any reactive curing agents, the entire process of mixing, milling, and grinding is simplified. They may also be extruded to obtain a uniform mix prior to being ground to the proper powder size.

The application techniques for vinyl powder coatings are the same as those used for the epoxy powder coatings. They may be applied by either the fluidized bed technique or by electrostatic spray. Where properly applied over a thoroughly clean surface, the vinyl powder coatings can have all of the good properties found in lacquer-type coatings. Most of the powdered vinyl coatings, however, are somewhat thinner than many of the vinyl lacquers. Again, these coatings are important to the corrosion engineer only because equipment is sometimes received that has been coated in this manner.

Surlyn and Nylon Powder Coatings

A newer application of the 100% solids technology lies in the application of Surlyn and Nylon powders developed by DuPont by means of newly developed flame spray equipment. While the equipment is similar to that used for flame spraying zinc and aluminum wire, it differs in that the ability to apply uniform films without pinholes and holidays is dramatically improved. The melted powders also have great affinity for edges which results in improved resistance to edge corrosion. The products are applicable at high film thicknesses and have good color ranges with very good color retention.

100% Liquid Epoxy Coatings

One hundred percent solids liquid epoxy coatings have been a goal for some time. Ideally, they would be epoxy coatings that are sufficiently thin in viscosity so that they could be applied to either structures or equipment by normal spray equipment in the field. There are a number of high-solids epoxy coatings that have been developed. Many of these, however, do contain some exempt volatile material in order to reduce the viscosity of the epoxy resins to a point where they can be handled. There are also some 100% solids epoxy coatings applied from two-headed spray equipment where the catalyst and the epoxy are mixed at the point of spray. Many of the epoxy compounds used in this case are heated during the application process, thus the reaction with the curing agent is usually rather rapid. Heavy film thicknesses can be achieved this way, although in some cases, this has been a hindrance rather than an advantage. Unless every care is taken during the application of such materials, adhesion and disbonding problems can result.

While it is true that 100% solids epoxy coatings are now available, "user friendly" truly 100% solids epoxy are still in the minority. The properties of the 100% solids epoxy coatings that are available are similar to those of the solvent-applied epoxy coatings of the more chemical-resistant type. Of particular interest to the chemical tank lining industry is the development of 100% solids novolac epoxies. The chemical, heat, and water resistance properties of 100% solids novolac epoxy coatings are similar to the high-solids novolac epoxy coatings. The major advantage is the ability to achieve higher dry film thickness (DFT) in one-coat applications that would otherwise require two or three coats with high-solids novolac epoxy coatings. The major disadvantages are the need for plural component heated airless application equipment and the higher application skills required. They are not "user friendly."

Plastisols

Plastisols are 100% solids in that they are essentially vinyl resin milled into a plasticizer, which does not solvate the vinyl resin until heat is applied. The amount and type of plasticizer determines the physical as well as chemical characteristics of the plastisol. One common use of plastisols is in the product finish field where plating racks, trays on the interior of automatic dishwashers, and other similar objects are coated. The coatings in these cases are subject to continuous and difficult operating conditions. Many plastisols are used for lining objects that can be heated, as well as for lining pipe. Much plastisol-lined pipe has been used by the mining industry for tailing pipe and for pipe handling of strongly corrosive solutions such as copper sulfate ($CuSO_4$).

The chemistry of this coating is relatively simple. The powdered vinyl resin is mixed into the plasticizer or combination of plasticizers where it remains suspended in a very viscous state. It is then applied to its intended object, and both are heated to the point where the plasticizer solvates the resin and is absorbed into it. The vinyl plasticizer mixture becomes homogeneous with the vinyl resin, and the plasticizer completely dispersed, one within the other.

Chemical characteristics depend on the plasticizer used since it is a major part of the coating film. The vinyl resin itself is generally a homopolymer of vinyl chloride, which is extremely resistant. However, when a large amount of plasticizer is included, chemical characteristics can be reduced considerably, depending on the plasticizer involved. Plastisols are ordinarily rather soft, rubber-like coatings and are applied in rather thick films (from 30 to 125 mils), so that the end result is a flexible, resilient coating having the benefits of an appreciable thickness. These properties have led to its successful use as lining for pipe of some substantial size in mining operations. The resilience of the coating, as well as its chemical resistance, provide a protection against the abrasive and corrosive mine liquids.

Rubber Linings

Rubber linings are a very critical material for extremely corrosive services. Since their application is very different from organic or inorganic linings applied for immersion service, the entire subject of rubber linings is dealt with in Chapter 20, "Elastomeric (Rubber) Linings."

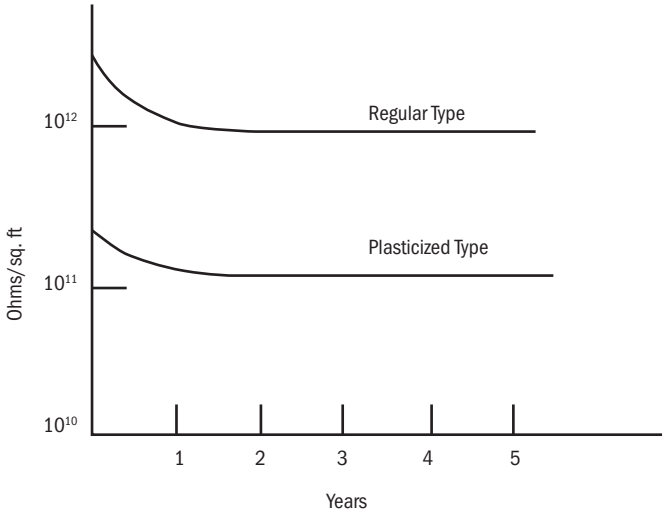


FIGURE 5.35: Electrical resistance rates for coal tar enamel. Source: Kemp, W. E., "Coal Tar Enamels Coatings for Underground Pipeline," *Materials Protection* (June 1970).

Furan Materials

A corrosion engineer may conceivably face a problem where furan products could serve as a valuable solution. Furan resins have one of the greatest potentials of any of the synthetic organic compounds available for the corrosion protection field. They have a broad span of chemical resistance, ranging from strong acids to strong alkalies, with good resistance to solvents as well. Their temperature resistance is well above other organic resins. On the other hand, furan resins cure explosively, are brittle and brash, have poor adhesion characteristics, and are black. Recent research, however, has led to a reduction of the materially negative characteristics without changing the valuable properties of these compounds. There presently are patents on over 1,000 of these materials, although from a practical industrial standpoint, there are only a few that are of value. These primarily are based on furfural, furfuryl alcohol, or combinations of the two.

The source of furfural, the base of furan resins, is vegetable matter that contains cellulose and hemicellulose. The cellulose compounds are built up from long-chain sugar units, mainly pentosans (xylan and araban) and hexosans (mannan and galactan). Of these components, the pentosans serve as the major source of furfural.

A pentosan is a five-carbon sugar with vegetable sources of corn cobs, oat hulls, cottonseed hulls, bagasse rice hulls, and so on. The chemical formation of furfural and furfuryl alcohol from pentosans consists of: (1) acid hydrolysis of the raw cellulose, which contains the pentosans producing pentoses; (2) continued acid hydrolysis of the pentose to furfural; and (3) catalytic hydrogenation of the furfural to furfuryl alcohol (Figure 5.35).

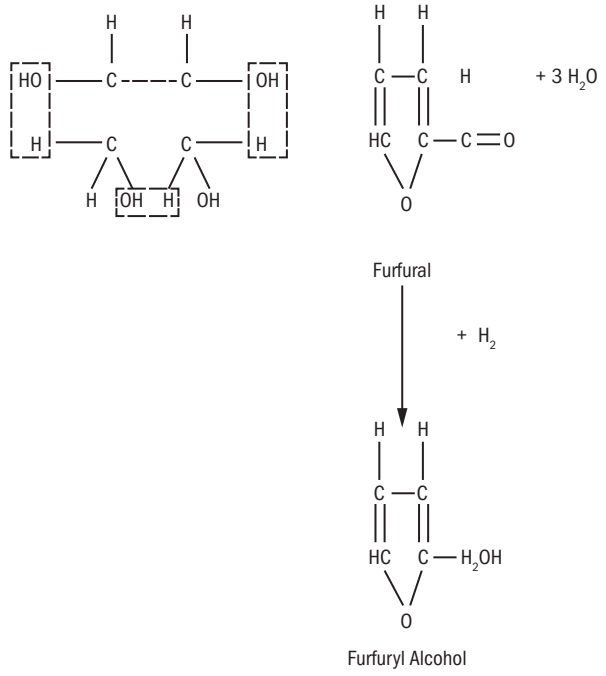


FIGURE 5.36: Chemical formation of furfural and furfuryl alcohol.

Furfuryl alcohol is the primary basic material for furan resins, and it is a mobile, amber-colored liquid. It is extremely sensitive to strong acids and polymerizes readily in their presence. The effect of hydrogen ion concentration on the polymerization process of furfuryl alcohol was studied many years ago when it was found that the rate of polymerization is a simple function of pH, at least during the early stages of the reaction. The first step in the reaction is one of intermolecular dehydration, which depends upon condensation between the hydroxyl group of one molecule of the alcohol with the labile nuclear alpha hydrogen atom of another molecule, as shown in Figure 5.36.

There are two stages of a furan resin: a liquid stage and a hard, cross-linked solid stage that constitutes the ultimate product. The first liquid stage is the one used in most industrial products, which is later reacted to the solid state as desired. The furfuryl alcohol or furfuryl alcohol-furfural resins are fluid or viscous liquids, dark in color with a reddish-black appearance, and generally stable in storage under normal conditions for extended time periods. Further polymerization takes place with the addition of catalysts to the furfuryl alcohol resins. When catalyzed to the final thermoset polymer, the resin becomes black.

Chemical resistance is one of the furan resin's outstanding characteristics since it is not limited to any one type of chemical reaction. Furan resins are resistant to strong acid solutions at high temperatures, strong alkali solutions, most salt solutions, and many solvent-type materials as well. Some of the specific properties of the furan resins are as follows.

Water Resistance

The water resistance of furan resins is excellent. Furan resins have been

made into acid-resistant cements for use in the steel industry to line acid pickling and rinse tanks in galvanizing plants and continuous steel strip lines. They have remained unchanged for many years, even though temperatures range from 69 to 85 °C.

Inorganic Acids

Furan resins have shown excellent resistance to most inorganic acids at temperatures as high as 90 °C for periods of many years. Concentrated H_2SO_4 is the exception. Concentrations above 60% of sulfuric are not recommended.

Oxidizing Conditions

Oxidizing conditions represent the one area where furan resins are deficient. Furan resins generally are not satisfactory for exposure to strong oxidizing chemicals such as hypochlorites, hydrogen peroxide (H_2O_2), chlorine dioxide (ClO_2), and chromic acid.

Organic Acids

The furan resins have very good resistance to organic acids, even at high temperatures. These include lactic, oxalic, and many fatty acids.

Alkalies

Furan resins demonstrate excellent resistance to alkalies in general. Many chemical tanks containing strong NaOH have been constructed using furan resin mortars and carbon brick.

Salt Solutions

Very good resistance to continuous exposure to most salt solutions at 90 °C is another characteristic of furan resins. Those salts that hydrolyze and release oxidizing acids are the only exception.

Solvents

Furan resins generally are resistant to most solvents, particularly where the resins are cured at above ambient or room temperature. Resins should not be cured at room temperature for extended periods. Also, materials such as aniline and methylene chloride tend to soften the resins over a period of time.

Animal, Mineral, and Vegetable Oils

Furan resins are unaffected by mineral, animal, and vegetable oils.

TABLE 5.18 Compression Strength in psi at Various Temperatures

Temperatureee, °C	22	65	95	120	150	175
Crosslinked Furan	10.572	13.863	14.691	13.331	12.908	10.466
Polyester	16.172	18.577	16.476	13.588	9.554	7.366
Epoxy Polyamide	7.706	10.059	2.059	1.116	806	136

Source: C.G. Munger, I. Metil, Industrial Applications of Furan Resins, Presented at Third Inter American Congress on Chemical Engineering, Mexico City, Mexico, October 1966.

Temperature Resistance

Temperature resistance is one of the outstanding properties of furan resins, since little heat distortion occurs with these resins even at temperatures as high as 190 °C. This is shown in Table 5.18 where the compressive strength of furan is compared with polyester and epoxy polyamide resins exposed to the same temperature conditions over the same period of time. The furan resin maintains its original compressive strength from ambient temperature through 175 °C, while a substantial change is evident in both of the other resinous materials.

The broadest use of furan resins for corrosion applications is in the steel and chemical industries where chemical-resistant cements are made. Furan has been used for a number of years primarily as acid-proof cement used for laying up brick in acid-pickling tanks in steel plants. These are large installations operated on a continuous basis with steel passing through the hot H_2SO_4 solution at a rapid rate. In these cases, the furan cement not only is utilized for its acid resistance, but also for its ability to retain its properties under strong, hot acid conditions, remaining sufficiently tough and adherent to the brick so that abrasion and impact from the steel has limited effect on the structure.

In addition to the acid pickling tanks and continuous acid strip mills in steel plants, there are many other similar tanks throughout the industry using equivalent acid-proof construction. In steel galvanizing, the steel must be pickled in a way similar to that in the steel mills. Rinse water tanks are also needed and lined in a similar way, since the rinse water is hot and gradually picks up sufficient acid to create a very corrosive condition. Chemical companies, particularly heavy chemical plants, use several tanks of this type for storage of a variety of severely corrosive liquids. Stacks in chemical processing and paper mills are lined with acid brick and furan mortars, as are many floors that are subject to continuous exposure to corrosive solutions. Some furan components have been formulated into troweling compounds and used for application on pump bases and similar areas where active corrosion exists.

The furan materials are versatile corrosion-resistant compounds. While there can be significant problems with their use, they may, in some instances, provide the only practical answer to a severe corrosion problem.

As evident from the foregoing discussion, 100% solids coatings, with the possible exception of 100% solids liquid epoxy coating, are primarily specialty products that are only for limited use in specific situations. They cannot be sold for general plant maintenance or other similarly broad purposes. Nevertheless, they can perform where other materials would fail or have short useful lives. Table 5.19 gives a summary of the general properties of the 100% solids coatings.

Corrosion-resistant organic coatings have numerous and varied properties, which are necessary to match the variety of corrosion conditions that exist. For this reason, organic coatings are the most widely used method of corrosion protection available. Without such versatility, adequate corrosion protection for modern industrial structures and equipment would be very difficult.

TABLE 5.19: 100% Solids Coatings: General Properties

100% Solids	Furfural							
Properties	Coal Tar Enamel	Asphalt Enamel	Polyester	Epoxy Powder	Liquid Epoxy	Vinyl Powder	Vinyl Plastisol	Alcohol Resins
Physical Properties	Hard	Somewhat Resistant	Hard	Hard	Hard, Tough	Hard, Tough	Soft, Rubbery	Hard, Tough
Water Resistance	Excellent	Very Good	Good	Good	Good	Good	Good	Excellent
Acid Resistance	Very Good	Very Good	Excellent	Good	Good	Good	Very Good	Excellent
Alkali Resistance	Good	Fair, Good	Poor	Very Good	Very Good	Good	Very Good	Excellent
Salt Resistance								
Solvent Resistance (Hydrocarbons)								
Aliphatic	Good	Poor	Very Good	Very Good	Very Good	Very Good	Good	Excellent
Aromatic	Poor	Poor	Fair	Very Good	Very Good	Fair	Poor	Excellent
Oxygenated	Poor	Poor	Poor	Good	Good	Poor	Poor	Good
Temperature Resistance	60 °C (140 °F)	50 °C (122 °F)	65 °C (150 °F)	93 °C (200 °F)	93 °C (200 °F)	60 °C (140 °F)	60 °C (140 °F)	120 °C (248 °F)
Weather Resistance	Poor	Good	Good	Good (Chalks)	Good (Chalks)	Very Good	Very Good	Good
Age Resistance	Excellent	Very Good	Good	Good	Good	Very Good	Very Good	Good
Best Characteristic	Water Resistance	Water and Weather Resistance	Acid and Oxidizing Chemical Resistance	General Water and Alkali Resistance	General Chemical and Alkali Resistance	General Chemical Resistance	Water and Chemical Resistance	Temperature and Acid Resistance
Poorest Characteristic	Weather Resistance, Black	Solvent Resistance, Black	Alkali Resistance	Critical Application	Critical Application	Critical Application	Adhesion	Adhesion, Brittleness
Recoatability	Poor	Good	Fair	Poor	Difficult	Good	Good	Good
Principle Use	Lining and Coating Pipe	Waterproof Structures	Tank Lining	Exterior Pipe Coating	Chemical Lining	Chemical-Resistance Product Finish	Pipe Lining	Cement for Acid Proof Brick

TABLE 5.20: Polysiloxane Terminology

Silicon	The element (Si)
Silane	Substituted silicon compounds
Oxysilane	Silicon compounds with at least one substituent: an alkoxide, hydroxide, or aryloxide
Silicate	Metal salt of silicon–oxygen anion
Siloxane	Compounds with 2 or 4 oxygens bonded to silicon
Polysiloxane	Polymer with silicon–oxygen backbone
Silicone	Polysiloxane with organic substituents on each silicon, typically two
Organic	Carbon-based compounds: polymers with carbon-carbon units in the backbone

Source: "Development in High-Performance Protective Coatings: Polysiloxanes." *American Paint and Coatings Journal* (August 1995).

Polysiloxanes

One of the more intriguing developments in protective coatings technology during the 1990s has been the creation of a new generic class of high performance resins based on siloxane chemistry. For purposes of clarity, Table 5.20 gives definitions of the chemical terminology used in this technology.[6]

In coatings compositions, the typical resins using the silicon-oxygen bond as the repeating unit in the backbone are silicones and silicates. The term polysiloxanes can include silicones, but is used here in its broadest sense; that is, any polymeric structure that contains repeating silicon– oxygen groups in the backbone, side chains, segments, or cross-links, regardless of substitution on the silicon atom. Oxysiloxane refers to a silicon-based structure in which the silicon is bonded to up to four alkoxide or hydroxyl groups, thereby rendering that structure reactive to certain condensation reactions. The oxysilane may be monomeric, polymeric, or a pendant group of a larger molecule.

This chemistry has been applied to create pure polysiloxane network compositions having maximized thermal and chemical resistance; pure polysiloxane compositions offering extended weatherability and appearance retention; and "hybrid" systems in which properties of a traditional resin have been selectively and significantly upgraded. Examples of these developments include the following.

Heat-Resistant Polysiloxanes

Compositions containing pure polysiloxane resin networks have been formulated that provide heat resistance in excess of 1,100 ◦C (2,000 °F). Typical formulations contain micaceous iron oxide (MiOx) as the major filler component. The resin/pigment ratio is as close as possible to the critical pigment volume concentration (CPVC) and the product cures by hydrolytic polycondensation at ambient conditions without need for any baking.

Chemical Resistant Polysiloxanes

This technology can be used in an essentially inorganic formulation that behaves like a zinc silicate without the acid-exposure and chemical-reactivity limitations of IOZs. Tank lining formulations with a broad range of resistance to solvents, organic acids, and mineral acids, are possible.

Ultraviolet Resistant Topcoats

By using appropriate blends of silicone intermediates and oxysiloxane cross-linking agents, topcoats similar in appearance to polyurethanes have been formulated. Polysiloxane acrylic topcoat blends have been formulated which meet or exceed the ultraviolet resistance properties of polyurethanes.

Oxysilane-Cured Epoxy

The incorporation of polysiloxane in the epoxy resin matrix has produced significant new properties for epoxies not heretofore possible; namely, inherent compatibility with IOZ silicate primers and combined build properties and ultraviolet resistant properties into one single topcoat over the zinc silicate primers. The penetrating properties of the formula, along with its inherent compatibility with IOZ primers essentially eliminates the gassing and bubbling problems normally associated with traditional epoxies applied over IOZ primers.

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6 Corrosion-Resistant Zinc Coatings

Zinc is a unique and very useful metal, particularly when in the form of a thin coating. It can be used as a pure metal coating or it can be combined with other materials and still provide full corrosion protection when applied over steel surfaces. Metallic zinc is resistant to most atmospheric conditions, yet it remains sufficiently reactive to cathodically protect steel where zinc and iron are in contact. It does not develop a continuous and inert oxide film, as does aluminum. The aluminum oxide film makes an aluminum surface non-reactive and thus prevents the degree of cathodic protection (CP) developed by zinc.

This characteristic of being relatively inert to atmospheric conditions, yet sufficiently reactive to protect steel is unique. Another important advantage of zinc is that it is readily available. In fact, among the nonferrous metals, zinc is one of the least expensive and one of the most readily available.

While there are other metals that also can be used to coat steel (e.g., magnesium, aluminum, and calcium), none of them have proven to be as useful or as effective as zinc. Over a million tons of zinc is used in the United States annually, and approximately half of that tonnage is used as a coating to protect steel. The majority of it is used for galvanizing or electrodeposited zinc coatings. Approximately 10% of the tonnage used for coatings is applied in the form of zinc-rich coatings. Approximately 10 million tons of steel is coated in the United States each year with some type of zinc coating.

Protection by Zinc Coatings

Zinc coatings are protective in two different ways: they serve as barriers and also as galvanic protectors of steel surfaces, regardless of the type of zinc coating involved. Metallic zinc protects steel from corrosive attack by most atmospheres by acting as a continuous and long-lasting barrier between the steel and the atmosphere. Zinc has a much lower corrosion rate than steel, so that in all except very polluted (acid or alkaline) atmospheres, the coating of zinc will provide protection against rust for long periods of time. Historical data to prove this point have been released in reports by the American Society for Testing Materials and by the Zinc Institute as a result of actual zinc coatings service and field tests.

Table 6.1 gives the estimated life of zinc-coated products in the atmosphere for various thicknesses of zinc. These are only estimates, but they do indicate that, when applied as a continuous film, zinc does provide corrosion protection in proportion to the thickness of the coating. The greater the thickness (up to an optimum point), the longer the time before the underlying steel will begin to corrode.

TABLE 6.1: Estimated Life of Zinc-Coated Products in the Atmospheres

Thickness (in)	Weight in oz/ft^2 of surface[A]	Life in Years under Atmospheric Conditions					
		Rural	Tropical Marine	Temperate Marine	Suburban	Urban	Highly Industrial
0.0036	2.00	50	40	35	30	25	15
0.0023	1.25	35	30	25	20	17	9
0.0018	1.00	25	20	15	12	10	7
0.0011	0.60	10	8	7	5	4	3
0.00066	0.37	7	6	5	4	3	2
0.00044	0.25	5	4	3	3	2	1

[A]In the case of galvanized steel sheets, the weight of zinc is specified in terms of total zinc on both sides of the sheet (i.e., a 2-oz. sheet has 1 oz. of zinc per ft^2 of surface).

Source: Zinc Controls Corrosion, Z1-51-10M/71 (New York, NY: Zinc Institute, Inc., 1971), p. 11.

There are several different methods of applying zinc to steel surfaces (Table 6.2). Each of these processes has its own unique characteristics, in spite of the fact that the protection is derived from metallic zinc. The processes are generally complimentary rather than competitive in nature so that each one fits a specific need.

TABLE 6.2: Principal Methods of Corrosion Protection with Zinc	
1.	Galvanizing a. Hot Dip b. Continuous Line Galvanizing
2.	Electrogalvanizing
3.	Zinc Plating
4.	Sherardizing
5.	Zinc Spray
6.	Zinc Coating a. Organic Zinc Rich b. Inorganic Zinc

Application of Zinc Coatings

Galvanizing

Galvanizing is the primary process by which zinc is applied to steel. Two different French engineers first suggested it at approximately the same time (1840).[1] Since then, its use has steadily increased.

Galvanizing is the process of cleaning steel free of all mill scale or other impurities and then dipping the steel into molten zinc. The molten zinc wets clean steel very readily and alloys with the steel, making a strong bond between the zinc and the steel surface. One of the great advantages of galvanizing is that once the object is dipped, removed, and cooled, the process is finished and the galvanized object can be handled without fear of damage. The hot dip galvanized coatings are rugged and provide an impervious and long-lasting barrier against most atmospheric corrosion processes.

Hot Dip Galvanizing After Fabrication

Hot dip galvanizing is the process with which the corrosion engineer will probably have the most contact. It is the earliest of the methods to be used for zinc coatings and, like many simple processes, is quite effective, continuing to be used year after year with only minor improvements. It is a flexible process in that it can apply zinc to steel parts ranging from extremely small ones such as nuts and bolts to large fabricated pieces such as small tanks, containers, transmission towers, pole line hardware, guardrails, and other structures.

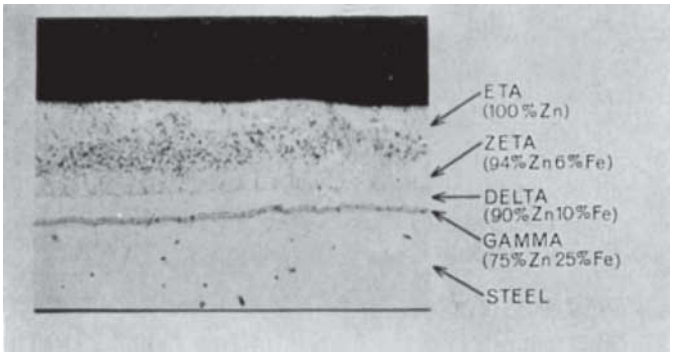


FIGURE 6.1: Photomicrograph of a section through a typical hot dip galvanizing coating showing alloy layers. Source: *User's Guide to Hot Dip Galvanizing for Corrosion Protection in Atmospheric Service (TPC-9)* (Houston, TX: NACE, 1983), p. 1.

As mentioned previously, the hot dip galvanizing forms an alloy with the steel that provides for maximum adhesion between the two metals. Figure 6.1 is a photomicrograph of a hot dip galvanized coating on a steel surface. Starting with the basic steel at the bottom, which is 100% iron, there is an adjacent, thin layer that is approximately 75% iron and 25% zinc. The next layer is approximately 90% zinc, the third layer is approximately 94% to 95% zinc, and the final layer, which is the thickest, is pure zinc. There is not any real line of demarcation between the iron and the zinc, but rather a gradual progression of iron and zinc alloy from the pure iron to the pure zinc. This provides a powerful bond between the two materials.

The structure of the zinc coating and its thickness depend on the composition and physical condition of the steel being treated as well as the temperature, time in the bath, and other factors, some of which are under the control of the galvanizer. Heavier coatings tend to be deposited on rough surfaces or coarse grain steel. The total thickness of the alloy layer tends to be slightly greater in corners and similar areas than it is in hollows. The thickness of the coating can be controlled by the length of time in the bath and the speed by which it is removed. Many times when a thin coating is required, the zinc is mechanically wiped from the surface as the object is being removed. Small parts and threaded parts are often centrifuged after being hot dipped in order to remove the excess zinc.

Some other elements also may be added to the galvanizing bath. Tin and antimony give a spangled effect, and some lead added to the bath also is considered desirable. Aluminum aids in the ductility and adds to the corrosion resistance of the coating. The thickness of zinc applied by the hot dip process usually varies from a maximum of 2.75 ounces per square foot down to an ounce or less per square foot. If the steel is thoroughly cleaned, a continuous coating is formed over the entire surface. Even the rivets, welds, and edges of complicated fabricated steel structures are well covered. One of the disadvantages of hot dip galvanizing is the possibility of warping the steel structure due to the heat of the galvanizing bath. There also is some possibility of the embrittlement of malleable cast iron. Such difficulties, however, usually can be overcome through proper galvanizing techniques. All in all, it is a very useful process, particularly for complicated, relatively lightweight objects or steel fabrications.

Continuous Line Galvanizing

Continuous line galvanizing is a process of hot dip galvanizing developed in the 1930s, whereby coils of sheet steel could be continuously hot dipped. A small amount of aluminum is added to the zinc bath, which provides a coating with essentially no iron zinc alloy, yet one of good adhesion and sufficient ductility to allow for deep drawing and folding without appreciable damage to the coating. Nearly all of the hot dip galvanized sheet steel that is used in metal building fabrication is produced by the continuous strip method. Approximately 6.5 million tons of steel a year are coated by this process, which accounts for the greatest use of zinc for corrosion protection.

The weights of coatings produced by this process vary from 2.75 ounces of zinc per square foot down to as low as 0.5 ounces per foot. The Zinc Institute standard for galvanized sheet is 2 ounces of zinc per square foot. In the case of galvanized sheet, 2 ounces per square foot refers to both sides of the sheet. This equals 1 ounce of zinc per square foot on each surface.

The zinc coating applied by this process is considerably different from the hot dip coating in that there is little alloying of the steel with the zinc. Figure 6.2 is a photomicrograph of continuous strip line galvanizing, which shows a distinct demarcation between the two metals.

Electrogalvanizing

Electrogalvanizing is an essentially cold process compared to the heat involved in hot dip galvanizing. Most electrogalvanizing is continuous and is applied to sheet, wire, and electrical conduit or similar objects. It produces a thin, pure zinc coating that has excellent

adherence. The coating is smooth, free of spangled characteristics, and can be readily prepared for painting by phosphatizing. Electrogalvanized steel is generally painted since it is applied as a relatively thin film. The coating produced on strip coils or sheets generally have a coating weight of from approximately 0.06 to 0.2 ounce per square foot. This is a thickness of 0.0005 to 0.00017 on each side of the sheet. Electrode-position steel offers a process for applying zinc coatings to parts that cannot be hot dipped. It is especially useful where high processing temperatures may injure the part.

Electrogalvanized steel can easily be prepared to receive organic coatings. Many organic coatings have good adhesion to the zinc surface, and the zinc base tends to increase the life of the organic coating over the surface, as compared with a similar coating applied to steel alone. This is similar to the effect that inorganic zinc (IOZ) coatings have on the life of organic coatings.

For outdoor surfaces, electrogalvanized products are commonly painted to increase corrosion resistance and protection of the thin zinc coating. Such protection is adequate for many mild services.

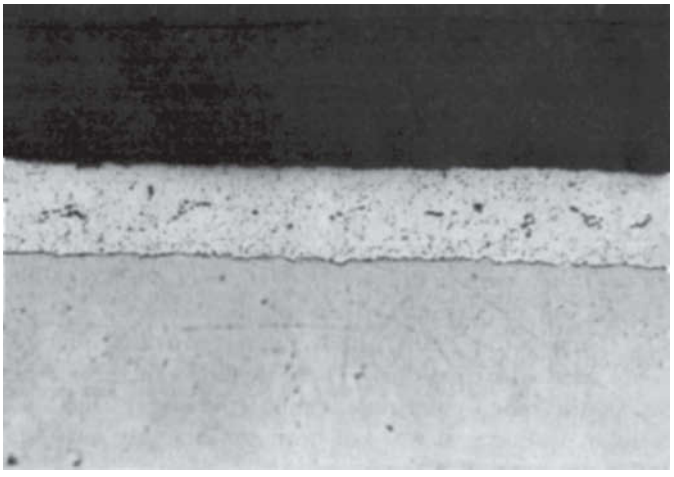


FIGURE 6.2: Photomicrograph of a continuous galvanized coating cross section. Aluminum addition minimized alloy layers, provides uniform coating. Source: Zinc Institute, Inc., New York, NY.

Zinc Plating

Zinc plating is similar to electrogalvanizing, although it is not continuous and is applied as a batch process. In zinc plating, the plating process and time in the plating bath also may control the thickness of the zinc. This is an effective method of applying zinc to small objects. Barrel plating of many small objects at the same time is a common process where the parts are tumbled in a barrel that is in the plating bath.

The normal plated zinc coating is dull gray in color and has a matte finish. The coating is pure zinc and is of uniform composition. It adheres by means of a metal-to-metal bond and is not alloyed.

Sherardizing

Sherardizing also is a process for relatively small parts. It applies zinc coatings to clean steel by rotating the parts in a sealed drum in the presence of zinc dust and at a temperature in the range of 700 to 800 °F (371 to 426 °C). Tubing, conduit, nuts, bolts, and small castings are handled in this manner. This is the process that was most commonly used earlier in the 20th century. At the present time, however, it is rarely used in the United States.

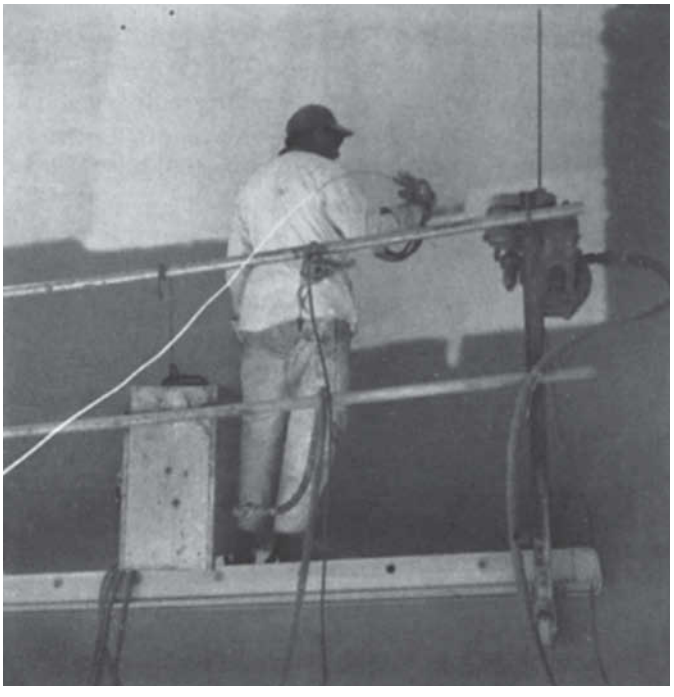


FIGURE 6.3: Metallizing is one way of applying a zinc coating. Molten zinc is sprayed at high pressure onto a clean steel surface. Source: Metalweld, Inc., Conshohocken, PA.

Zinc Spray (Spray Metallizing/Thermal Spray)

Zinc spraying is a process whereby zinc is melted in the spray gun and is atomized and projected onto a steel surface. The steel is usually grit blasted to a minimum of NACE No. 1/SSPC-SP 10 Near White Metal[2]/ISO Sa 2.5 Very Thorough Cleaning[3] with an angular anchor profile of 2.0 to 3.0 mils (50 to 75μm). The thermal sprayed zinc should be applied as soon as possible after the surface has been prepared in order to reduce oxidation on the steel and to make sure of an effective metal-to-metal bond. The bond can be affected both by the oxidation and many times by the temperature of the steel at the time the zinc spray is applied. Some experienced operators prefer to heat the surface from 79 to 93 °C (175 to 200 °F) before starting application. This improves the bond with the base metal because the heating opens up the grains of the metal, thus creating better penetration of the thermal sprayed zinc or aluminum.

Thermal spraying of zinc is accomplished by one of three methods. One is the wire process in which zinc wire is fed into the center of a very hot gas fed flame. (Zinc powder can also be fed into the gas flame). A stream of compressed air disperses the molten metal and sprays it out of the nozzle in a fashion similar to the spraying of coatings. The zinc wire or powder is fed continuously into the gun as long as the gun is operating. Sprayed zinc of these types can be applied to structures of almost any size or shape and can be done either on site or in a plant. Coating of the steel is dependent on the gun operator and strict care is required in order to obtain a smooth and even film over the surface. Zinc spraying is one of the only satisfactory methods of depositing a heavy zinc coating of 0.01 in (0.25 mm) or more on the steel surface (Figure 6.3).

A second method of flame spraying zinc is arc spraying, in which an electrical current between two wires in the spray gun causes the tips of the zinc wire to melt when they touch. The molten zinc is transported to the substrate being sprayed by low-pressure compressed air. Arc spraying is easy to learn, portable, and fairly simple to maintain. The spray pattern is wider than with a gas-fed flame so productivity is better. A third method is plasma spraying, in which gases such as argon, nitrogen, helium, or hydrogen pass through a nozzle and are ionized by an electric arc. The core temperatures are typically greater than 10,000 °C (18,032 °F), well above the melting point of any material. This process injects powder into the flame.

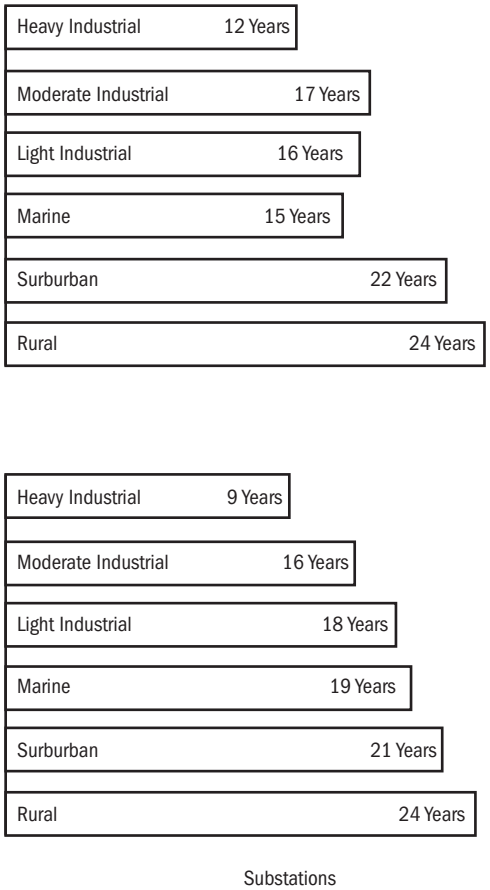


FIGURE 6.4: Average service life. Years before first painting of galvanized transmission towers (75 companies) and of galvanized substations (87 companies). Source: Zinc Controls Corrosion, Z1-51-10M/71 (New York, NY: Zinc Institute, Inc., 1971), p. 11.

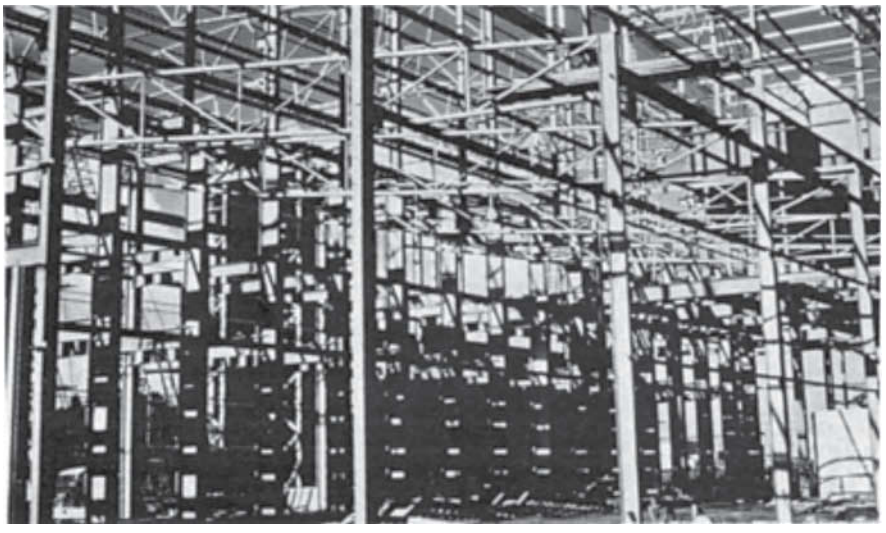


FIGURE 6.5: Thousands of edges, corners, and bolt heads make this electric substation extremely difficult to protect. IOZ or galvanizing, applied before erection, is a practical answer to long-term corrosion protection.

Zinc spraying is difficult in cavities, depressions, corners, and similar areas. Due to the porosity of the molten metal application, zinc spray is usually sealed or used as a base for an organic topcoat.

One of the older, yet continuing, uses of zinc coatings and galvanized steel has been by electrical utilities. Hundreds of thousands of major transmission towers have been protected by hot dipped zinc galvanizing. Thus, a good record of the life of hot dip galvanized coatings has been kept by this industry (Figure 6.4).

The steel frame in an electric substation in Figure 6.5 is typical of the complex structures on which zinc coatings or galvanizing does an excellent job of corrosion protection. Such structures could not be satisfactorily protected by organic coatings alone because of the hundreds or thousands of linear feet of edges, corners, welds, rivets, and so on. Only a coating with the properties of zinc can provide the corrosion protection required. These properties are summarized in Table 6.3.

Zinc Dust Coatings

When the galvanizing process was first used in the mid-1800s, it had one substantial drawback. This was the inability of zinc to be applied to large, existing structures or new structures that were too complex to fit into a bath of molten zinc. The size and weight of structures, both substantial factors in the galvanizing process, increased several times during this period. Structures also were becoming more costly and processes were becoming more corrosive, so that a substantial need was developing for zinc coatings that could be applied to large or existing structures. The use of zinc dust as a basis for an anticorrosive coating was conceived in two areas of the world at approximately the same time (i.e., 1930s): zinc dust was incorporated into organic coatings in Europe and it also was being tried as an anticorrosive in inorganic coatings in Australia.

Organic Zinc-Rich Coatings

The development of organic zinc-rich coatings in Europe came slightly before its counterpart in Australia and, in many ways, proceeded more rapidly. Drying oils were the first type of materials used that, for the most part, were not entirely successful. One such zinc dust product is a Federal Specification, TT-P-641G,[18] in which Type 1 is a zinc dust, zinc oxide, linseed oil paint for outdoor exposures. It is used for air- drying only and is recommended as a primer or a finish coat for galvanized steel, particularly where the galvanizing has started to show rust penetration and pinpoint rust on the steel surface. It is specified that this product has a minimum weight of 23 lb/gal.

Type 2 included in this specification is a zinc dust, zinc oxide, phthalic alkyd resin coating, which may be either air dried or baked at temperatures up to 300 °F. This is a so-called heat-resistant paint and is often used as a coating for low-temperature stacks. It also can be used as either a primer or a finish coat under outdoor conditions where corrosion is not too severe. A minimum weight per gallon of this product is specified at 16 lb.

Type 3 is a zinc dust, zinc oxide, phenolic resin paint that may be air dried or baked, again at temperatures up to 500 °F.Because of the phenolic resin, this coating may be used for water immersion and other similar conditions. It has a minimum weight of 16.4 lb/gal.

During the 1930s, many other resin and oil types were used with zinc dust. These included such materials as polystyrene, chlorinated rubber, vinyl resins, and similar products. It was not until considerably later that zinc dust was used with phenoxies, epoxy resins, epoxy esters, and silicones.

The degree of variation in the performance of coatings depended primarily on the vehicle. In general, the performance is in direct proportion to the resistance of the vehicle to corrosive conditions. Some early tests of the organic zinc-rich coatings illustrate the type

TABLE 6.3: Summary of Zinc Coating Properties

Process	Typical Products & Specifications	Zinc Coating Weight Range
GALVANIZING		
Application	Sheet Strip ASTM A525-79[4]	1.20–2.75 oz/ft^2 of sheet
Hot dip galvanizing is most commonly used for coating steel with zinc. It is employed on a wide range of items from heavy structural to house hardware, individual fasteners, etc.	Roofing Sheets ASTM A361-76 (1981) el[5]	1.20–2.75 oz/ft^2 of sheet
	Structural Sheets ASTM A446-76 (1981 el[6]	1.20–1.75 oz/ft^2 of sheet
Technique *Two hot dip galvanizing techniques are available:*		
1. Continuous galvanizing of sheet, strip, or wire. Modern continuous galvanizing allows unterrupted passage of carefull prepared sheet strip or wire through a bath of molten zinc. This results in an exceptionally good zinc-to-steel bond.	Wrought Iron ASTM A163—withdrawn 1972[7]	1.20–1.75 oz/ft^2 of sheet
	Tube & Pipe ASTM A120-84[8]	2.00 oz/ft^2 of sheet
	Wire Strand ASTM A476/A476M-00 (2009)[9]	0.15–3.00 oz/ft^2 of sheet
2. Hot dip galvanizing (after fabrication). Items to be coated are dipped into a bath of molten zinc. This technique is particularly suitable to irregularly shaped articles.	Farm & Right of Way Fencing	0.20–0.80 oz/ft^2 of sheet
	ASTM A116-11[10]	
Properties		
1. Galvanized coatings are metallurgically bonded to the iron or steel base. Length of the coatings protective live is directly proportional to thickness applied. 2. Properly treated galvanized surfaces form an ideal permanently bonded base for paint. 3. Galvanized coatings withstand rough usage on applications such as highway guard rails. 4. Continuous glavnized sheet can be severely formed without damage to the coating. 5. Prepainted galvanized steel sheet can be fabricated without damage to the paint film. A range of colors is available. 6. Prepainted glavanized siding is available for residential or industrial applications.	Chain Link Fence Fabric ASTM A392-11A[11]	3.2–2.0 oz/ft^2
	Products fabricated from rolled, pressed, forged steel shapes, brass, and strip ASTM A123M-12[12]	2.0–2.3 oz/ft^2
	Coatings, nuts, bolts, washers, pole line hardware ASTM A153/153M-09[13]	1.0–2.00 oz/ft^2
	Transmission towerd nults and bolts ASTM A394-08el[14]	1.25 oz/ft^2
ELECTROGALVANIZING		
Application	Assembled Steel Products ASTM 123/123M-12	1.00–2.00 oz/ft^2 of sheet
Generally used for wire, conduit, hardware, and fasteners.	Sheet and industrial fasteners	0.0015-0.001 in
	Chain link fence fabric woven after plating ASTM A392-11A (hot-dep also)	1.2–2.0 oz/ft^2
Technique		
Zinc coating is electrodeposited. Usually think coatings, but heavier coats can be built up		
Properties		
Bright, durable adherent coating when phosphate treated provides an excellent base for paints and finishes		
METALLIZING		
Application		
1. Hot dip galvanizing is unavailable 2. No distortion of welded sections is permissible 3. High alloy steels are used 4. Coating thicknesses must vary 5. Repairs to galvanized surfaces are needed	Large structures, bridges, fabricated assemblies, conduit NACE No. 12[15]/AWS C2.23M[16]/ SSPC-CS23.00[17]	0.003–0.016 in
	American Welding Society AWS C2.23M	0.001 in. thickness equals 0.5 oz/ft^2 of surface
Technique		
After steel grit blasting, molten zinc is sprayed on surface. Zinc may be powder, wire, or molten		
Properties		
Coating may be in shop or at site. Excellent as paint base.		

Note: (1) Coating weight requirements on sheet and strip are in ounces per ft^2. of sheet (both sides inclusive [i.e., 2 ft^2 of surface]); (2) "Seal of Quality" galvanized steel sheet carries 2 ounces of zinc coating to meet the specification of Zinc Institute; and (3) one ounce of zinc per ft^2 of surface is equivalent to a coating thickness of 0.0017 in (0.043 mm).

Source: "Zinc Controls Corrosion," 21-51-10M/71 (New York, NY: Zinc Institute, Inc., 1971), p. 11.

of variable results that were obtained. The following test directly compared zinc-rich coatings made from drying oil, chlorinated rubber, styrene, and epoxy. The equivalent formulations were exposed in seawater:

1. Immersion in Florida seawater, four years: (a) drying oil-type zinc-rich coating—coating was completely dissipated, panel was solid rust; (b) chlorinated rubber zinc-rich coating—rust starting at scribe and edges, some active anode-type corrosion along edges; (c) styrene-type zinc-rich coating—severe edge pitting, scribe badly corroded with pits ¾ in (19 mm) wide, one or more penetrating the panel; and (d) epoxy zinc-rich coating—edges corroding with active pitting, scribe has several small pits.
2. Seacoast atmosphere, eight years and six months: (a) drying oil-type zinc-rich coating—general pinpoint rusting, 80% failure; (b) chlorinated rubber zinc-rich coating—light carbonate deposit, otherwise okay, no score corrosion; (c) styrene-type zinc-rich coating—light score rusting, pinpoint rusting on edge of panel; and (d) epoxy zinc-rich coating—light score rusting, pinpoint rusting near bottom edge.

The effectiveness of the various coatings was rated as follows.

1. Chlorinated rubber zinc-rich coating
2. Epoxy zinc-rich coating
3. Styrene-type zinc-rich coating
4. Drying oil-type zinc-rich coating

The drying oil coating is obviously a failure because of the breakdown of the vehicle due to the alkaline zinc reaction products. However, the more resistant vehicles under other environmental conditions might have performed equally with the chlorinated rubber types.

The early commercial zinc-rich products that were used for corrosion resistance were based on chlorinated rubber. It was an ideal resin inasmuch as the resin itself is rather heavy, contains a sizable amount of chlorine, and thus aids in the suspension of the heavy zinc dust. It was primarily a lacquer-type material and therefore dried rapidly, providing a base coat that could be quickly followed by other topcoats.

Later (1940s), epoxy resins became available and were soon found to provide a good vehicle for zinc-rich coatings. Today, there are two epoxy-type vehicles that make up the majority of the organic zinc-rich products presently in use. These are based on the epoxy polyamide resins and the phenoxy resins. The phenoxy resin is a long-chain thermoplastic resin that has epoxy groupings at the ends of the molecule. Each of these is a very resistant material, particularly to alkalies, so that any alkaline reaction of the zinc would not have any effect on the vehicles. Since the 1970s and particularly during the 1990s, zinc-rich moisture cure polyurethane primers gained a significant market share for maintenance of structures, particularly in cold, humid locations.

These organic vehicles generally have good dielectric properties, which makes it necessary for the zinc to be in sufficient quantity so that when the coating is dry and ready for use, the zinc can be in particle-to-particle contact throughout the film. It is generally conceded that the dry film in an organic zinc-rich coating must contain 90 to 95% zinc by weight in order to have the zinc in particle-to-particle contact. The zinc particles must be in contact from the base metal clear through to the surface of the coating in order for the coating to be conductive and to prevent corrosion by CP (Figure 6.6).

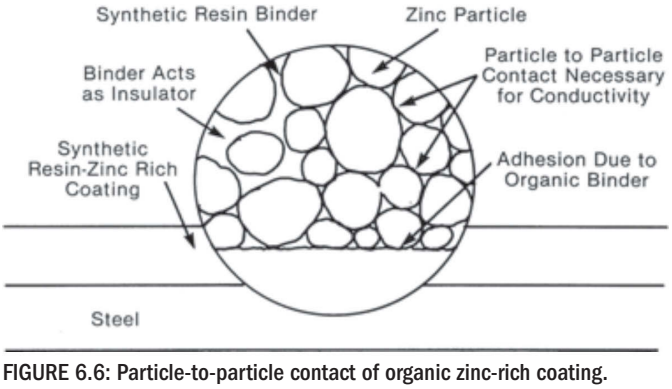


FIGURE 6.6: Particle-to-particle contact of organic zinc-rich coating.

There is little chemistry involved in the formation or formulation of organic zinc-rich coatings other than to provide a resistant vehicle that does not react with the zinc. The chemistry consists primarily of the curing of the vehicle. The zinc exists within the film as a heavy loading of pigment. The formation of the film is therefore very similar to any organic coating, with the exception that the volume of pigment within the vehicle is, of necessity, high. Once the coating is formed, only the zinc on the surface reacts to form ions to provide CP. Once ionized, it may react with other atmospheric ions to form such compounds as zinc oxide, zinc hydroxide, zinc carbonates, and so forth, on the surface of the coating.

Characteristics of Organic Zinc-Rich Coatings

Organic zinc-rich primers have some important characteristics, particularly as related to and compared with the inorganic zinc coatings.

Compatibility

The most outstanding characteristic of organic zinc-rich primers is their compatibility with both organic and steel surfaces. This is extremely important in coating repair and may be important during original construction where many different types of surfaces are involved, which all require excellent corrosion protection. Organic zinc-rich coatings may extend from bare steel out over various primers and topcoats (organic or inorganic) and provide adhesion to each surface. They should be compatible with oleoresinous topcoats as well as synthetic resin types, which is not possible with IOZ coatings.

Cathodic Protection

Organic zinc-rich coatings do provide limited CP, as long as the formulation is such that particle-to-particle zinc contact is maintained.

Application

With an organic binder, the application of organic zinc-rich coatings covers a very wide range of conditions. Organic binders may be fast or slow drying, and curing conditions can vary widely, depending on the requirements of the application.

Binder Resistance

A binder in an organic zinc-rich primer may be more or less chemical resistant, depending on the binder and its use requirements.

Chlorinated rubber, epoxies, polyurethanes, or vinyls are those which would provide chemical resistance; silicones provide weather and temperature resistance; while some alkyds provide intermediate temperature resistance and good weather durability. Epoxy esters are used primarily as cold galvanizing compounds for the touch-up and repair of welds in galvanized steel. Examples of epoxy ester zinc primers are products described in Mil-P-21035B[19] and C[20] and Mil-P-46105.[21] Numerous organic binders can be used, depending on the intended use of the zinc-rich coating. Probably the best known vinyl zinc rich primer is the Corps of Engineers specification CWGS-09940 Formula VZ-108d used on their locks and dams with very good results.

Surface Preparation

It often is claimed that the organic zinc-rich primers are less subject to critical surface preparation than are the IOZ materials. This may be true for the initial application since they would be less subject to problems from organic contamination. On the other hand, eliminating the organic contamination factor, light rust coloration on the steel surface to be coated may be more easily tolerated by an IOZ coating than by an organic-based material. This is due to the ability of the IOZ vehicle to thoroughly wet the oxide and to react with it.

Inorganic Zinc Coatings

Zinc has proven its effectiveness as a corrosion-resistant coating, not only as galvanizing, but to a lesser degree, by the organic zinc-rich coatings. Nevertheless, prior to the advent of IOZ coatings, maintaining industrial and marine structures was a difficult and continuous chore. There was no effective long-time protection for large or existing new structures. Coatings were applied and reapplied at short intervals in order to maintain structures in a safe condition for satisfactory operation.

IOZ coatings, as a single coat applied to a clean steel surface, have completely changed the old concept of paint and repaint on a continued basis in order to maintain critical industrial and marine structures. IOZ has proven its resistance to corrosion in the Arctic, in the Tropics, and in all of the intermediate climates. One of its first uses was in the marine area, on offshore structures and ships, as well as onshore structures along seacoasts throughout the world. It continues to be the standard of the industry in these areas for long-term corrosion protection.

IOZ coatings have been one of the true technological developments of our time that has made a real and positive impact on modern society. While this impact is not as dramatic as that of television or space travel, IOZ coatings nevertheless have made a solid contribution toward the preservation of scarce materials, thus eliminating the need for the replacement of existing structures, reducing the cost of steel structures, saving labor, reducing the energy required for metal replacement, and providing new structures with a substantial increase in life expectancy.

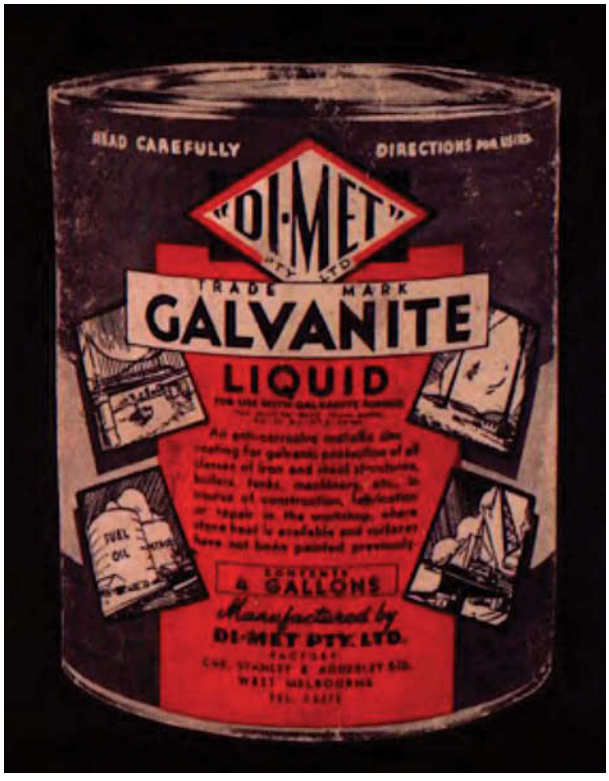


FIGURE 6.7: Victor Nightingall's original IOZ.


FIGURE 6.8: First application of inorganic zinc coating on above ground pipeline near Sydney, Australia..

Development of Inorganic Zinc Coatings

Credit for this contribution of IOZ coatings is given to Victor Nightingall of Australia, who first mixed zinc dust with sodium silicate to make a coating that could replace galvanizing (Figures 6.7, 6.8, and 6.9). He spent several of the last years of his life studying ways in which a chemical compound could be made to duplicate the durability of zinc ores and at the same time provide long-time corrosion protection. Nightingall's goal is well stated in one of the opening paragraphs in his United States patent on inorganic coatings.

> Protective coatings for metals surfaces must meet several requirements if they are to be considered effective. Such coatings must be continuous and impervious to corrosive elements, must be sufficiently hard to withstand the normal abrasion and mechanical shock to which metal articles are frequently subjected, and must have a high degrees of adherence to the surface of the metal article. If a coating does not adequately meet these requirements, it fails to qualify as a protective coating. This is particularly true with respect to protective coatings for ferrous metal articles where a single flaw in the coating will permit widespread corrosion and even disintegration of the ferrous article beneath the coating.[22]

A reference was made in a previous paragraph to the patent of zinc ores. Nightingall's idea was that if he could form a coating that would closely simulate the chemical characteristics of willemite or zinc silicate, then he would be able to accomplish his goal. He was a man of purpose who set out to make his approach to the problem work. The following is a quotation from his paper on dimetalization in 1940.



FIGURE 6.9: Inspection of original field test of an IOZ coating after eight years of exposure.



FIGURE 6.10: Morgan Wyalla pipeline in Australian bush country. IOZ is used as protection against grass and brush fires.



FIGURE 6.11: Morgan Wyalla pipeline crossing salt marshes near the Spencer Gulf in Australia.

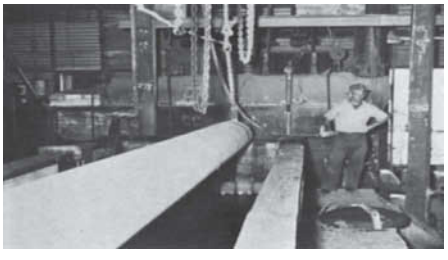


FIGURE 6.12: Pickling steel pipe for IOZ application.

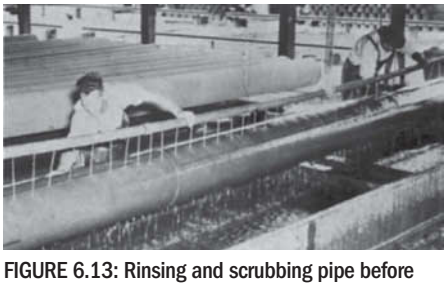


FIGURE 6.13: Rinsing and scrubbing pipe before coating application.

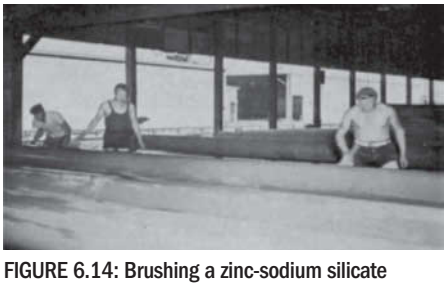


FIGURE 6.14: Brushing a zinc-sodium silicate mixture on to a pipe with 6-inch brushes.

> When the right ingredients had been determined by research in one of the zinc-iron silicate ores, it was found that a coating painted or spread on a pickled iron surface would dry in quite a short period of time, usually about half an hour; and that this coating, when dry, would have placed all the chemicals in their right proportions and molecularly closely associated together, but this was nothing more than a mechanical method of placing the requirements of the chemical reaction in position on the iron surface, and if in this stage, the article was again wetted with water, the coat would dissolve and the zinc washed away. To complete the chemical reaction, it was necessary to place the completed iron goods in an oven and heat to a temperature over and above 180 °F, the reason for this being that to complete the molecular combination of a silica, zinc, and iron, it is necessary that this should be done in the presence of a body that will bring about a release of silicic acid when a rapid silication of silica-zinc iron takes place; such a body was found to be carbon dioxide.[23]

He did this by mixing a rather alkaline sodium silicate with zinc dust and a small amount of red lead and sodium bicarbonate. This was the start of the IOZ coatings as we know them today. The billion or more square feet of surface that is presently protected by these zinc coatings were the result of the effectiveness of these early and very crude products.

The Morgan Wyalla Pipeline

The coating of the Morgan Wyalla pipeline, which is the most famous 250-mile (402-km) pipeline in inorganic silicate history, was negotiated in 1941 to 1942 and completed in 1944.(1) The negotiations included the 20-year guarantee on the coatings. This was completed with only the experience with the Woronora pipe section to rely on. The Woronora and the Morgan Wyalla pipelines were thus the beginning of the present era of IOZ coatings.

(1) The Morgan Wyalla waterline runs from a small pumping station at a point called Morgan on the Murray River in South Australia across the Australian bush to the Spencer Gulf and a town named Port Perie. Here, it runs around the Gulf to the site of a steel mill at Wyalla. The steel mill was installed as a World War II measure, and the Morgan Wyalla pipeline supplied it with water.

Today, after more than 50 years, the Morgan Wyalla pipe is still in excellent condition with its guarantee never having been challenged. In fact, a parallel line was constructed and an IOZ coating of the same type was used for its protective coating. The pipeline runs through the Australian bush country and grasslands with its large population of emus, kangaroos, and sheep (Figure 6.10). The corrosion there is not severe, but since the line is aboveground it is subject to severe brush fires. (Both the tall grass and the eucalyptus brush are explosive in the dry season.) The pipe also runs through a humid zone along the Spencer Gulf, where it is subject to salt marshes and salt beds. The crystallization of the salt, in fact, has severely spalled the concrete pipe supports. The exterior of the all-welded pipe is subjected to practically all forms of corrosive atmosphere except direct immersion in water or salt water (Figure 6.11).

The coating used was a very simple formula made at the time the pipe was coated. As for surface preparation, the pipe was pickled, freed of mill scale (Figure 6.12), scrubbed with fiber brushes to remove the black pickling deposit, and rinsed with dilute phosphoric acid (Figure 6.13).

As soon as this process was completed, the coating was mixed by weighing about 10 lb of sodium silicate and a small amount of sodium bicarbonate into a bucket. Twenty lb of zinc dust and about 2 lb of red lead followed, and the whole thing was stirred vigorously with a stick. When mixed, it was then applied to the exterior pipe surface with 6-in (152-mm) brushes (Figure 6.14). The coating was well worked onto the surface to eliminate holidays. The pipe was then moved in front of a large burner, which blew flame, hot air, and combustion products into the pipe at one end, and out the other (Figure 6.15). This procedure raised the temperature of the steel

pipe to be between 300 ° and 500 °F. The time involved amounted to approximately a half-hour per pipe.

Since the Morgan Wyalla line was designed to transport water, its interior also required coating. This was done by spinning a concrete lining on the interior of the pipe.

The pipe was supported on rubber belts, which tended to polish the zinc coating where it spun on the belt (Figure 6.16). There was apparently no loss of thickness at this point, and, after 60-plus years of exposure, there is no evidence of coating imperfection or breakdown in these areas (Figure 6.17).

The Nightingall–McKenzie conviction that the zinc coating was a permanent one was entirely borne out by the guarantee period passing in 1965. In 1970, the South Australian government duplicated the original Morgan Wyalla line, using the same type, although somewhat more refined, exterior coating. A section of the first line near Wyalla was inspected firsthand in 1972 after 28 years of service. The pipe was in perfect condition and showed no evidence of rusting, chalking, or any change due to long exposure to the atmosphere (Figures 6.17 and 6.18).

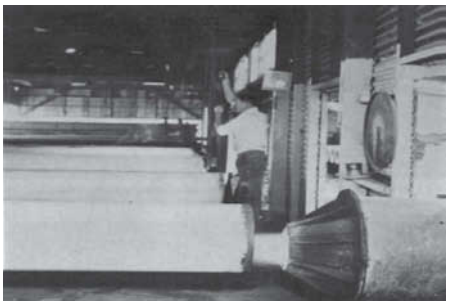


FIGURE 6.15: Stoving a coated pipe by flame and combustion products from large open burner. The coating was cured in approximately a half-hour.

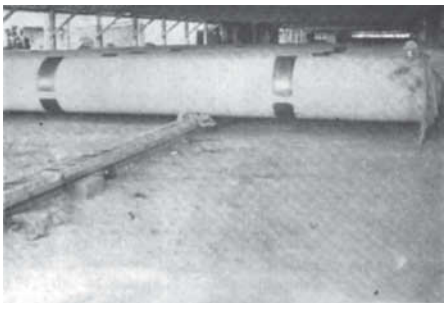


FIGURE 6.16: The burnished areas on a zinc silicate coating were caused by pipe rotation on rubber belts at about 400 rpm during the concrete lining process.

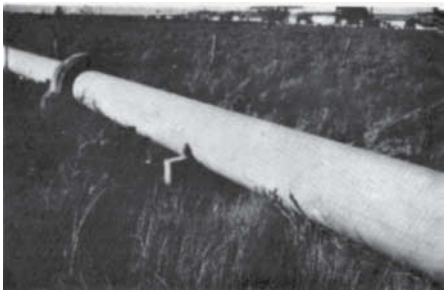


FIGURE 6.17: Morgan Wyalla pipeline in 1972 after 28 years of service. A steel mill can be seen in the background.



FIGURE 6.18: Close-up of Morgan Wyalla pipeline after 28 years of service. A longitudinal weld displays the excellent protection offered by the original, rather crude coating.

Early United States Research Work

Following the inspection of the Morgan Wyalla line in 1949, it was recommended that the dimetalization process be brought to the United States. As mentioned previously, the original Australian inorganic zinc silicate required stoving (heating to 350 °F for a half-hour or more). While stoving proved effective on several different installations, it was soon noted to have a severe limitation. It could not be applied to large structures, such as offshore drilling platforms, ships, large storage tanks, refinery structures, or even to relatively small equipment such as workboats, fishing boats, and other such items. Several years of intensive research was carried out in the United States to develop the first practical IOZ coating, which could be applied without stoving and to any existing structure by ordinary painting methods. There were a number of early attempts to apply the coating by spray and then to cure it through the use of heat. One application was on approximately one mile of bypass water piping that was coated on the exterior and heated in the same manner as the pipe had been heated in Australia. This pipe and the coating lasted for several years, but because it was handled by bulldozers and other similar equipment, both the coating and the pipe wore out after a few years of service.

Several installations also were made where portable weed burners were used to bring about a cure of the coating. While the steel temperature never did rise a great deal, the water vapor and the carbon dioxide (CO_2) in the combustion products undoubtedly provided some limited cure. Some of these applications actually lasted several years before pinpoint rust started.

The original laboratory work in the United States was an intensive study of the chemical processes involved in silicate chemistry with the object of obtaining a cure for the zinc silicate, which would take place at ambient temperatures and under the widely varying weather conditions that exist throughout the industrial and marine world. This not only included sodium silicate, but also studies of potassium silicate, lithium silicate, ethyl silicate butyl titanate, borates, phosphates, and other similar chemicals. There were many attempts to use various salt solutions as a cure. These were primarily fairly concentrated solutions in water or alcohol of magnesium chloride, zinc chloride, aluminum chloride, and some soluble phosphates. One manufacturer during this period actually recommended that the coating be washed with seawater in order to bring about a cure. These trials, including the seawater, had some basis in fact, as the following diagram suggests.

$$2Zn + NaCl + 3H_2O \rightarrow ZnOZnCl_2 + NaOH + 2H_2O \qquad (6.1)$$

The zinc oxychloride or the basic zinc chloride is insoluble, and this material, together with zinc carbonate, which would undoubtedly be part of the reaction products, could provide a sufficiently insoluble product so that the coating would hold together until further zinc silicate reactions could take place.

Actually, none of these curing procedures worked very well and only indicated that a post-cure was possible. Finally, it was determined that a solution of phosphoric acid neutralized with an amine would hydrolyze when in contact with the zinc silicate so that a slow and thorough cure was obtained. The final post-cure material was dibutylamine phosphate, and the resulting product using this phosphate cure had all of the good characteristics of the stoved IOZ, as originally conceived by Victor Nightingall. This product marked the beginning of the IOZ revolution, and it is still recognized today as the standard of the industry with an exceptionally long life under very

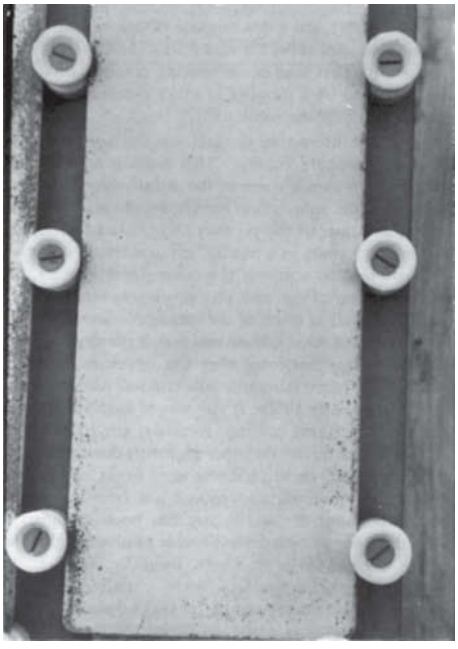


FIGURE 6.19: The original Australian formulation (stoved) shows pinpoint failure just beginning after 25 years of exposure at the 80-ft lot at Kure Beach, NC.

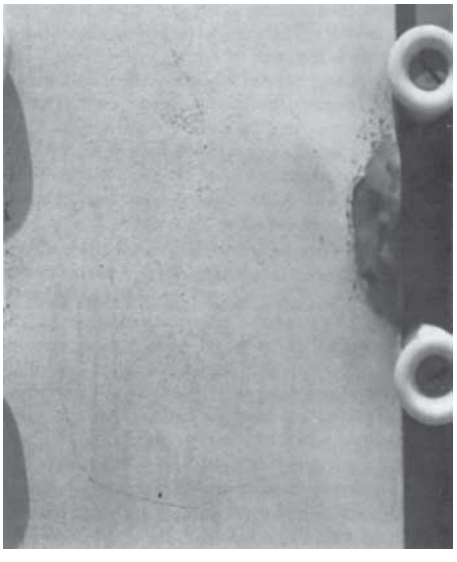


FIGURE 6.20: Post-cured IOZ after 25 years of exposure at the 80-ft lot at Kure Beach, NC. The damaged area on the right was the result of a hurricane 10 years after installation. Only limited rusting has occurred after several years of marine exposure.

difficult corrosion conditions. That the post-cured product was equivalent to the heat-cured Australian formulation is demonstrated in Figures 6.19 and 6.20.

Research on IOZ coatings has continued by many companies throughout the world. Several of the materials tried include different sodium oxide to silica ratios of sodium silicate, potassium silicate, lithium silicate, ammonium silicate, various phosphates, titanates, borates, zinc oxychlorides, magnesium oxychlorides, colloidal silica, various silica colloids in solvents, ethyl silicates, cellosolve silicates, and combinations of these.

Much of the research effort up to the present time has been directed toward simplifying the product and its application and developing products that will self-cure. Not only has the research resulted in self-curing products, but also in single-container or single-package products where the silicate and the zinc are combined in a single container ready for application in a similar manner to standard paints. One of the early materials of this sort was a dry mixture of dry sodium silicate and zinc powder to which water was added just prior to the time of application.

Another interesting product was the development of the zinc phosphate coating. This coating actually went beyond the research stage to the point where it was applied to some substantial structures. It also was self-curing, and tests of the product show it to be unaffected even after 15 years in a marine atmosphere. It again was overshadowed by some of the other developments, plus the application of the zinc phosphate was not as easy or straightforward as some of the other products.

The use of ethyl silicate was one of the developments that took place not long after the development of the original post-cured IOZ and was patented in the late 1950s or early 1960s. It also served as the basis of the first self-curing zinc coating. The ethyl silicate products have been extensively used throughout the world and have been modified by many different companies to provide products that they believe to be superior to others. Basically, however, the products are all formulated with partially hydrolyzed organic silicates and modified by various small amounts of soluble metal salts.

The effective products, which are presently on the market, are based on sodium silicate, ethyl silicate, potassium silicate, lithium silicate, and colloidal silica. The single package systems are primarily based on partially hydrolyzed ethyl silicate, as are a number of the two package products. That many of these products have proven effective is indicated in Figures 6.21 through 6.24. These test panels, exposed for eight years in a marine atmosphere, compare four different IOZ vehicles. The protection offered by each of these applied in an equivalent thickness appears to be almost equivalent after the eight-year exposure period at Kure Beach, North Carolina. Only the colloidal silicate-based product shows beginning pinpoint corrosion.

Table 6.4 shows a series of interesting combinations of silicate coatings. Many of these have proven most practical and successful. Progress has therefore been made in the last 50 years, from the original product, which was made by mixing the individual ingredients just prior to application, to the present finished IOZ products, which are in a single package and may be used essentially like paint. These zinc coatings have spurred a coating revolution, which has developed to the point where coating maintenance is minimized even under sever corrosive conditions, and even painting crews are no longer retained aboard ship since most required repair or maintenance is done in drydock. Critical industrial structures have been in service for 20 years or more without any maintenance. A review of IOZ coatings in "Coating Service Life and Maintenance Cost," CORROSION/86 paper no. 28724 shows the economic benefit for a single coat of IOZ along with other coating systems and galvanizing. IOZs, when overcoated, have increased the life of organic topcoats several times over that of the organic material alone.

Composition of Inorganic Zinc Coatings

IOZ coatings, whether composed of sodium silicate, potassium silicate, lithium silicate, colloidal silica, or hydrolyzed organic silicate, are reactive materials from almost the moment that they are applied. IOZ coatings are in a state of constant change. While the degree of change depends to a great extent on the atmosphere to which they are exposed, there is nevertheless a slow continuing reaction that takes place up until the time when the zinc in the coating has practically been consumed in protecting the steel over which it is applied. In certain cases, the surface of IOZ coatings can become inactivated by the accumulation of zinc salts on the coating surface to the point where the coating becomes an inert film rather than one that protects by CP.

Some of the typical zinc reactions are:

$$Zn\ (\text{metal}) + H_2O \rightarrow Z^{++} + 2e^-$$
(the normal corrosion reaction for zinc) (6.2)

$$Zn + 2H_2O \rightarrow Zn(OH_2) + H_2 \quad (6.3)$$

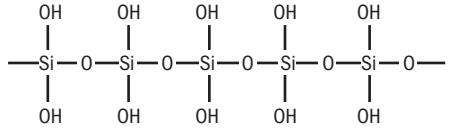
$$Zn + H_2O + CO_2 \rightarrow ZnCO_3 + H_2 \quad (6.4)$$

$$2Zn + 2NaCl + 3H_2O \rightarrow ZnOZnCl_2 + 2NaOH + H_2 \quad (6.5)$$

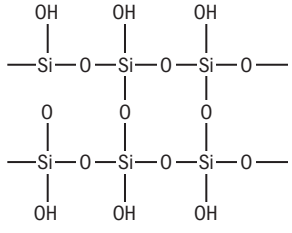
Galvanized surfaces or pure zinc reacts with the CO2 and oxygen in the air to form zinc carbonate or zinc oxide on the surface almost as soon as it comes out of the galvanizing bath. The original bright zinc surface, after a few days in the weather, becomes a dull gray, and will even, at times, accumulate a rather substantial quantity of white salts on the surface. While the initial reaction takes place rather quickly and visibly, it is entirely a surface phenomenon and only progresses at an extremely slow rate over many years, even in fairly corrosive atmospheres.

The IOZ coatings are considerably more complex than metallic zinc in their reactions to the atmosphere. They are composed of powdered metallic zinc, which is mixed into a complex silicate solution so that silicate chemistry is actually the key to the reactions, and to the cure which takes place within the IOZ coating. The chemistry of silica, which applies directly to the IOZ coatings, is explained by E.G. Rochow in a paragraph on polysilicic acids as follows.

> Since silicon forms no classical double bonds to oxygen, it is characteristic of all non-ionic compounds of silicon with oxygen to form siloxane chains and networks in which each oxygen atom is bound to two different silicon atoms. It follows that metasilicic acid and disilicic acid must be polymeric, and that it is but a short step from their structures (with a few terminal OH groups) to those of the polysilicic acids (with still fewer terminal OH groups). Thus the polymeric H_2SiO_3 may be represented as:



> and that cross-linking with neighboring chains will correspond to condensed or polysilicic acid with –OH content:



> The cross-linking can be occasional (in the lower polysilicic acids), frequent (in the more highly condensed acids) or even complete (in SiO_2) itself. Since Si—OH groups are inherently acidic, as is shown so clearly in the organosilanols (all of which are more acidic than their carbinol counterparts), all condensed HO-bearing siloxane structures may be expected to be weakly acidic in relation to proportion of Si—OH groups they contain.
>
> In the more condensed polysilicic acids it is quite possible that the interior of each small particle is nearly completely cross-linked with interlocking Si—O—Si chains, but still the surface oxygen atoms necessarily are unsaturated and will accept hydrogen, so that the outside of the particle must still be covered with weakly acidic Si—OH groups. In this sense there is no distinction between highly condensed polysilicic acids and colloidal silica.[25]

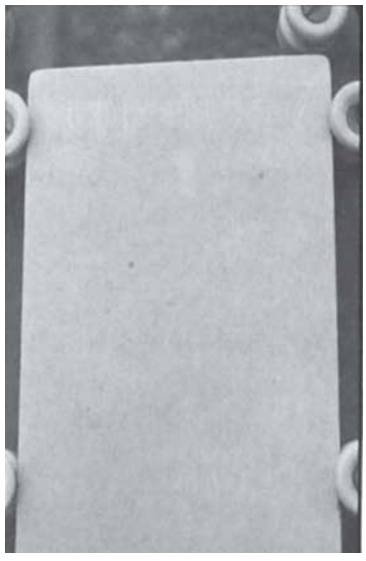


FIGURE 6.21: Post-cured sodium silicate zinc coating after eight years of exposure in a marine atmosphere.

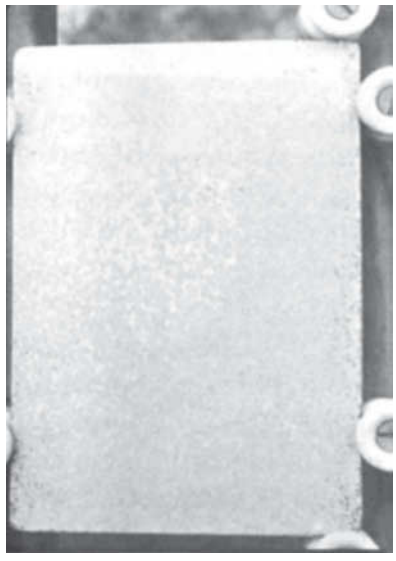


FIGURE 6.22: IOZ coating based on colloidal silica after eight years of exposure in a marine atmosphere.



FIGURE 6.23: Self-cured water-based IOZ silicate coating after eight years of exposure in a marine atmosphere.

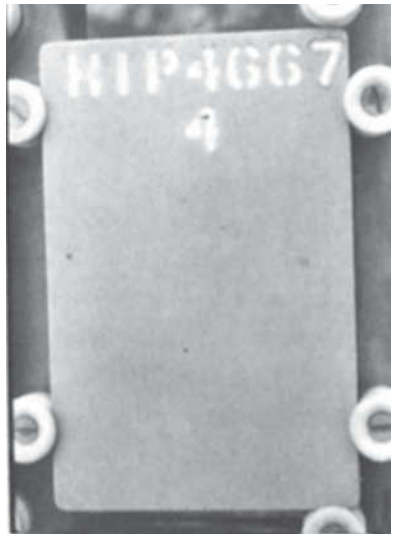


FIGURE 6.24: Ethyl silicate based IOZ coating after eight years of exposure in a marine atmosphere.

With this chemistry in mind, it becomes obvious that in spite of the different starting point (e.g., sodium silicate, potassium silicate, lithium silicate, ethyl silicate, or colloidal silica), the ultimate reaction product as it exists on the steel surface is quite similar for each one of the coatings. Each vehicle, water soluble or organic silicate or colloidal silica, reacts or hydrolyses to form a polymer of silicic acid, and when zinc is added to the system, a silica oxygen zinc polymer is created. This combination is very insoluble and forms the strong matrix surrounding the zinc powder to form the coating. Since the silicic acid is a mild acid, and since it is known that iron ions will be formed when iron is exposed to water or moisture, it is reasonable to assume that in addition to the zinc reacting with the silicic acid, iron ions from the sandblasted steel surface also will react with the silicic acid to form an insoluble reaction product at the interface of the metal and the silicate coating. This provides the basis for the adhesion of the coatings as well as for their excellent resistance to undercutting by corrosion.

Reactions of Different Silicate Types

The actual reaction, starting from the time the coating is applied to the surface, is somewhat different for each type of silicate, even though the end product appears to be similar for each of the various zinc silicates. The exception is the post-cured coating.

TABLE 6.4: Typical Examples of Various Zinc-Rich Coating Formulations

Type	Vehicle	Pigment	Weight Ratio Pigment/Vehicle
	Water-Based Inorganic Zinc-Rich Coatings		
Post-Cured			
A	3.2 ratio sodium silicate; 22% SiO_2; sodium dichromate	Zinc dust + red lead	2.8
B	3.2 ratio sodium silicate; 24% SiO_2; potassium dichromate	Zinc dust	3.2
Self-Cure Potassium Silicate			
A	2.9 ratio potassium silicate; 14% SiO_2; manganese dioxide; sodium dichromate	Zinc dust	2.9
B	2.4 ratio potassium silicate; 9.25% SiO_2; acrylic emulsion	Zinc dust	2.0
C	2.8 ratio potassium silicate; 18% SiO_2; quaternary ammonium hydroxide; soluble amine; carbon black	Zinc dust + red lead	2.8
D	3.2 ratio potassium silicate; 15% SiO_2; quaternary ammonium hydroxide; soluble amine; carbon black Self-Cure Lithium Silicate	Zinc dust	2.5
	Lithium-sodium silicate; 19% SiO_2;	Zinc dust + iron oxide	3.3
	Sodium dichromate		
Self-Cure Silica Sol			
	Silica sol; 32% SiO_2; soluble amine potassium dichromate; carbon black	Zinc dust + red lead	4.1
Self-Cure Quaternary Ammonium Silicate			
A	Quaternary ammonium silicate; 32% SiO_2	Zinc dust	2.5
B	Quaternary ammonium silicate; sodium silicate; 20% SiO_2	Zinc dust	2.5
	Solvent-Based Inorganic Zinc-Rich Coatings		
Self-Cure			
A	Partly hydrolyzed ethyl silicate; 10% SiO_2; clay fillers	Zinc dust	2.2
B	Partly hydrolyzed ethyl silicate; 22% SiO_2	Zinc dust	3.4
C	Basic hydrolyzed ethyl silicate; 15% SiO_2; clay fillers	Zinc dust + iron oxide	2.4
D	Polyol-Alkyl Silicate; 20% SiO_2	Zinc dust	2.2

Source: Steel Structures Painting Manual, Vol. 1, Chapter 5, Section 2, "Zinc-Rich Primers" (Pittsburgh, PA: Steel Structures Painting Council, 1966).

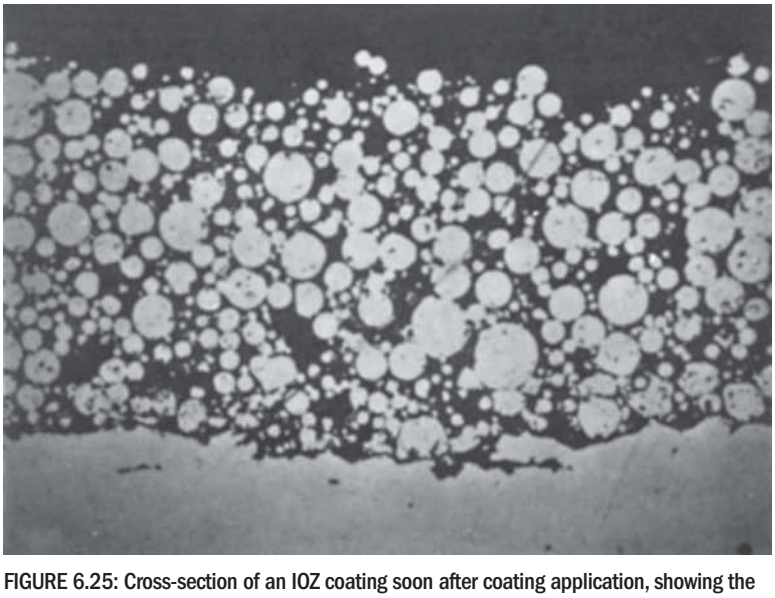


FIGURE 6.25: Cross-section of an IOZ coating soon after coating application, showing the character of the sandblasted surface (bottom).

Coatings based on sodium or potassium silicate or ethyl silicate or colloidal silica (since the latter is usually stabilized with sodium or potassium hydroxide) react as follows. The initial reaction is that of concentration of the ingredients as the water evaporates from the coating. This brings the zinc and the silica compounds into close relationship and provides for the initial deposition of the coating on the surface. This initial reaction is an important one since this is the time at which the coating thoroughly wets the metal surface and is in intimate contact with the steel. Should there be organic contamination on the surface, this wetting does not take place and the coating will have no adherence, beginning at the initial deposition of the coating.

The second reaction to occur takes place shortly after the coating deposition. This is the initial insolubilization of the coating caused by the reaction of zinc ions with the silicic acid to form the initial zinc silicate. Only a few zinc ions are necessary for the silicic acid to become insoluble, even though there are a number of other acid groups on the polymer that can react at a later time. The coating is now a solid insoluble coating on the metal surface. Even so, it is not completely reacted.

The third stage of the reaction is one that occurs over a period of time, which can be just a few hours, days, weeks, or months to come to completion, depending on the type of silicate and the ratio of the silicate to the alkaline metal. The third reaction is the continuing activity of carbonic acid, formed by CO_2 and moisture in the air, acting on and within the coating to complete the formation of the zinc silicate matrix. The coating, as originally formed on the surface, is shown in Figure 6.25.

The action, which forms the zinc silicate matrix within the coating and surrounding the zinc particles, does not react all of the zinc within the coating. Zinc ions are formed from the surface of the zinc particles. These diffuse into the silicate gel forming the insoluble matrix; however, there is also a layer of zinc silicate surrounding each of the zinc particles. In many ways, this is the way cement reacts in concrete. The water hydrates the cement particle primarily on the surface and forms a matrix between and around the sand and rock particles in concrete. The center of the cement particle remains unhydrated until the concrete is cured for a month or more. Likewise, most of the zinc is left as metallic zinc within the coating (Figure 6.26).

This does not mean that the original does not contain pores or is porous, as evidenced by the problems involved organic coatings over newly applied IOZ. Air reactions (e.g., the reaction of CO_2, water, and carbonic acid continue, forming zinc carbonate and zinc hydroxide within the coating and within the porous areas within the coating). This is the reaction that decreases the porosity over a period of time and makes the final coating into a continuous film (Figure 6.27).

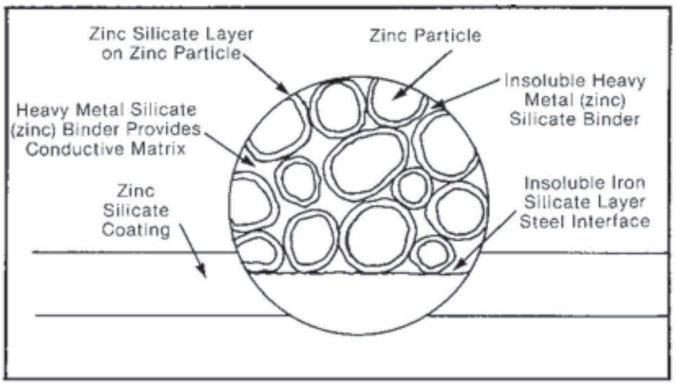


FIGURE 6.26: The zinc silicate matrix within the IOZ coating and surrounding the zinc particles does not use all of the zinc within the coating.

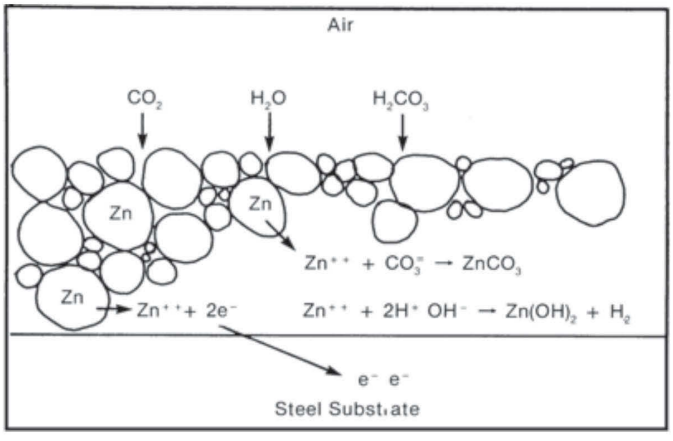


FIGURE 6.27: Continuing reaction of CO_2 and H_2O within the IOZ coating. These reactions provide the mechanism for continued corrosion protection by cathodic protection, as well as filling the coating voids with the zinc reaction products.

Reactions in the Formulation of Various Inorganic Zinc Coatings

There are essentially four different general chemical reactions that take place in the formation of various zinc coatings. The first, the reactions of the post-cured IOZs, are as follows.

1. The first step is primarily the dehydration process in which the water, which is the basic solvent for the silicate, evaporates from the clean steel surface, leaving the zinc and the alkaline silicate on the surface as a coating. At this point, when the coating is free of water, it is very hard and metallic. Scraping with a coin merely polishes the zinc in the coating. It is not, however, cured to water insolubility.
2. Once the initial drying process has taken place, a solution of an acid amine phosphate salt is sprayed or brushed over the surface of the coating in order to thoroughly wet out the surface with the curing compound.
3. The next reaction consists of the acid salt gradually neutralizing the sodium in the sodium silicate solution and creating a mildly acidic condition on and within the coating. This neutralization of the sodium opens up the reactive silica groups to which the sodium was attached.
4. This neutralization of the sodium opens up the reactive silica groups to which the sodium was attached.
5. The addition of the acidic phosphate solution on the surface of the zinc coating ionizes the zinc in the coating, as well as the lead oxide, which is mixed with it. As this takes place, there occurs a rapid reaction between the active silica groups and the lead and zinc, which insolubilizes the silica matrix and forms some zinc and lead silicate polymers from the basic molecular structure of the silicate.
6. The acid phosphate also reacts with the ionized zinc and lead to form very insoluble zinc and lead phosphates. This reaction forms the zinc and lead phosphates within the silicate matrix. At this point, the coating has become insoluble to water, and unaffected by exposure to weather.
7. Following the application and reaction of the curing agent, most of the remaining soluble salts on the surface are removed with clean water. This reduces the sodium phosphate and the amine salts so that the majority of all soluble materials are removed from the coating. The coating at this point is dense and non-porous, as well as being insoluble in water and unaffected by marine atmospheres. At this stage, it can be readily overcoated with organic coatings.
8. While insolubility has been achieved, along with resistance to weathering and marine activity, the curing of the coating continues. The complete cure comes gradually over a period of many months with the reaction of CO_2 and water on the coating further reacting the silica matrix with the zinc ions, which are formed by the carbonic acid. This reaction is well known and increases the toughness, hardness, and adhesion of the coating over a period of many months or years.

Figure 6.28 traces the initial solution through the initial cure and on to the final carbon dioxide cure.

TABLE 6.5: Curing Rates of Potassium vs. Lithium Silicates

Type	Temperature Fahrenheit	Relative Humidity	Time to Water Insoluble
Potassium Silicate	59	90	6.5 hours
Potassium Silicate	77	25	2.5 hours
Potassium Silicate	104	40	6.5 hours
Lithium Silicate	77	25	1.67 hours
Lithium Silicate	122	50	17 minutes

Source: "Designing VOC Compliant Silicates," CORROSION/90, paper no. 477 (Houston, TX: NACE, 1990).

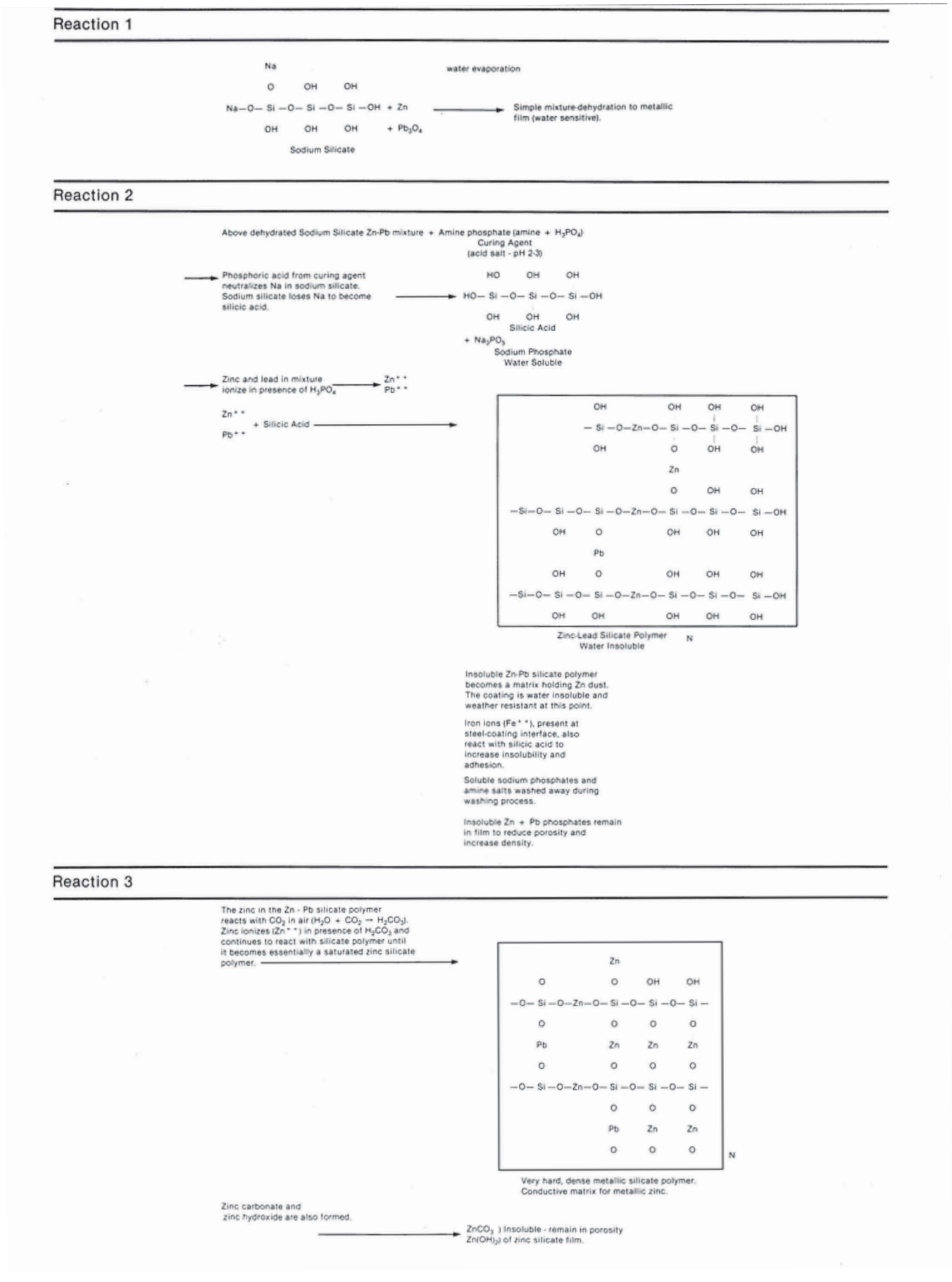


FIGURE 6.28: Model of the probable internal reactions taking place during the curing of a post-cured IOZ coating.

The second type of coating, the water-based sodium, lithium, or potassium silicate self-curing coating, generally reacts as follows. First, the alkali silicates become concentrated through the evaporation of the water. This provides the initial drying and primary deposition of the coating. In this case, the alkali silicate is much less alkaline than might be the case in the post-cure coating, so that more of the silicate is in the form of a polysilicate acid. This allows for faster reaction of the zinc into the coating and forms the basis for the self-cure. Other metal ions also may be included to speed up this self-curing process. The use of lithium silicate significantly speeds curing to water insolubility as compared to potassium silicate as shown in Table 6.5.[26]

Water based potassium silicate IOZ formulae with silicate to alkaline metal ratios in excess of 3.9:1 pigmented with inorganic zinc pigment meeting the requirements of ASTM D52027 Type III are known to cure in as little as 2 hours at ambient temperatures of at least 70 °F (21 °C) and relative humidity in excess of 50%.

During the drying phase, the air temperature, relative humidity, and air movement are critical factors in achieving water evaporation. In one case, evaporation occurs slowly into the air, in another case, not enough water arrives at the surface to be evaporated.

A typical water-based IOZ coating may contain 3 to 5 lb or more of water per gallon of coating. A gallon of coating covers 300 to 400 ft^2 at 3 mils (75 µm) dry film thickness (DFT). Initial drying time at 70 °F and 50% relative humidity is 6 minutes or less, which equates to a water evaporative rate of 0.16 lb/ft^2 per hour. Drying time vs. evaporative rate would be as shown in Table 6.6.[5]

If an arbitrary but safe minimum evaporation rate to achieve satisfactory film formation is selected at 0.02 lb/ft^2 per hour, the maximum relative humidity vs. surface temperature and air velocity would be as shown in Table 6.7.[28] Air movement/ventilation is significant for initial drying since most normal atmospheric environmental conditions have a relative humidity above 40% or 50% during the day.

Although initial drying is important, re-wetting by dew condensation or rain before sufficient insolubilization of the binder can also be detrimental to the coating. Spot water condensation on the coating can result in spot discoloration. General condensation on the coating surface with rundown can result in binder leaching and a subsequent powdery coating. Rain can result in washing and removal of the coating. The magnitude of damage to the coating is dependent on the degree of insolubilization attained when water contact occurs, the amount of water, and the contact time.

TABLE 6.6: Drying Time Vs. Evaporative Rates

Water-Based Inorganic Zinc			
Evaporative	Dry Time (minutes)		
Rate (lb/ft2 h)	3mils	6 mils	9 mils
0.16	6	12	18
0.10	10	29	30
0.06	17	34	51
0.02	50	100	150
0.01	100	200	300
0.001	1,000	2,000	3,000

Source: "Designing VOC-Compliant Silicates," CORROSION/90, paper no. 477 (Houston, TX: NACE, 1990).

TABLE 6.7: Minimum Safe Evaporation Rates to Achieve Satisfactory Film Formation of Water Based Inorganic Zinc Coatings

	Maximum Relative Humidity %					
Air Velocity	@ Surface Temperature (°F)					
(mils/h)	40	50	60	70	80	90
0	*	12	36	55	68	76
3	33	53	70	78	83	87
5	50	65	77	82	87	90

*Evaporation rate below 0.02.

Dehumidification in tank lining work has become an accepted practice. Most all railroad hopper car coating work is done under cover with the ability for both temperature and some ventilation control. Many steel fabrication shops have covered application areas and some temperature control available. Many shipbuilding operations have facilities under cover for preparing and coating block sections with some temperature control and ventilation.

The second reaction is the insolubilization of the silicate matrix through a reaction with zinc ions from the surface of zinc particles, and probably some reaction with iron ions from the sandblasted steel surface. As the zinc reacts into the silicate or silicic acid polymer, the coating becomes insoluble, forming a silica-oxygen-zinc polymer. This is the basis of the matrix that holds the zinc powder in place (Figure 6.25).

The third reaction that takes place in the coating is the one that occurs over a long period of time, making it a matter of days, months, or years before the final saturation of the silicate polymer with zinc occurs. This continuing reaction is the result of humidity from the air, condensation of moisture on the surface, or rain, which creates a very mild acidic condition and continues to reduce the alkali and aids in the ionization of the zinc so that it continues to react with the silicate acid polymer. This reaction gradually proceeds through the coating to the interface of the steel, increasing the adhesion of the coating to the steel surface and making the coating extremely dense and metal-like. Over a period of time, zinc carbonate and zinc hydroxide are formed on and within the coating (as was shown in Figure 6.27) to decrease any porosity that might exist and to form the film into a continuous coating.

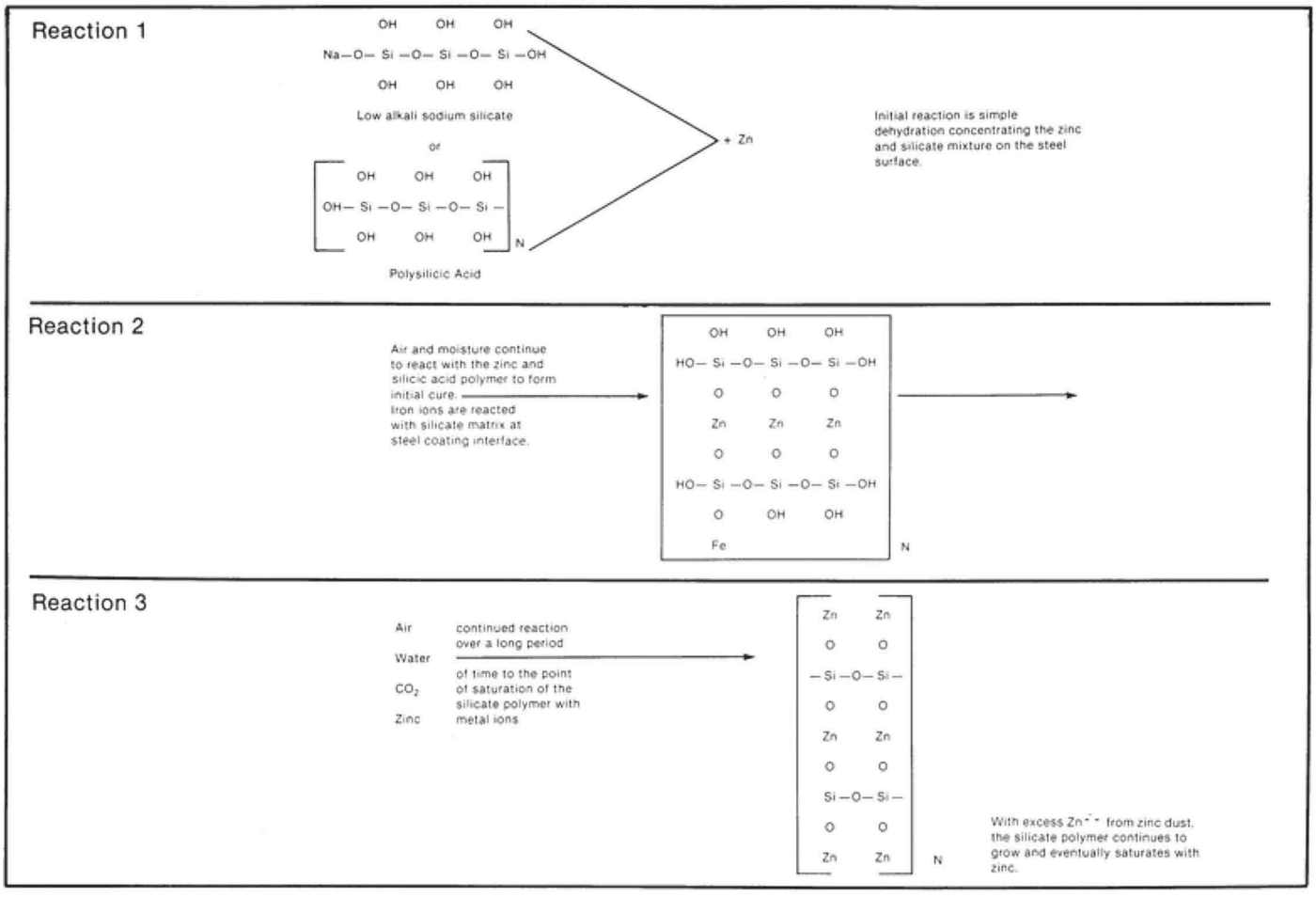


FIGURE 6.29: Model of the probable internal reactions of a water-based self-cure of a colloidal silica self-cure IOZ coating.

The third type of inorganic coatings is the organic silicate type. The general reactions for formation of the coating are similar to the water-based self-cure products. There is, however, a sufficient difference to make it worthy of description. The first step consists of applying the hydrolyzed ethyl silicates and zinc mixture to a sandblasted steel surface. The initial reaction involves the evaporation of the solvent in the organic silicate vehicle, leaving the organic silicate mixture on the metal surface.

In the second reaction, which is the one that takes place during application or shortly thereafter, the moisture from the air continues to hydrolyze the ethyl silicate to silicic acid. This then reacts with the zinc, and possibly other metal ions that have been added to the mixture, to give the coating its initial insolubility. The organic silicate coatings are noted for their rapid resistance to water, which is due to both the precipitation of the ethyl silicate zinc mixture on the surface, and the rather rapid reaction that takes place in a humid atmosphere, as outlined in reaction 2.

The third reaction (the long-time curing mechanism) is similar to the reactions that take place with the other IOZ coatings. The polysilicic acid further polymerizes and further reacts with zinc and the other metal ions that may be incorporated in the formula. These other metal ions are incorporated as very small quantities primarily for initial cure, although some (e.g., lead) tend to improve the silicate film over a period of time (Figure 6.29).

The fourth type of IOZ coating (i.e., the ones made with colloidal silica) reacts similarly to the second type of IOZ coating already described. In the case of colloidal silica, it is primarily the silicic acid polymer, which is stabilized with an alkali such as sodium or potassium hydroxide. The primary different lies with the greater concentration of polysilicic acid. As Rochow stated, "There is no distinction between highly condensed polysilicic acids and colloidal silica."25 The reactions are therefore essentially the same for both the sodium or potassium silicate self-cure and the colloidal silica self-cure (Figure 6.30).

One additional type of zinc silicate has been used extensively and reacts in a somewhat different fashion due to the alkali silicate from which it is made. This is the lithium silicate-based coating. Reaction 1 is similar to the other alkali silicate coatings. Reaction 2 is different in that the lithium hydroxides in the film react with carbon dioxide, readily forming lithium carbonate. This is a very insoluble product and becomes part of the inorganic film. As the lithium carbonate is formed, acid groups are created on the silica polymer, which react with the zinc and any other heavy metal ions present. The lithium zinc silicate coating is somewhat less porous than those coatings based on sodium, potassium, or ammonium silicate where the alkali reaction products are soluble. Lithium carbonate, which is very insoluble, is then rapidly formed. This aids in reducing porosity. Reaction 3 is similar to those of the silicate-type coatings previously described.

Additives Used in Inorganic Zinc Coatings

There are a number of vehicle additives that are incorporated by various manufacturers to improve their inorganic zinc coatings in one way or another. Dean Berger, in Current Technology Review—Zinc Rich Coatings,28 describes a number of these additives.

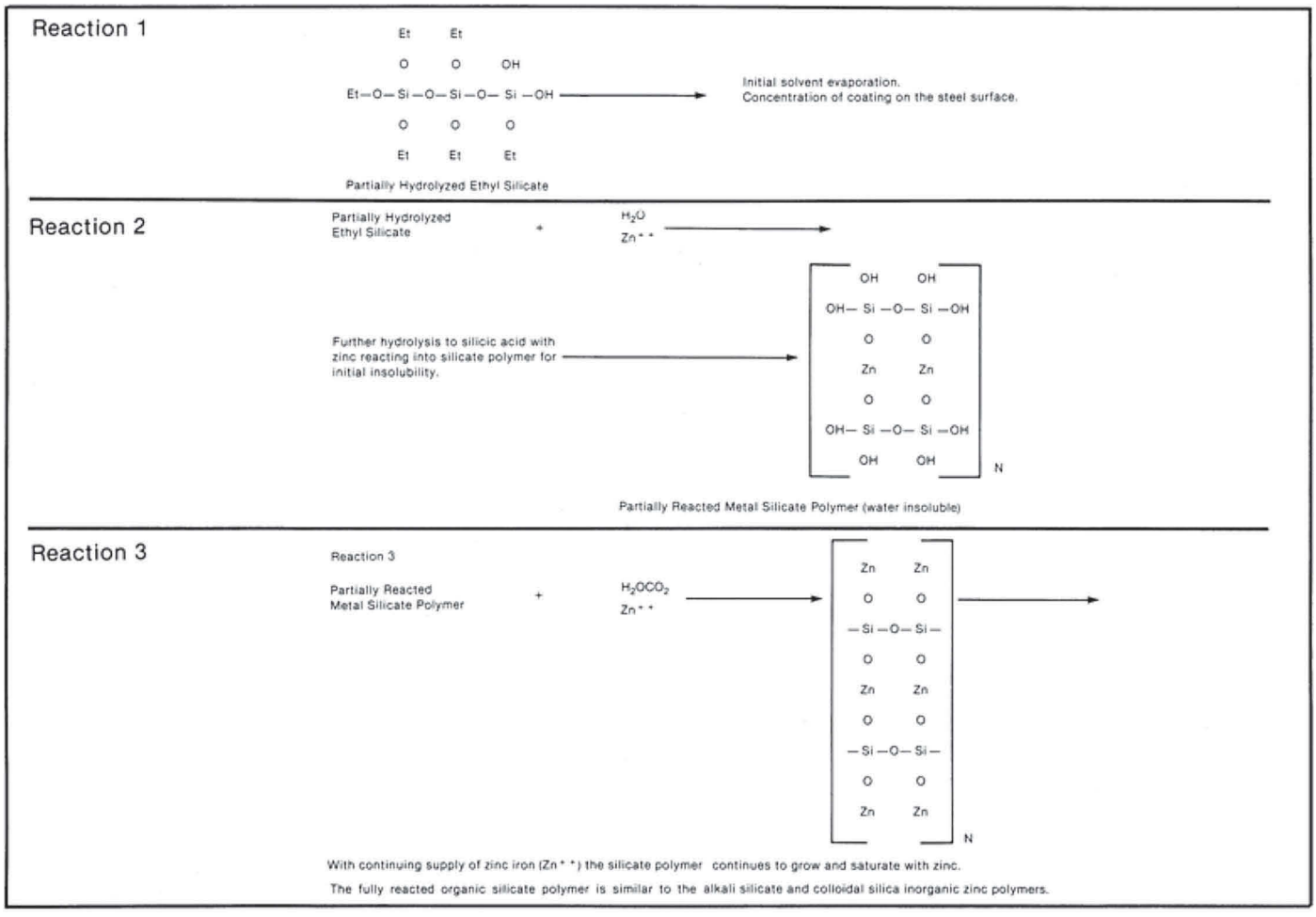


FIGURE 6.30: Model of the probable chemical reactions within an organic silicate zinc coating.

In U.S. Patent 3,392,036, McLeod offers several vehicle modifications using trimethyl borate with a siloxane. It can be shown that these materials will react with partially hydrolyzed ethyl silicate in the presence of moisture to form a complex borosilicate. A boron content of five to 20 percent of the silica is useful. The ethyl dimethylsiloxane is used to help prevent mud cracking of the applied zinc-rich primer.

The first polyvinyl butyral-modified ethyl silicate zinc-rich paint is described by Robert A. Rucker of Zinclock in U.S. Patent 3,392,130. This product offers extremely good flexibility of the final film. In addition, it is easy to apply and to top coat. It will not, however, withstand high temperatures. D. P. Boaz (Standard Paint) also used this technology plus borates and silanes, in U.S. Patent 3,730,746. Combinations of cellosolve silicates with borates, glycols and silanes are mentioned as vehicles for zinc paints in Patent 2,147,299 to Anderson and 2,147,804 and 2,147,865 to Gordon McLeod and in South Africa, Patent 71/3993 to Nils Trulsson.

Aaron Oken of DuPont, in U.S. Patent 2,649,307 described a borosilicate vehicle for zinc-rich paint. Dean Jarboe of Plaskem described a tri-methyl borate and aluminum oxide modified zinc- rich paint in U.S. Patent 3,412,063.

The use of two ethylhexoic acid and monoethanolamine was described by Blake F. Mago in U.S. Patent 3,634,109 to Union Carbide. The amine salt is used to partially hydrolyze the ethyl silicate. W. R. Keithler of Plaskem described the use of di-2-ethyl-hexylamine in U.S. Patent 3,202,517 and described the first zinc- rich based on an amine hydrolysis.

Various colored zinc-rich paints are described by Robinson in British Patent 1,205,394. Napko and Carboline also introduced zinc-rich paints of various colors. One-coat protection was offered in earth tone colors and a top coating was not required. Corrosion resistance was not as good as originally thought and their use has largely disappeared in the United States.[28]

Pigmentation

Zinc Nitride Formation

There is also a rather obscure chemical reaction that takes place during the formation of zinc dust, which may also be a factor in the insolubilization and the curing of IOZ dust coatings. This reaction begins during the formation of the zinc dust. Zinc dust is formed by the distillation of liquid zinc and the condensation of zinc vapor into a large chamber. The temperature of the zinc vapor and the temperature of the chamber regulates the size of the zinc particles.

There are three principal materials from which zinc dust is manufactured. These are zinc dross (which is the waste [surface skimmings] from the galvanizing process), scrap die castings (primarily from the automotive industry), or prime zinc ingots. The first two represent the most common sources of zinc dust. Since the dust is formed by the distillation of the zinc, very few contaminants carry over into the dust itself. The reaction product under discussion, however, may come from two sources: (1) the ammonium chloride used as a fluxing agent on the top of galvanizing baths, and (2) nitrogen from the air. At the temperature of the distillation of the zinc, there is some zinc nitride formed on the surface of the condensing particles. When subject to moisture, this little-known compound can hydrolyze to zinc hydroxide and ammonia.

That this compound exists and breaks down into zinc hydroxide and ammonia under ambient temperatures and humid conditions has been verified. For instance, zinc dust was stored for several weeks or months at temperatures from 25 to 35 °C (750 to 95 °F) in a

high-humidity area. During this storage process, ammonium gas developed in the zinc containers, creating enough pressure to actually bulge the tops of the metal containers. When they were opened the emerging strong ammonia odor was unmistakable. Also, the reaction of zinc nitride with moisture is the reason for the use of the desiccating packages of silica gel, which are found in almost all containers of zinc dust used for zinc coatings. Zinc nitride is very reactive and has been responsible for the instability of liquid zinc silicate coatings shortly after they are mixed and prior to application. When ammonia is found in a zinc container and the zinc is mixed with the silicate liquid, the solution becomes grainy and therefore, unusable. This reaction is prevented by the desiccant in the can, which absorbs any moisture that may enter the can due to the high humidity on the outside of the can vs. the zero humidity in the can's interior. Moisture is actually pulled through the mechanical joint on the lid of the can.

$$Zn_2N_3 + 6H_2O \rightarrow 3Zn(OH)_2 + + 2NH_3 \quad (6.6)$$

This nitride water hydrolysis also may play a role in the original insolubulizing reactions of the coatings, and possibly in the continuing reactions that take place with time. The zinc nitride hydrolyses and zinc ions are formed, which can react with the silicate molecule, helping to polymerize it and causing it to become insoluble.

Grades of Zinc Dust

Zinc thus enters into a number of different reactions in the IOZ coatings. Some of these reactions, such as the absorption of moisture and the ionization of zinc in the various vehicles, is due to the fine particle size of the zinc that is used in the coatings. Actually, there are several grades of zinc dust that are used for pigments. For so-called regular coating grade, which has the largest average particle size, the zinc particles range from approximately 6 to 10 η, with a median size of 7.6 η; an intermediate grade, which is used in some formulations has a median particle size of 6.3 η; and a superfine grade, which has a median particle size of 4.5 η and a range of 2 to 5 η. There is yet another grade, used primarily in the automotive industry for the zinc coating of critical automotive parts. This has a median particle size of 5.5 and a range from 4.5 to 6.5 η. This grade, however, is not particularly important in the coating of large structures, pipes, tank exteriors, and so on, for corrosion protection. There is one additional grade of zinc dust developed for high solids solvent based inorganic zinc coatings "course grade" having an average particle size range of 7 to 12 η.

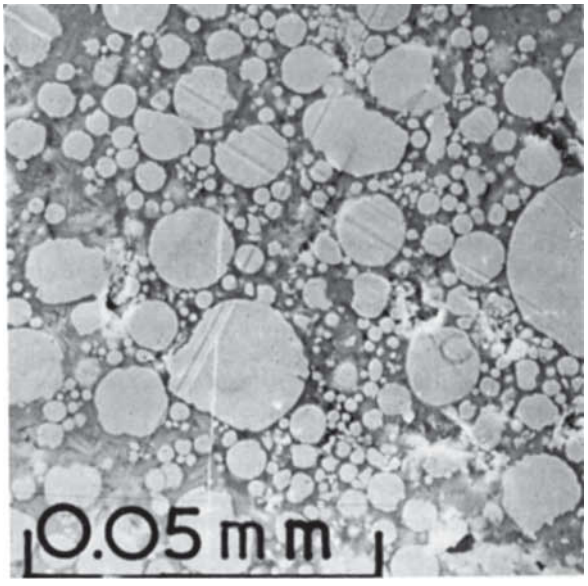


FIGURE 6.31: Cross-section of an IOZ coating showing typical packing characteristics of the zinc particles.

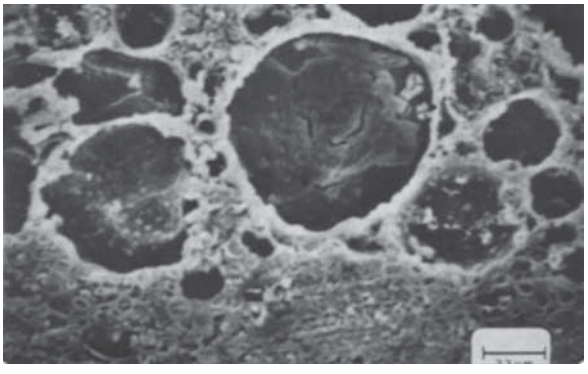


FIGURE 6.32: SEM photograph of a cross section of a zinc silicate coating showing silicate matrix and the zinc reaction products surrounding the zinc particles.

The regular coating grade is used in most of the water-based inorganic coatings and many of the ethyl silicate-base two-package systems. The superfine grade is primarily used in the single packaged systems and primarily for improved suspension of the zinc dust in the vehicle. Since these materials are prepackaged and must remain in the container for considerable periods of time, the settling of the zinc dust is extremely important. The finer grades improve this property.

Two grades of zinc dust, the regular and the superfine grade, are also often mixed in order to obtain a more uniform gradation of particle size throughout the coating and to minimize porosity by the packing of the zinc particles. This process is probably best demonstrated by relating the zinc dust coating to concrete. In concrete, the aggregate is graded in such a way that the fine sand particles pack in between the larger rock particles to form a concrete with a maximum density. The same packing princi- ple is applied to the use of zinc dust in zinc dust coatings. The size of the zinc particles also makes a difference in the surface area of metallic zinc subject to chemical reactions, with, as might be expected, the finer particle size having some increased reactivity over the larger particle size. Low-lead (less than 0.01) grades of superfine zinc with particle size from 2.5-4.0 η are available to meet government restrictions on lead content. These are listed as ASTM D520 Types 1, 2 & 3.

The packing characteristics of zinc dust are illustrated in Figure 6.31, which is a photomicrograph of a cross section of an IOZ film and demonstrates the typical distribution of the particles in the coating. The various sizes of zinc dust are well distributed throughout the film, forming a dense structure of the zinc aggregate. The area between the zinc particles is filled with the silicate matrix and, as it reacts with the zinc ions, it becomes a very strong binder, both to the metal surface and in and around the zinc particles. This is shown in Figure 6.32 where the area between the zinc particles and surrounding zinc particles is filled with the reactive zinc silicate.

Manufacture of Zinc Dust

The manufacturer of zinc dust determines the sizes of the zinc particles and thus the various grades. As was previously stated, zinc dust is manufactured according to the distillation process. This consists of melting the metallic zinc in a retort. The zinc is heated to the distillation point where the zinc metal evaporates and forms a zinc gas. The metallic gas is then transferred from the retort into a relatively large metal condenser where the zinc gas cools and is precipitated as a fine zinc dust.

The control of this process is critical in the determination of various particle sizes. The controllable variables consist of the temperature of the gas, the temperature within the condenser, and the speed by which the gas is propelled from the retort into the condenser. This; of course is determined by the zinc gas pressure. As might be expected, oxidation to zinc oxide is not desirable. Therefore, the retort and the condenser must be kept as free of oxygen as possible in order to precipitate the zinc metal without a large content of zinc oxide on the surface. The control of the process determines the particle size, the particle size distribution, and the content of zinc oxide on the surface of the particles.

Pigments Other Than Zinc

There are a number of other pigments, in addition to zinc dust, which may be incorporated into any given formulation for an inorganic zinc coating. Lead oxide, or red lead, was one of the first materials used in the formulation for the original Nightingall work in Australia. The red lead not only reacted into the final silicate matrix as lead silicate, but also apparently helped to regulate the speed of the reaction once the silicate and the zinc dust were mixed. The addition of the lead oxide appears to increase the hardness and toughness of the inorganic film, as well as improve its resistance. The addition of the red lead also slightly changes the color of the zinc coating to a light reddish-gray, which aids in visibility when it is applied over a sandblasted surface.

Iron oxide is incorporated in some IOZ coatings. In this case, it is primarily used as a secondary, nonreactive pigment in order to change the color of the coating to one that is slightly reddish, which again differentiates it from the color of the sandblasted steel during application. Yellow dyes are also used to change the color of the coating as it is applied to one that is slightly green, which also differentiates it from the color of the sandblasted steel during application. Both colors are fugitive, in that they gradually degrade leaving the original zinc color.

Some chromates are added to the IOZ formulations primarily to control the speed of reaction of the zinc dust with the vehicle, such as preventing spot rusting during initial drying and curing of water-based IOZ under high-humidity conditions. Chromates are also corrosion inhibitors and, as such, may in some small way aid the zinc in providing a corrosion-resistant coating. Chromates have generally been removed from the latest water-based IOZ products because of government restrictions. Barytes has been used as an inert pigment, both to reduce the cost of the zinc powder and to decrease the porosity of the applied film, thus decreasing the blister formation in the organic topcoats.

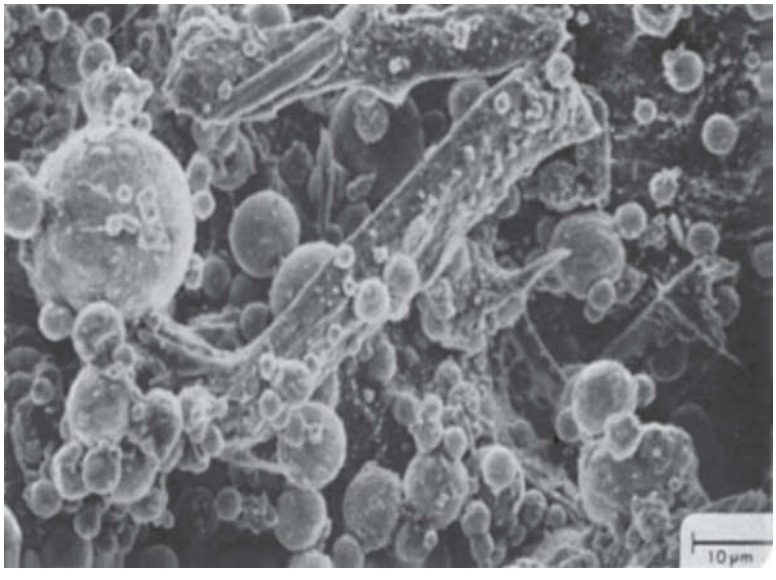


FIGURE 6.33: SEM photograph of reinforcing pigments in a solvent-based IOZ film, showing the size relationship of the reinforcing pigments to the zinc dust.

A number of various color pigments have been added to IOZ coatings in order to change not only the color from the light gray of the zinc, but to attempt to add some decorative character to the coating itself. Because of the large quantity of zinc dust used in an IOZ coating, changing the color with a small amount of pigment is difficult, since the zinc itself masks the other color to a great degree. Second, when sufficient amounts of these color pigments are added so that a substantial color change can be made, the amount of zinc in the coating is diluted and the corrosion-resistant characteristics of the coating itself tend to be reduced.

Some of the other chemical reactions that take place in the coating also reduce the effectiveness of color pigments. Formation of zinc oxide and zinc hydroxide on the surface of the coating over a period of time tends to reduce the effectiveness of the color pigments. The primary color pigments that are effective are based on inorganic oxides, such as iron and chrome oxide. Some black pigments have been added in order to change the color of the basic zinc gray.

There are quite a number of inert pigments that are added to the zinc dust in order to provide reinforcing for the coating. This tends to increase the coating toughness and to reduce mud cracking where the coatings are applied at too great a thickness. The materials first used were ascicular type pigments, such as asbestine or very fine asbestos fiber, but the ban on asbestos as a health hazard has eliminated this film forming additive. Short glass filaments also have been tried. Mica is frequently used for this purpose. White Portland cement, while not totally inert, has been used successfully (mostly in epoxy modified formulae), again for cost reduction and film formation with reduced porosities. Many of the commercial formulations contain these and other reinforcing material, such as proprietary mineral fibers (Figure 6.33).

Another inert pigment, which has been widely acclaimed for use with IOZ coatings, is di-iron phosphide. It is claimed that 30% or more of the di-iron phosphide can be used as a substitute for zinc in zinc coatings, and a number of commercial products contain some of this material. There have been some good test results in the area of 30% substitution. However, there is considerable controversy as to the full effectiveness of the substituted material, as compared with non-substituted zinc coatings.

There is one area, which appears to be well documented, and this is the property of weldability. The di-iron phosphide is a conductor, and many of the zinc coatings, both inorganic and organic, where weld-through characteristics are a requirement, contain the di-iron phosphide pigment. This has been particularly true in the zinc-rich coatings used by the automotive industry where spot welding is of vital importance. Norbert Intorpe described some of the automotive uses of zinc-containing di-iron phosphide in a paper entitled "Enhanced Zinc-Rich Primers,"[29] as follows.

> Major U.S. automotive companies have been using zinc-rich primers containing di-iron phosphide pigment since 1974. These primers are applied to automobiles in areas where extra corrosion protection is required. Because di-iron phosphide pigment is highly conductive, both

electrically and thermally, it also improves spot welding. This is an important benefit in the automotive industry, where spot welding is so widely used.

Spot weld tests were made on steel sheet coated with zinc-rich primers containing various levels of di-iron phosphide. The welding rate was 15 welds per minute until 2,000 consecutive welds are produced. Weld nugget size was measured at intervals of 250 welds. Results show that the formulation containing 40% di-iron phosphide with 60% zinc passed the test with a nugget size of 0.61 to 0.69 cm (0.24 to 0.27 in) at 2,000 welds. One hundred percent zinc-rich primers typically result in nugget sizes of 0.46 to 0.56 cm (0.18 to 0.22 in) for the same number of welds. Since weld strength is directly proportional to nugget size, the advantages provided by including di-iron phosphide in the primer formulation is quite apparent.

The increase in diameter of the electrode face, measured after 2,000 welds was 0.05 to 0.15 cm (.02 to .06 in) when a primer containing 40 di-iron phosphide was used. This can be compared with a 0.05 cm (.02 in) increase in the electrode face diameter after only 1,250 welds were made when a 100% zinc-rich primer was used.

Since electrode wear is attributed to the combination of copper with zinc vapor, which results from the low melting point of zinc, decreasing the amount of zinc in a primer with the use of di-iron phosphide pigment can also reduce the amount of electrode wear. This is important because electrode wear decreases electrical current density and weld strength. Furthermore, by including di-iron phosphide in a zinc-rich coating system:

1. Welding can be performed on coated steel in applications where it was previously not possible.
2. Coatings with higher film thicknesses can be welded (unusually heavy coatings occasionally occur in production operations, causing the welding process to stop due to the loss of electrical conductivity).
3. Welding speed can be dramatically improved without sacrifice to weld strength.[29]

Types of Inorganic Zinc Coatings

Preconstruction Primers

One of the important anticorrosive uses for IOZ coatings has been their use as preconstruction primers. These materials are a little different in formulation from the full thickness IOZ coatings; on the other hand, they are formulated with the same basic materials as are used with the standard zinc coating. The primary difference is that they are formulated to be applied at approximately ½ to ¾ mil (12 to 17 η) in thickness and are usually applied by automatic spray equipment. The low DFT is used to minimize the coating's influence on welding and cutting speeds. The purpose of the IOZ preconstruction primer is to provide a corrosion-free surface for steel during its prefabrication and fabrication stage. The majority of these types of coatings have been used in the marine industry where the steel plate or steel shapes, as they enter the shipyards, are automatically blasted free of mill scale and rust. Within a matter of minutes, the steel is sprayed with the preconstruction primer on both sides of the plate before the plate is transferred to storage or to the fabrication area. The coating must dry quickly so as not to be damaged by handling with large magnetic lifting devices.

The preconstruction use of the IOZs requires that they be tough and abrasion-resistant, inasmuch as the steel plate and shapes are handled continuously through the fabrication stage with heavy equipment. The coating must be easily welded and cut both by hand and by automatic welding and cutting equipment. There should be little or no burn back at the welds or cut areas, and the life of the coating should be such that it fully protects the steel from any corrosion for the full period of construction up to the point where additional coatings are applied. The preconstruction primer can act as a base for topcoats, or it can be lightly blasted and followed by additional IOZ coatings for maximum corrosion resistance. Secondary surface preparation with power tools is commonly done on areas that will not serve in immersion conditions. It is in use by many shipyards and other fabrication facilities, where it not only performs as required but provides a light gray surface with good visibility during fabrication as well.



FIGURE 6.34: IOZ preconstruction primer applied to deck plates showing an automatic weld. Note the minor burn-back at the weld edge and the lack of any pinpoint corrosion after two years of service. The reddish color was used to contrast the color of the blasted steel.

Figure 6.34 shows the application of a preconstruction primer to deck plates with the automatic weld between the plates. This photograph was taken almost two years after the application of the preconstruction primer and, even with all of the abrasion that takes place on the deck, there was little or no wear-through of the thin primer and no corrosion to the steel itself. It provided an excellent base for an additional IOZ coating following a light blast of the surface to remove surface contamination and to prepare the weld areas. Surface preparation for the final coats was reduced to a minimum by the use of this material. New formulations invented during the 1990s have reduced the porosity of these preconstruction primers to the point that dust, dirt, and oil pick-up is reduced and both cutting and welding speeds are dramatically improved.

Figures 6.35 through 6.40 demonstrate the application and handling of the preconstruction primer in a steel fabrication shop.

The rolling of steel also is common during the fabrication process, and it demonstrates the excellent adhesion and abrasion resistance of the preconstruction primer. Such treatment is not uncommon in tank fabrication or in shipbuilding, and the coating must withstand such treatment without appreciable abrasion damage or corrosion after fabrication.

Advantages of Inorganic Zinc Preconstruction Primer

There are a number of advantages to using an IOZ preconstruction primer, particularly where large volumes of steel are to be coated. The two principal reasons for using a preconstruction primer have to do with surface preparation.

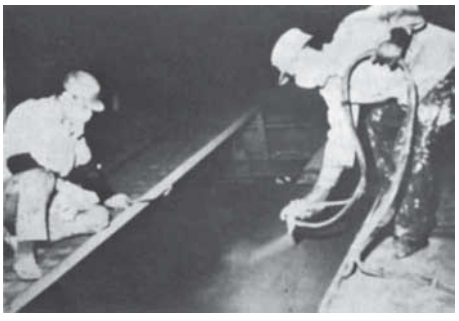


FIGURE 6.35: Manual application of IOZ preconstruction primer.

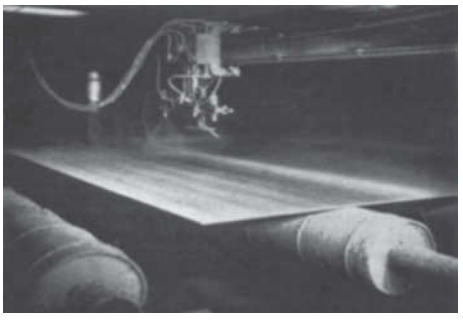


FIGURE 6.36: Automatic application of IOZ pre-construction primer.

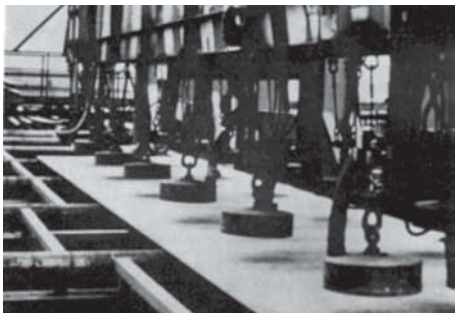


FIGURE 6.37: Magnetic pickup of IOZ-coated plate directly after application. Coating is solid but uncured with no damage due to pickup.

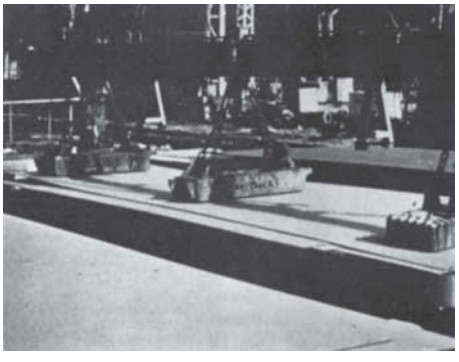


FIGURE 6.38: Magnetic handling of IOZ-coated plate during fabrication.

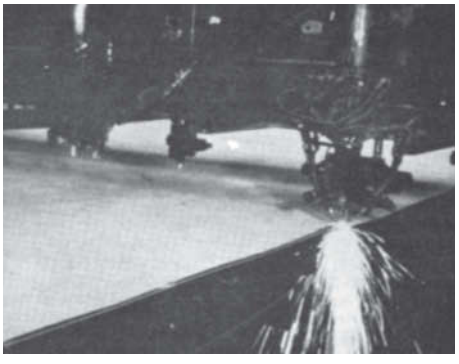


FIGURE 6.39: Automatic cutting of IOZ-coated plate. Primer is 18 to 25 µm (0.75 to 1 mil) in thickness. Note the absence of white zinc fumes.

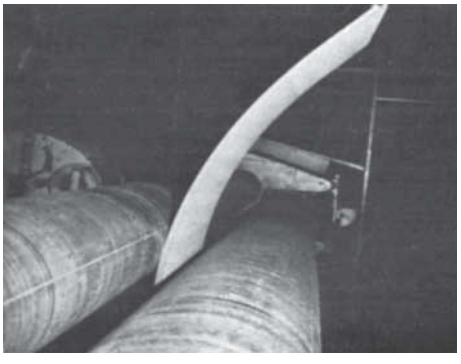


FIGURE 6.40: Forming plate coated with IOZ preconstruction primer. Formed plates show excellent corrosion resistance.

1. Preparing steel by blasting is most economically done by automatic blasting processes. Large volumes of steel can be handled and blasted at a very low cost before it is cut and fabricated into larger or more complex sections. The difficulty is the retention of this surface preparation over a long period of time.
2. The IOZ primer is applied as the steel plate or section comes out of the automatic blast machine. Often, the steel is preheated so that it is slightly warm—a few degrees above ambient temperature. The time lapse between blasting and coating is less than one minute, so that the blasted surface is immediately protected. With the coating thickness less than 25 η (1 mil), it dries to handle very rapidly, particularly if the steel is warm. Newer formulations have allowed the application of 12 to 18 η (1/2 to 3/4 mil) where the size of the ship allowed a completed fabrication time of less than nine months. The whole blasting and coating process is very low cost as compared to hand blasting after fabrication.
3. Where the IOZ preconstruction primer is applied evenly, the steel can be stored, formed, cut, welded, and fabricated, and still be corrosion-free after many months or even years. This retains the original low-cost surface preparation so that additional full-scale blasting is not required.
4. The original IOZ primer can be recoated with a full thickness coat of IOZ by brush blasting to remove any surface contamination and to blast the welds, cut surfaces, and other areas, down to bare metal. Many organic topcoats can be applied directly to the preconstruction primer by merely washing or steam cleaning the surface and spot blasting the welds. The original intact IOZ primer provides a good base for any of the above coatings.
5. An added advantage of the IOZ preconstruction primer is its light color. Template marks, punch lines, and other construction marks are easily visible, making the cutting and fabrication work much easier.

There are essentially three types of zinc based preconstruction primers. The first type, water-based inorganic preconstruction primers, have exceptional corrosion resistance and have high abrasion resistance. They are excellent for application to warm steel; on the other hand, they are not as satisfactory for cold steel under highly humid conditions.

The second type is based on the solvent-based inorganics, either single package or two-component, and is a common type in current use. It gives excellent results under cold and under high-humidity conditions, and may be applied readily by automatic airless equipment. It does not harden as rapidly as the water-based primers, but nevertheless may be handled within minutes after application.

The third type is the organic-based zinc-rich preconstruction primer. It is an easily applied material. It is much slower to harden than the IOZ preconstruction primers and never reaches the hardness of the inorganics. Applied in the same thickness range, it is much more subject to abrasion and is somewhat less durable than the inorganic-based coatings.

The restrictions on VOC emissions in the 1990s has led to the development of several water-based epoxy/acrylic organic preconstruction primers with good protection and welding and cutting properties. Generally, these only can be counted on for much shorter duration of full protection compared to the IOZ preconstruction. More recently water-based high-ratio potassium silicate (WB HRZS) IOZ pre-construction primers have been used extensively to meet even the most stringent volatile organic compound (VOC) emissions regulations. These require special 3M or Devilbiss spray guns with Delrin polymer non-stick components to prevent gun plugging caused by the reaction of the silicate with the metallic gun parts. Airless spray guns are not recommended by the coating manufacturer.

Single Package Inorganic Zinc Coatings

The development of the IOZ single package products has been a breakthrough in the application and handling of IOZ coatings. The original single package products were recommended primarily for use where the IOZ was to be coated, as their durability was not comparable to the two-package in organic zinc products, either water-base or solvent-base. The single package products are based on the solvent-base or organic silicate IOZ materials. As might be expected, the manufacturer of these products is more critical, with particular attention having to be given to the storage life of the mixed material prior to use. Continued research has improved these materials until they approach the durability of the organic base inorganics with the advantage of single-package handling.

The chemistry involved in these single-package products is similar to that of the organic silicates. The formulations have evolved in such a way that any reaction is delayed until after the application of the product and its exposure to humidity in the air. Once the initial drying stage has been complete (i.e., the removal of the solvent and the initial deposition of the coating), the humidity of the air is then able to react with the organic silicate and zinc in the same manner as previously described for the ethyl silicate base products. Some additional information as to the reaction that takes place is provided by Dean Berger in a review paper as follows:

> U.S. Patents 3,615,730 and 3,653,930, and Dutch Patent 6,900,749 describe amine initiated hydrolysis and colloidal suspension of silica in various solvents. This technology led to the first commercially produced, single-package zinc rich paint.
>
> Some interesting aspects of U.S. Patent 3,653,930 include the use of amines, such as cyclohexylamine or triethanolamine. These amines provide a hydroxyl source that is non-reactive with the organic polysilicate vehicle.
>
> When the coating is applied, the amine reacts with the atmospheric moisture to yield OH ions. The alkyl silicate then undergoes basic hydrolysis to form the polysilicate matrix and the resulting alcohol by-product is lost by vaporization.

$$RHN'_2 + H_2O \rightleftarrows RNH_3 + OH^-$$

$$C_2H_5O\left[\begin{array}{c} O \quad C_2H_5 \\ | \quad | \\ -Si-O- \\ | \\ OC_2H_5 \end{array}\right]C_2H_5 + OH^- + H_2O \rightarrow$$

$$\rightarrow N(Si_2O_5) + N(C_2H_5OH)^{(2)}$$

> It has been found that gas evolution may be controlled by adding a few percent of 1-nitropropane. Thus, it is suggested:
>
> $$Zn + H_2O \rightarrow Zn(OH)_2 + H_2$$
>
> $$CH_3{-}CH_2{-}CH_2{-}NO_2 + 3H_2 \rightarrow CH_3CH_2CH_2NH_2 + 2H_2O$$
>
> 1-Nitropropane
>
> Close examination, however, indicates the following combined reaction likely:
>
> $$3Zn + 4H_2O + RNO_2 \rightarrow 3Zn(OH)_2 + RNH_2$$
>
> Red lead has also been found to reduce the gas evolution of such inorganic single package systems. The patent further claims the use of non-polar solvents, which contribute to non-settling characteristics of the paint. In addition, a cyclic ketone is also claimed as a hydrogen scavenger.[28]

There are a significant number of manufacturers in the United States manufacturing IOZ coatings, each of which have at least a slightly different product from the others. Table 6.8 gives the range of the type of products available and shows some of the variations between the different commercial products. The products on this list do not necessarily mean that they are equivalent in effectiveness. However, they all can be considered to be supplied by reputable manufacturers.

(2) Author's Note: The $N(SiO_2)$ represents the silica matrix or polymer, but without the zinc in the molecule. With zinc, as would be the case in an inorganic zinc coating, the silica polymer would be as represented in the model of probable chemical reactions within an organic silicate zinc coating previously shown. The $N(C_2H_5OH)$ represents the alcohol produced by the hydrolysis reaction and which evaporates out of the coating.

There have been many attempts to use metals other than zinc to provide an inorganic coating. None of the other common metals react in the same way that zinc does. Metallic aluminum and metallic magnesium are both cathodic to steel and therefore should, if formed into a coating, provide an effective corrosion-resistant product. This, however, has not been the case. Even when used as a pigment in an organic-based coating, the results have not been comparable to a zinc base coating. Zinc is a uniquely reactive metal, and the other metals just do not react in the same way, either in combination with silicic acid to form an inorganic film or in being able to develop a cathodic surface over a steel substrate. None of the efforts to use these other metals have been even reasonably successful in the formation of the basic coating or in obtaining corrosion resistance.

Inorganic Zinc Versus Galvanizing

Although IOZ coatings are made with metallic zinc, they should not be considered a metallic coating (e.g., galvanizing). There has been considerable discussion and controversy with regard to IOZ coatings and galvanizing, with most of the proponents of either material taking a rather strong stand in favor of their particular product. Actually, IOZ coatings and galvanizing should not be considered competitive. Rather, they should be considered complementary, since both of them provide an excellent corrosion-resistant application under the conditions where each one operates best. They are two entirely different concepts of coating, even though they both rely on metallic zinc for the basis of their corrosion resistance. Both are chemically bonded to the metal surface, the galvanizing by an

TABLE 6.8: Typical Inorganic Zinc Coatings and Compositions

		Ounces					
Coating Type	Powder #/Gal (Two-Component)	Zinc Dust #/Gal	Volume Solids %	Mil Sq. Ft. Coverage	DFT Mils	Zinc Dust per ft^2 at DFT	Pigment Other Than Zinc
Preconstruction Primer—Single Package	N.A.	6.91	35.0	561	.75	0.15	——
Preconstruction Primer—Water Base	14.15	14.00	35.0	561	.75	0.30	——
Water Base—Post-Cure	23.0	19.89	66.2	1052	3	0.90	Red Lead
Water Base—Self-Cure	25.0	21.62	75.4	1209	3	0.86	Red Lead
Water Base—Self-Cure	19.4	16.78	67.8	1088	3	0.74	Red Lead
Organic Base—Self-Cure	14.94	14.79	66.1	1060	2.5	0.56	Iron Oxide
Organic Base—Single Package	N.A.	10.0	50.0	800	2.5	0.50	——
Organic Base—Self-Cure	14.6	14.6	62.3	1000	3.0	0.70	——
Organic Base—Self-Cure	18.0	16.82	65.0	1042	2.5	0.65	Celite
Organic Base—Self-Cure	15.0	12.0	63	1010	2.5	0.475	Celite

amalgam of zinc and iron; whereas IOZ coatings are bonded by a chemical compound of iron and silica. Actually, galvanizing can be considered an IOZ coating and, in many ways, it will do the same things that an IOZ-rich coating will do.

There are also some basic differences. The zinc in an IOZ coating is not continuous as it is with galvanizing. It is made up of many individual zinc particles, which are surrounded by and reactive with an inert zinc silicate matrix. This matrix is very chemically inert and, except for very strong acids or alkalis, is unreactive with most environmental conditions where coatings would be used. This does not mean that in an acid atmosphere the zinc in the IOZ coating might not be dissolved. However, because it is in a chemical-resistant matrix as discrete particles completely surrounded by the matrix, the solution of the zinc is slowed down in a major way. On the other hand, zinc in galvanizing is pure zinc, and any acid in the atmosphere reacts directly with it with no inhibition of the reaction, as is the case in the IOZ coating. This is an important difference between the two materials and is the reason why, under many difficult corrosion conditions, the IOZ coating will have a much longer life than the galvanizing under the same conditions. This has proven to be the case not only in laboratory testing over a number of years, but also in both industrial and marine atmospheres.

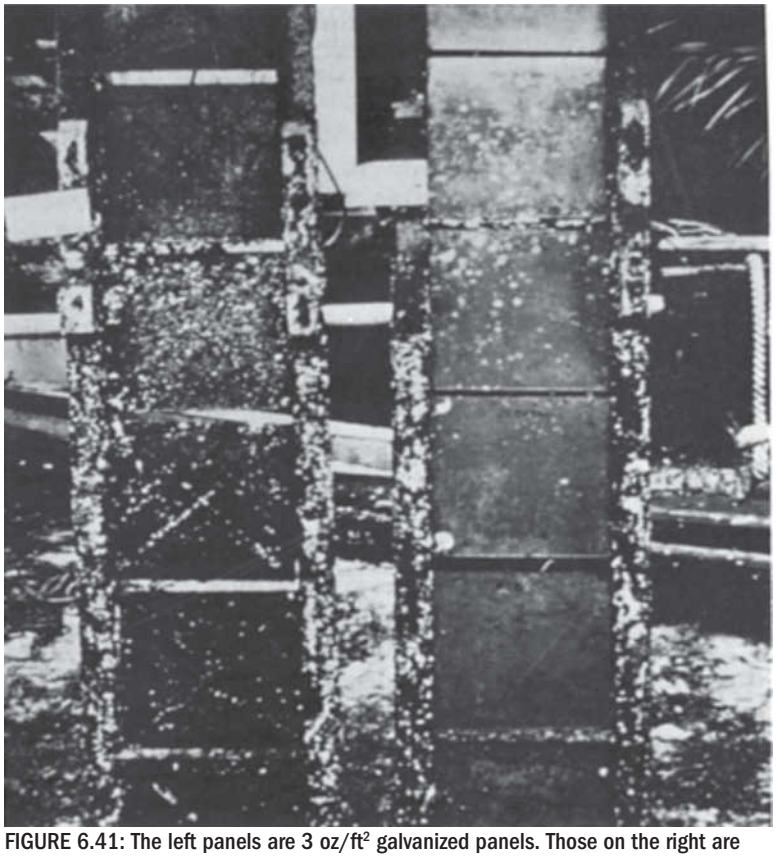


FIGURE 6.41: The left panels are 3 oz/ft^2 galvanized panels. Those on the right are 75 µm (3 mils) water based IOZ. Exposure time was two years in tidal seawater conditions. Note that the galvanized panels are completely covered with pinpoint rust. However, there is no corrosion evident on the IOZ panels, even in the scribes.

Figure 6.41 shows the direct comparison of an IOZ coating and a three-ounce-per-square-foot hot dip galvanized coating under tidal conditions. In this case, the top panels were continuously just above the high tide level. The lower panels were continuously immersed. These panels were exposed for two years with no appreciable corrosion on the three mils IOZ coatings compared with an almost complete breakdown of the metallic zinc coating (galvanizing) by pinpoint rusting. Many similar tests have been run with similar results.

Inasmuch as the zinc in a zinc coating is surrounded and interlocked into an inert matrix, the coating has controlled reactivity and controlled conductivity. This was shown in a test in which inorganic zinc panels and galvanized panels were placed in a dilute acid solution and coupled to a plain iron panel. Both the voltage that developed and the current flow were measured. In the case of the volt- age developed, both the IOZ and the galvanizing developed a potential of approximately 0.5 V, showing that the zinc in each one provided the same potential under these conditions. On the other hand, when the current flow was measured between the coated panels and the bare steel, the IOZ coating provided 52 milliamps of current, while the plain zinc surface provided 92 milliamps of current, thus showing that the metallic zinc was considerably more reactive than the zinc, which was protected by the IOZ matrix (Figures 6.42 through 6.45).

While galvanized surfaces provided a malleable zinc surface, the IOZ coating, because of the hard, rock-like character of the zinc silicate matrix, results in a much harder and more abrasion-resistant coating than the metallic zinc. All of the above differences generally indicate, on an exposure-for-exposure basis, that the IOZ will tend to have a longer life span under most conditions than will the normally galvanized steel surface.



FIGURE 6.42: Post-cured IOZ silicate panel coupled to a plain steel panel in a dilute acid solution developed a potential of approximately 0.5 V.

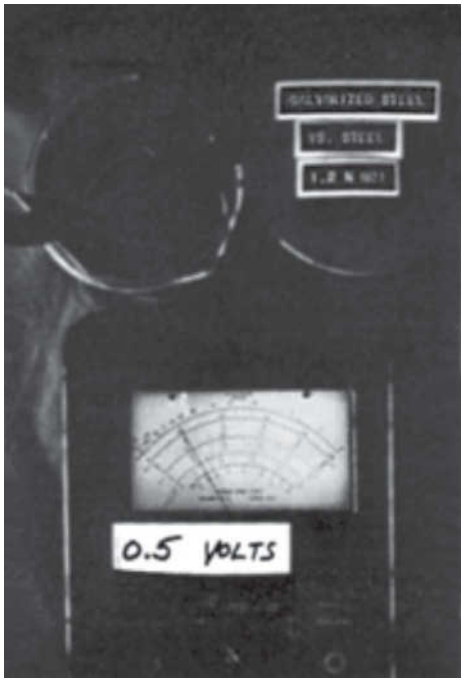


FIGURE 6.43: Galvanized steel panel coupled to a plain steel panel in a dilute acid solution developed a potential of approximately 0.5 V.



FIGURE 6.44: Cured IOZ silicate panel coupled to a plain steel panel in a dilute acid solution developed a current flow of 52 milliamps.

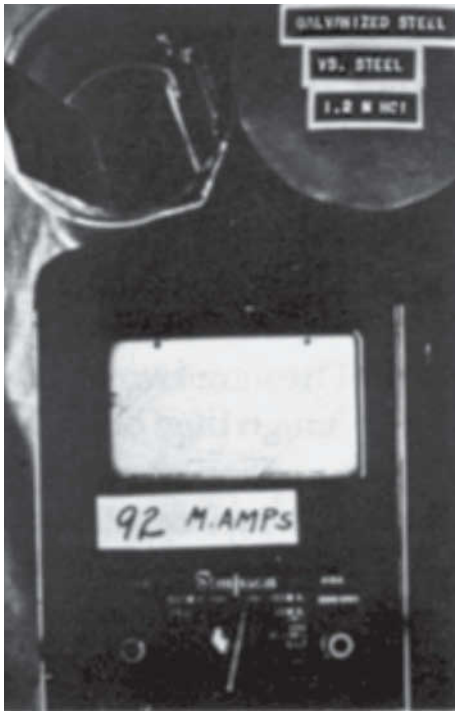


FIGURE 6.45: Galvanized steel panel coupled to a plain steel panel in a dilute acid solution developed a current flow of 92 milliamps.

Characteristics of Inorganic Zinc Coatings

A number of the characteristics of coatings have been discussed. However, it appears useful to list the major general characteristics of IOZs as a whole so that they may be compared with the many organic coatings described in previous chapters.

Corrosion Resistance

As mentioned in a review of the chemical characteristics of IOZs, their general and chemical resistance is extremely good compared with metallic zinc by itself. This characteristic simply cannot be overemphasized since galvanizing has been a standard of corrosion resistance since the beginning of the 20th century.

Cathodic Protection

One of the most significant properties of IOZ coatings is the CP they provide. The simple test of a zinc-rich coated panel connected to a steel panel in an indicator gelatin bath is ample indication of this characteristic, as discussed in earlier chapters. Other tests where bare areas are left on a coated panel and the panel immersed in a conductive solution show the same protection to the bare area. The inorganic matrix is conductive and allows the zinc to go into solution in a controlled manner, making it anodic to steel and thus able to cathodically protect any breaks that may occur in the coating. Eventually, any minor holidays, pinholes, scratches, or scars heal by the formation of zinc reaction products, such as zinc hydroxide and zinc carbonate. This action is important since it provides an added increment of protection to damaged areas of the coating.

Weather Resistance

An IOZ coating, being completely inorganic, is unaffected by weathering, sunlight, ultraviolet radiation, rain, dew, bacteria, fungus, or temperature. Since it is essentially inert to these weather-oriented factors, the coating does not chalk or change with time. The IOZ film remains intact and with essentially the same thickness, even after many years of exposure. This has been demonstrated by making pencil marks on the coating shortly after application. After 10 years of marine exposure, the pencil marks were still intact and readable. Any surface change in the coating would have eliminated such marks in a short period of time. Thickness measurements made over a several-year period also show no change, even under severe weathering conditions.

Undercutting

The prevention of undercutting of a coating on steel is also an important anticorrosive property. Organic coatings generally do not have it. IOZ base coatings do prevent rust from undercutting. Both galvanizing and zinc silicate coatings have this property. As explained previously, the galvanized coating is amalgamated with the iron. Zinc silicate coatings provide this adhesion by the inorganic binder chemically reacting with the underlying steel surface in a similar way to its reaction with the surface of the zinc particles. This reaction occurs at the interface between the steel and the coating, forming a permanent chemical bond between the two. This is the

property responsible for the effectiveness and life of the coating in addition to the prevention of undercutting of the coating by corrosion. This adhesion cannot be overemphasized since the majority of organic coating failures under severe corrosion conditions is by under film corrosion starting at small breaks in the coating. This property of the IOZ base coat multiplies the effective life of an organic topcoat several times.

Figure 6.46 shows two steel panels coated with a two-coat epoxy, which were exposed for more than a year in a very humid, slightly acid industrial area. The panels were adjacent to each other and subject to equivalent conditions. Many similar tests as well as actual uses have proven the benefit of the IOZ base coat in protecting organic topcoats from undercutting and corrosion.

Shrinkage

Another important characteristic of IOZ coatings is that they do not shrink upon drying or curing as do organic coatings. Once applied, the inorganic material follows the configuration of the surface over which it is applied. This is due to the method by which the film is formed and is a major advantage in overcoating rough, pitted, and corroded surfaces or rough welds. The liquid coating wets the metal surface well, and when applied, flows into the small imperfections in the surface. As the film forms, the water or solvent evaporates, leaving the coating in place on the surface. At this point, the coating has no strength or toughness, as do organic films; it merely lies on the surface. Any reduction in volume by solvent evaporation is in depth rather than parallel to the surface. The only exception is where the film is applied too thick, and then mud cracking occurs. Generally, no bridging of pits, cavities, or inside corners occurs (Figure 6.47). Zinc coatings have been observed that were applied over steel surfaces that were completely covered with corrosion pits, yet showed no evidence of bridging in the concave pit areas. This is an important characteristic in coating rough areas, welds, or previously corroded surfaces.

Temperature Resistance

IOZ materials are relatively unaffected by temperatures above the melting point of zinc. Used as a primer and topcoated with silicone-based topcoats, the combination has provided protection even at temperatures of 1,000 °F for long periods of time. Without topcoats, the IOZ coatings are usually recommended up to 750 °F (slightly below the melting point of metallic zinc) since rapid oxidation above the temperature will deplete the metallic zinc content in the coating and reduce protection. Top coating IOZ restricts rapid oxidation. Steel stacks, hot processing equipment, and similar structures have been fully protected for many years without coating breakdown.

One example of this concerns a steam exhaust muffler and water separator. It was heated with steam to 160 °C (320 °F) and then cooled with water to ambient temperature on a 20-minute cycle. During the steam exhaust, it was completely wet with water. This rather large steel installation was coated with a single coat of IOZ, which fully protected the surface for more than 10 years of this heating and cooling cycling.

Steel stacks from a large steam generator station, shown in Figure 6.48, serve as another example. They were adjacent to the seacoast and had already been in use several years with only one coat of IOZ to provide protection.

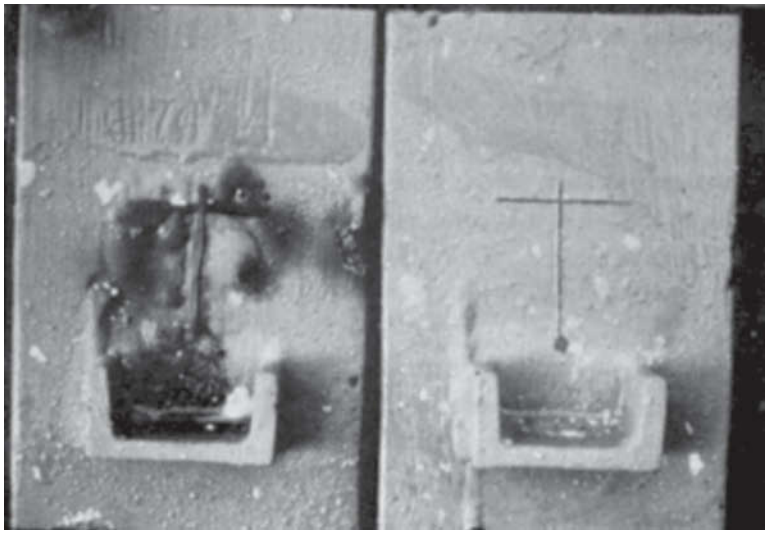


FIGURE 6.46: Condensation on two-coat epoxy panels. The right-hand panel was also coated with an IOZ primer. Note the heavy undercutting and blistering on the left-hand (epoxy only) panel.



FIGURE 6.47: Rough areas coated with an IOZ coating. Note the complete coverage of the deep pits and undercuts.

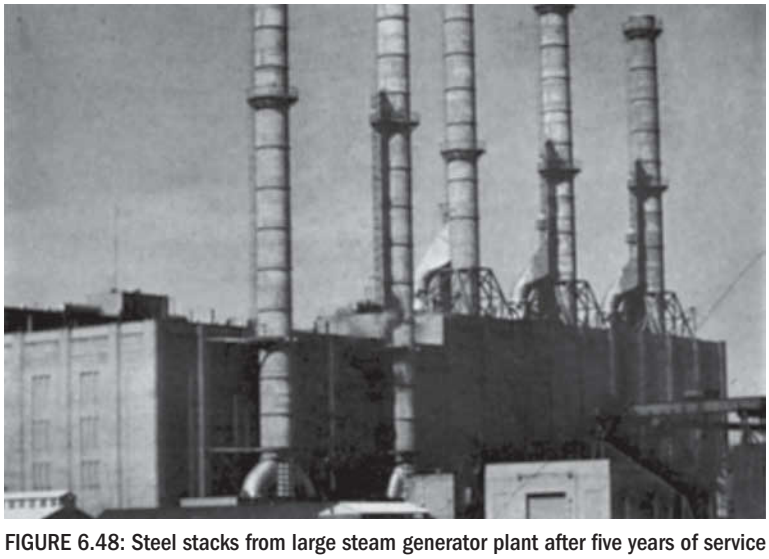


FIGURE 6.48: Steel stacks from large steam generator plant after five years of service coated with one coat of IOZ coating. The coating was applied to stack sections on the ground and then erected.



FIGURE 6.49: Steel stacks from large steam generator plant after five years of service coated with one coat of IOZ coating. The coating was applied to stack sections on the ground and then erected.

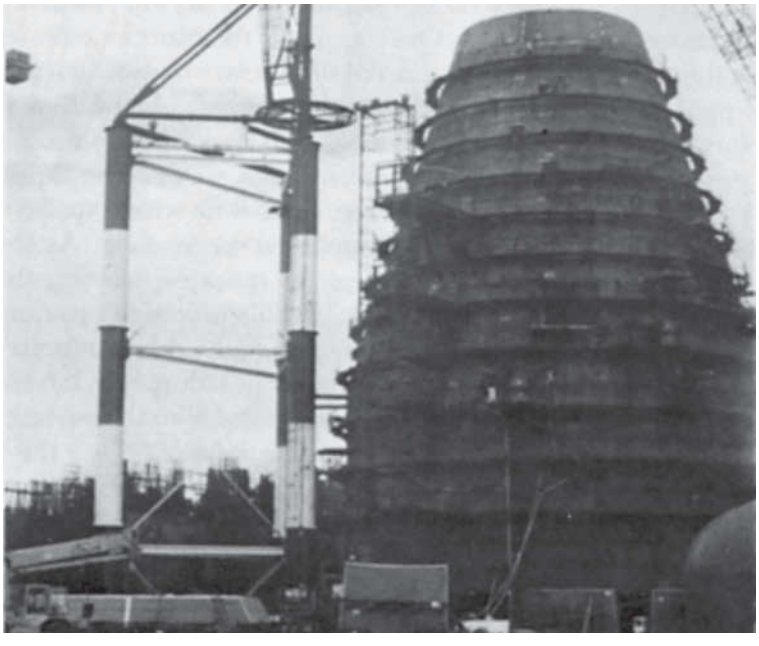


FIGURE 6.50: Typical atomic reactor shell prior to coating the interior and exterior with an IOZ coating.

Solvent Resistance

IOZ coatings, being completely inorganic, are unaffected by organic solvents, even the high-strength ones such as ketones, chlorinated hydrocarbons, aromatic hydrocarbons, and others. They also are unaffected by gasoline, diesel oil, lube oil, jet fuel, and many similar refined products. Therefore, they may be used alone or in connection with topcoats for continuous exposure to such chemicals. One coating manufacturer, for example, has all of its solvent storage tanks coated with IOZ to protect against rust contamination.

Generally speaking, water-based inorganics are preferred for continuous immersion in solvents. Some solvent-based inorganics may show slight softening when continuously exposed to ketone, ester, or similar solvents. The classic solvent use of water-based inorganics has been as a lining for refined oil ship tankers (Figure 6.49). These transport alcohols, toluol, and xylol, as well as all types of gasoline, jet fuel, and lube oil. They are, at the same time, subject to seawater washing.

Radiation Resistance

IOZ coatings are unaffected by gamma ray or neutron bombardment. These coatings have been exposed to atomic radiation up to and beyond 2 × 1010R without any change in properties. Table 6.9 indicates the comparison of IOZ coatings with several organic coatings in this regard. Most of the organic materials showed some failure at the indicated radiation dosage. The test on the IOZ and inorganic topcoat was discontinued without any evidence of failure. Figure 6.50 is typical of many of the reactor containment shells that are coated on both the interior and exterior with IOZ coatings.

Coefficient of Friction

The strong permanent bond to steel surfaces and the rock-like character of the inorganic film form a base that has proven to have excellent friction characteristics. Therefore, the IOZ coatings may be used as a coating for faying surfaces (friction interfaces between bolted or riveted structural steel sections) on structural steel buildings, bridges, towers, and so on. These joints are subject to severe weathering conditions, including both industrial and marine atmospheres, and corrosion often starts at the joints. Such areas are hard to prepare and hard to properly coat. On the other hand, IOZ coatings, because of their good friction resistance, can be applied before the joint is made, providing full protection both within and at the junction of the two steel sections. Organic coatings, and even galvanizing, act as lubricants and do not allow a proper coefficient of friction to be developed in the joint.

Table 6.10 provides some comparative figures based on actual tests of various surfaces. Note that the IOZ coatings provide a coefficient of friction equal to or above a sandblasted surface. Any coefficient of friction less than a sandblasted surface (0.47) is usually not acceptable for steel construction and is the reason for masking the joints on bolted or riveted structures, which are shop-primed with ordinary paint prior to erection.

Abrasion

This same property of a hard, metallic, abrasion-resistant surface is also important in areas of severe abrasion. The boot-topping and upper hull of a ship is a good example. Abrasion due to docking and mooring can be extremely severe in these areas. Where an IOZ coating is used as a permanent primer, even though the topcoats are abraded away, the zinc coating remains to provide full corrosion protection.

Fire Resistance

One of the important characteristics of IOZ coatings is their resistance to burning and fire. They will not support combustion because of their inorganic nature and will not burn even though exposed to severe flames. The welding and cutting of inorganic coated steel demonstrates this characteristic. This point also is dramatically demonstrated by their use on the missile launching structures and launching pads at Cape Canaveral and other launching sites. Even the extreme heat caused by the rocket launch does not cause the coating to oxidize or burn. Even petroleum storage tanks coated with IOZ that accidentally burned still had the protective coating intact after the fire was extinguished.

TABLE 6.9: Examples of Typical Coating Resistance to Radiation Based on Comparative Tests

		Radiation Resistance(A)	
Type	Substrate	Air	Water
Inorganic Zinc	Steel	2.2×10^{10}	Discontinued before failure
Inorganic Topcoat	Steel	1.0×10^{10}	Discontinued before failure
Epoxy Amine	Concrete	$> 3 \times 10^{9}$	$> 3 \times 10^{9}$
Epoxy Amine	Steel	6×10^{9}	–
Epoxy Polyamide	Steel	1.0×10^{10}	–
Epoxy Polyamide	Concrete	1.0×10^{10}	–
Modified Epoxy Phenolic	Steel	1.0×10^{10}	7×10^{9}
Modified Epoxy Phenolic	Concrete	3×10^{9}	3×10^{9}
Epoxy Surfacer	Concrete	1.0×10^{10}	–
Vinyl	Concrete	4.42×10^{9}	$5 \times 9 \times 10^{8}$
Vinyl Acrylic	Steel	5.6×10^{9}	–
Chlorinated Rubber	Steel	1×10^{8}	–
Chlorinated Rubber	Concrete	1.0×10^{10}	–
Urethane	Steel	5×10^{8}	–

(A)Rads—The unit of absorbed dose, which is 100 ergs /gram in any medium. For most organic materials, 1 RAD = 1 Roentgen; Roentgen = exposure dose; and RAD = exposure dose.

Source: C.G. Munger, "Coatings for Nuclear Plant," NACE Western Regional Conference (Seattle, WA: NACE, October 1974).

Welding

Joints and connections on steel structures usually are subject to welding, thus, there has been a great deal of pro and con discussion with regard to welding IOZ coated steel. The structural and physiologic problems of welding galvanized steel are well known, since some reduction of strength in the welds due to zinc inclusions result and the welding fumes cause various health problems for the welders.

TABLE 6.10: Actual Results of Coefficient-of-Friction Tests for Various Surface Conditions

Surface Conditions	Coefficient of Friction
Solvent Based IOZ Coating	0.52
Rusted and Wire-brushed Surfaces	0.51
Post Cured IOZ	0.48
Brushed Surfaces	0.48
Water Based IOZ Coating	0.47
Sandblasted Surfaces	0.47
Galvanized Surfaces	0.25
Rust Preventative Paint	0.11
Red Lead Paint	0.06

Source: W.H. Munse, "Static and Fatigue Tests of Bolted Connections Coated with Dimetcoat," Univ. of Illinois, Urbana, IL, private report to Ameron Corp. (March 1961).

Battelle Memorial Institute, along with several foreign laboratories, has made tests to determine both the effects of IOZ coatings on welds and the effects on welders. These tests have shown that the IOZ coatings can be welded without any reduction of weld strength either for preconstruction steel primers or full thickness (75 µm [3 mils]) IOZ coatings. High-speed production welding cannot be accomplished with full-thickness coats without some porous welds. Inorganic preconstruction primers or weld-through primers 18 to 25 µm (3/4 to 1 mil) do not cause any problem with the speed of cutting or welding. The welds obtained by either automatic or hand-welding techniques are equivalent to those on bare plate.

The following test results are indicative of the weld effectiveness using a submerged arc method. Test plates were welded using square butt joints with all surfaces, including the edges, coated with an inorganic steel primer. All tensile strengths of the welded specimens exceed the requirements of the American Welding Society Specification AWS D2.0-66.30 All welding materials, currents, voltages, and other information, are shown in Table 6.11. Speed changes within the range of 35 to 45 in/minute did not affect the results. Similar results also were obtained using a shielded metal arc and a gas metal arc.

Many millions of square feet of preconstruction primed steel have been cut and welded without creating hazardous working conditions. Nevertheless, carefully controlled tests were made to determine if any hazards were present. Another project was conducted in which the safety conditions when welding IOZs were thoroughly studied. Measurements of the zinc oxide, lead, and iron oxide content in a welding atmosphere were made with a Gelman GM4TM membrane filter. Measurements were made during the welding of vertical tee joints made in A-36 steel that was either uncoated or coated with standard IOZ and inorganic preconstruction steel primers. The filter was positioned about 12 in (0.30 m) from the tee specimen and slightly above it (i.e., in approximately the same location as the welder's face). The results are summarized in Table 6.12.

In general, the conclusions from the tests were as follows:

1. The concentration of zinc, iron, and lead in the air was well below the recommended threshold limits of 5, 0.2, and 15 mg/m^3, respectively.
2. The concentration of zinc in the fumes generated by welding uncoated A-36 and A-36 coated with post-cured IOZ increased from a background value of 0.09 mg/m^3 to 2.1 mg/m^3, respectively. The same results were noted when welding was performed on plate

TABLE 6.11: Submerged Arc Method

					Free Bend Test Gauge Reading		
	Amps	Volts	Speed I.P.M.	Tensile Strength PSI	Orig.	Final	% Elong.
Uncoated Steel	---	---	---	69,300	---	---	36.5
Uncoated Steel	---	---	---	70,020	---	---	34.0
Coated Steel	650/700	30/32	35	73,520	0.433	0.591	36.5
Oxweld 36	650/700	30/32	35	75,560	0.361	0.512	41.8
Unionmelt 50	650/700	30/32	45	73,580	0.290	0.413	42.4
	650/700	30/32	45	73,521	0.263	0.374	42.2
Coated Steel	650/700	30/32	35	72,971	0.414	0.611	47.6
Lincoln L61	650/700	30/32	35	73,797	0.409	6.571	39.6
781 Flux	650/700	30/32	45	74,260	0.249	0.335	34.5
	650/700	30/32	45	73,830	0.283	0.349	23.3

Note: Tensile strength base metal = 74,700 psi. Minimum acceptable elongation is 23%. All specimens passed.

Source: C.G. Munger, "Inorganic Zinc Coatings," Proceedings of II Symposia Sul-Americano de Corosao Metalica, Rio de Janeiro, Brazil, 1971.

coated with self-cured IOZ or preconstruction inorganic zinc primer.

3. The concentration of zinc in the fumes produced when welding galvanized A-36 plate was about three times that produced when welding IOZ, but was within the allowable limits.

Manual welding of an IOZ structure is not only possible, but practical. Even with the full thickness coatings of 75 µm (3 mils), proper welding procedures will provide welds with equivalent strength to uncoated steel. This makes structural repairs of IOZ coatings equivalent to the new surface.

These characteristics indicate that IOZ coatings are unique and different from any other corrosion-resistant coating on the market. It is no wonder then that these coatings have revolutionized the corrosion protection of steel structures of all types throughout the world. Not only do they provide longer and better protection, but their use as a base coat multiplies the life of organic topcoats many times over.

Types of Zinc-Rich Coatings

Industry Designations

TABLE 6.12: Analyses of Welding Fumes Collected with Gelman GM4 Filter (Within 23 in. of Welder's Face)

Elemental Metal	Threshold Limit	Not Coated		Post-Cured Inorganic		Self-Cured Inorganic	
	mg/m^3	mg	mg/m^3	mg	mg/m^3	mg	mg/m^3
Fe	5.0	0.20	3.7	0.95	1.1	0.05	1.1
Pb	0.2	0.005	0.09	0.005	0.10	0.002	0.4
Zn	15.0	0.005	0.09	0.10	2.1	0.10	2.1

Source: H.E. Pattee, R.E. Monroe, "Effect of Dimecote Coatings on Weldability of Selected Steels," *Welding J.* 48, 6 (1969): pp. 222s–230s.

The general properties of the various zinc-rich type coatings have been discussed so that the principal coating types can be more easily differentiated. In order to bring the whole area of zinc coatings into some kind of an organized picture, the Steel Structures Painting Council, in their Specification SSPC Paint 20,[31] describes the basic types of zinc-rich coatings that are in general use at the present time. There are two obvious types: Type 1, the IOZ-rich coatings; and Type 2, the organic zinc-rich coatings. These are outlined in the specifications as follows.

Type I-A: Inorganic post-curing vehicles—water-soluble and include alkali metal silicates, phosphates, and modifications thereof. These coatings must be subsequently cured by application of heat or a solution of a curing compound.

Type I-B: Inorganic self-curing vehicles—water reducible and include water-soluble alkali metal silicates, quaternary ammonium silicates, phosphates, and modifications thereof. These coatings cure by crystallization after evaporation of water from the coating.

Type I-C: Inorganic self-curing vehicles—solvent reducible and include titanates, organic silicates, and polymeric modifications of these silicates. These systems are primarily dependent upon moisture in the atmosphere to complete hydrolysis, forming the polysilicate.

Type IIA: Organic thermoplastic binder—solvent reducible resins including chlorinated rubbers, vinyls, etc.

Type IIB: Organic thermoset binders—solvent reducible resins including phenoxies, catalyzed epoxies, urethanes, styrenes, silicones, and other suitable resinous binders. The organic Type II vehicles covered by this specification may be chemically cured or may dry by solvent evaporation. Under certain conditions, heat may be used to facilitate or accelerate hardening.[32]

SSPC-Paint 30[33] covers weld-through IOZ primers.

AASHTO M300[34] is the standard specification for IOZ prmers used by the Federal Highway Administration.

Canadian Specification 1-GP-171[35] covers coatings, IOZ.

Holland Specification COT 16.61 (SB-2) covers alkyl silicate dust coating, heat resistant. The single component version is COT 16.81 (SB-1).

Australia has AS2105,[36] "Inorganic Zinc Silicate Paint."

NASA-KSC Spec F-0020[37] covers coating, organic and IOZ rich.

Such a variety of zinc-rich coatings is available for many reasons. One of the primary reasons is the wide variability of atmospheres around the world, which is a particularly important consideration during the application of the various coatings. In Japan and many other more northern areas, for instance, it is rather cool and highly humid during most of the year. Thus, it is difficult under many conditions to apply water-based materials. On the other hand, in the relatively dry, hot areas of the Southwestern United States and Mexico, there is difficulty applying solvent-based materials because of rapid drying and the formation of overspray. When the humidity is very low, they may not cure properly.

Basic use of the materials, as well as the conditions under which they are to be applied, dictate which type of formulation should be used.

Type 1-A

The Type 1-A post-cured coating has a broad range of applications. Not only is it a heavy-duty IOZ coating, but it has been used effectively on an almost worldwide basis, from the Arctics to the Tropics. It is a water-based material, so that wherever water will effectively evaporate from the initial coating, this product can be used. This initial evaporation is the key to the proper formation of the coating and to the development of the hard, metallic film characteristic of this coating type. It forms a good coating under either warm or cool conditions due to the use of the post-curing agent, which gives it a fast initial cure and insolubility as soon as the curing agent, has been applied.

These coatings generally are not usable when the water will not effectively evaporate from the coating system within a short period of time. Generally, the evaporation time should be between a few minutes and one to two hours. A longer drying period may cause the zinc to separate in the vehicle, which makes for a poor coating with little or no corrosion resistance.

It is also difficult to use and apply this coating where rain showers are frequent, since the coating must dry to a solid state and then be cured with the curing solution before additional water can come in contact with the coating. A rain shower on a Type 1-A coating prior to the application of the curing agent will break up the silicate gel into a powder and the coating becomes useless. Most of the Type 1-A coatings are most effective where they are used alone, without topcoats, since the removal of the curing agent residue is essential wherever topcoats are to be applied. On the other hand, after washing the post-cured solution from the coating, it is relatively nonporous, and topcoats are relatively easily applied without the difficulty of solvent penetration into the voids of the coating, causing solvent blistering.

Type 1-B

The Type 1-B self-curing IOZ coatings have a water base. They can be based on a number of different alkali silicates, or on phosphates or silicasols. Ammonium silicate coatings, for example, come under this type. As with Type 1-A, it is essential that the water be able to evaporate from the coating readily in order to form the initial film. Once this takes place, leaving a hard, metallic coating on the surface, the film becomes water insoluble in a short period of time and continues to cure to full hardness and adhesion by reaction with carbon dioxide and humidity from the air. Some of these formulations require more humidity for a complete cure than others. Many of these types of coatings are effective under warm, dry conditions.

One of their most useful applications has been on the interior of tanks and tankers under warm or hot climatic conditions. Since there are no solvents in the film, they can be applied on the interior of closed areas without difficulty. The water that evaporates from the coating itself creates sufficient humidity to continue the cure of the coating to its insoluble and useable state. These materials are not effective under cold, highly humid conditions where water will not properly evaporate from the surface within a reasonable period of time.

Type 1-C

The Type 1-C solvent-based, self-curing inorganic IOZ include many different formulations. The primary type, and the one in most general use, is the organic silicates such as partially hydrolyzed ethyl silicate. This coating type is widely used because it can be applied effectively under cold conditions where the humidity is also high.

This does not mean that it should be applied to areas where there is condensation on the surface, since this type of coating reacts readily with water, and water on the surface prior to its wetting the surface prevents the formation of a proper film or one with proper adhesion. In many areas of the world, however, the temperature and humidity are such that water does not readily evaporate during certain times of the day. These coatings do not generally form a film unless there is adequate moisture in the air to allow proper hydrolysis of the silicate.

Since these materials are also solvent-based, they are less effective than Type 1-A and Type 1-B under rapid drying, windy conditions. A powdery, dry film is the usual result when these materials are applied in a warm area with considerable air movement. A number of manufacturers have made formulations with slower evaporation than the usual ethyl silicate zinc coating. They also have made faster evaporating formulations for use under less favorable conditions.

There are two specific types of solvent-based inorganics, which are additional variations of the hydrolyzed ethyl silicate product. These are both assumed to be included in the Type 1-C category. The first is a single-package inorganic. As previously noted, this product combines all of the ingredients needed to form the coating, including the zinc, into a single package which can be opened, stirred, and used like paint. The product characteristics are generally similar to the two-package system, and the general curing mechanism is the same. Most of the single package products are used as primers for organic topcoats in areas where topcoats are necessary, either for additional protection or cosmetic purposes.

The second type is the modified IOZ primer. Here, the solvent-based (Type 1-C) inorganic is modified by the addition of a compatible organic resin, usually a vinyl butyral, which is soluble in alcohol solvents. The product characteristics are a compromise between the completely IOZ coating and the organic zinc-rich primers, with some of the good properties of each appearing in the modified product. Any deficiency that might come about would be due to the life of the organic resin incorporated into the system. The advantages claimed for this type of material are improved application properties, a smooth film, easy and rapid overcoating, adhesion to

most clean steel surfaces, and good repair properties for previously zinc-primed and overcoated surfaces. This type of product is usually used where topcoats are to be applied.

Type 2

SSPC Type 2 is the organic zinc-rich classification. These materials are made with many different organic vehicles. As previously discussed, the most important are those made from phenoxies, epoxies, urethanes, and chlorinated rubber. They can be applied under almost any condition where an organic vehicle applies effectively. However, they also are subject to all of the basic problems inherent in organic vehicles, such as weathering, undercutting, release of adhesion from water absorption, blistering, and so on. One of the useful applications of the organic-based zinc-rich coatings is as a repair primer for IOZ primers and galvanized surfaces, which have been topcoated and then damaged during use. Through the use of the organic zinc-rich primer, the zinc-base coating is maintained over the bare steel area, while the organic vehicle is compatible with the organic topcoats, allowing it to be feathered out over the edge of the existing organic material.

It is suggested that information be obtained on the total solids content, the theoretical and practical coverage, the percent of zinc in the dry film, the type of binder, and the scope and duration of actual field applications or field tests of the several materials, which may be considered for the job. Where there is a requirement for a high-performance coating, the best is none too good, and since materials cost is only a small part of the completed coating job, only the best materials for the purpose, not the cheapest, should be selected. The data suggested should be readily available from the manufacturer and can be a good basis for comparing the various zinc-rich coatings offered for a project.

Comparison of Zinc-Rich Coatings

There may be times when some test comparison of the various zinc-rich types of material is desired. There are always the relatively long-term tests, such as salt spray, the Cleveland humidity test, salt water, and immersion. However, these tests generally take a considerable period of time. One quick test is the so-called "V" type test. In this case, a panel approximately 4 by 12 in (102 by 305 mm) is abrasive blasted and prepared for coating. On the middle of one side is placed a "V" made from masking tape or cellophane tape, which goes from a point at the bottom to a 1in. width at the top. The panel is then coated and allowed to dry or cure, at which point, the "V" of masking tape is removed. The panel or panels are then subjected to weather conditions for periods up to a week and are observed daily. The measure of the test is the area of the "V," which is fully protected from rust or corrosion. This provides a quick comparison between different IOZ or organic zinc coatings. While it is not infallible, it does provide for a comparison that generally has correlated well with field results.

Figure 6.51 shows a series of different inorganic and organic zinc products, including galvanized steel, which were compared in this manner. These panels were exposed to 100% humidity for three days. The various coatings used on the panels, which were marked with identical "V" holidays, and their performances are summarized in Table 6.13.

This test can be considered a test of the activity of the zinc in the individual zinc-rich formulations and its throwing power or its ability to provide CP to bare steel areas. A numerical rating can be developed from the test by measuring the amount of the "V" from the bottom of the panel up to the point where there is a first indication of rust. The examples given are commercial formulations, and it must be stressed that every formulation will perform differently since this is simply a quick comparison test. It is used exclusively for the direct comparison of two or more materials; therefore it does not yield conclusions as to whether one generic type of zinc-rich paint is better than another.

TABLE 6.13: Coating Type and Performance for Test Panel

Type I	Zinc Lead Silicate Post-Cured	SSPC Type 1-A
Type Ii	Zinc Silicate	SSPC Type 1-B
Type III	Zinc Silicate	SSPC Type 1-B
Type IV	Zinc Phosphate	SSPC Type 1-B
Type V	Zinc Lead Silicate	SSPC Type 1-B
Type VI	Hydrolyzed Ethyl Silicate and Zinc	SSPC Type 1-C
	Epoxy and Zinc	SSPC Type 2
	Chlorinated Rubber and Zinc	SSPC Type 2
	Galvanized Steel	
After three days of exposure to 100% humidity:		
Order of Performance		
Type I	Zinc Lead Silicate	100% protection
Type V	Zinc Lead Silicate	100% protection
Type IV	Zinc Phosphate	100% protection
Type II	Zinc Silicate	100% protection
	Galvanized Steel	95% protection
Type III	Zinc Silicate	85% protection
Type VI	Hydrolyzed Ethyl Silicate and Zinc	70% protection
Chlorinated Rubber and Zinc		60% protection
Epoxy and Zinc		40% protection

Topcoating

Inorganic Topcoats

In many ways, the technology involving IOZ primers is similar to that of IOZ topcoats, except that the inorganic topcoats do not contain metallic zinc. Some of these topcoat products have been in service for a good many years in spite of the fact that these materials have never really "caught on" in the corrosion field. They have been used successfully, however, in chemical plants, refineries, storage tanks, and the interiors of steel stacks.

One of the larger geothermal plants, for instance, located south of Mexicali in Mexico at Cerro Prieto was coated with an IOZ base coat and an inorganic topcoat for over 10 years. The first section of the plant was coated with a post-cured IOZ coating followed by the inorganic topcoat in white, and is the section that has been in service for over 10 years. A second section has been added to the plant and, because of the excellent service in resisting the hot, sulfur-containing fumes and liquid, it has been coated in the same manner. Figure 6.52 shows one of the condensers in the plant, which has been in service for a 10-year period. Figure 6.53 shows a condensate tank in a chemical plant, which operates continuously at 250 °F. The white inorganic topcoat has maintained a clean white appearance for several years.

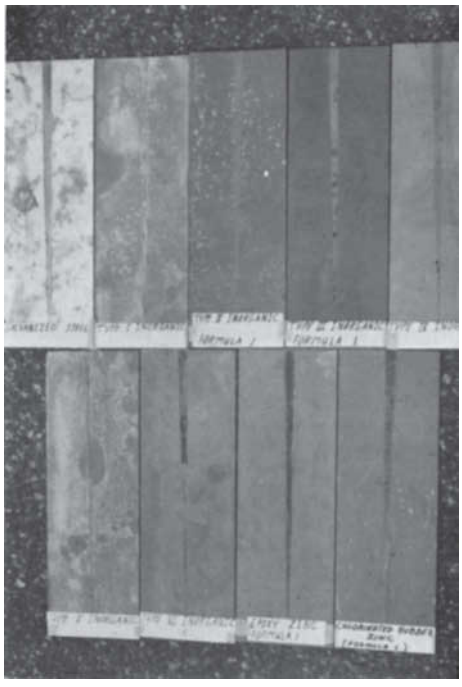


FIGURE 6.51: Various zinc-rich coatings compared by using the "V" method to determine the degree of initial protection to the bare steel. Note the difference in protection by the various coating types after three days of weather exposure. Note also the zinc reaction products that have covered some of the "V"s providing complete protection.



FIGURE 6.52: Barometric condensor located in a geothermal power plant coated with one coat of IOZ and one coat of inorganic white after approximately 10 years of exposure.

These inorganic topcoats may be made from either water-based or organic-based silicates, and represents an area where a major coating breakthrough has taken place with some widespread consequences. IOZ primers and polysiloxane topcoats can provide the two-coat anticorrosive coating systems with protection equivalent to or exceeding three coat zinc/epoxy/polyurethane systems.

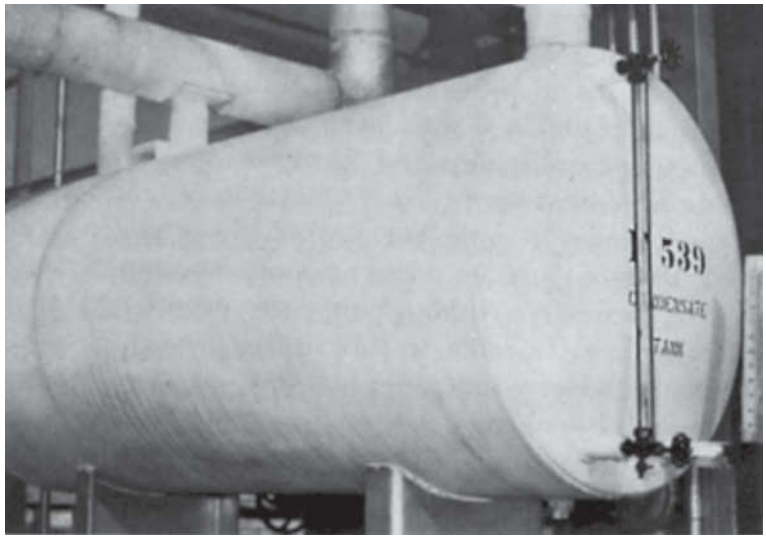


FIGURE 6.53: Condensate tank coated with IOZ base coat and white inorganic topcoat exposed to a chemical plant atmosphere.

Atmospheric Changes

As has been outlined previously, IOZ coatings change in the atmosphere. They change from their initial reaction, merely the evaporation of the solvent that laid down a rather porous film, to, upon aging, a much denser film. This can be seen in the scanning electron microscope photographs of a newly applied solvent-based zinc coating compared to a weathered coating of the same type and shown at the same magnification. Note in Figure 6.54 how the particles are laid down in a relatively discrete way; and the porosity that exists in the initial coating. Each individual zinc particle is visible, along with some of the ascicular reinforcing pigments. Some reaction has been started, as is indicated by the circle of light-colored reaction product around each of the particles of zinc. On the other hand, Figure 6.55 shows that after several years of exposure to the weather, the zinc particles are much less discrete; they look more as though they were encased in a matrix, and even some of the ascicular particles appear the same way. It appears to be a much denser film than that where the coating is initially applied.

A cross section of a similar coating, when newly applied, shows the porosity that exists in the coating all the way down to the metal surface. Figure 6.56 shows the discrete zinc particles as they are formed in the body of the coating, and the excellent wetting of the coating as it is applied over the sandblasted steel surface (the solid area at the bottom of the photograph). Note the manner in which the coating conforms to the sandblasted surface.

Figure 6.57 shows a solvent-based coating after it has been applied to the surface for several years. The cross section displays the individual zinc particles and thus indicates the buildup of the matrix around the zinc particles and, in general, the reduction of the porosity within the coating. Also note the continued excellent wetting of the steel surface and the appearance of a light reaction product at the coating-steel interface.

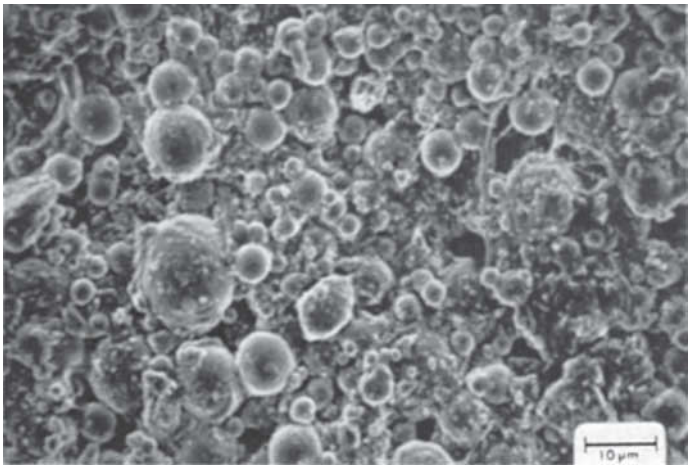


FIGURE 6.54: SEM photograph (surface view) of a newly applied solvent-based IOZ coating. Note the initial porosity.

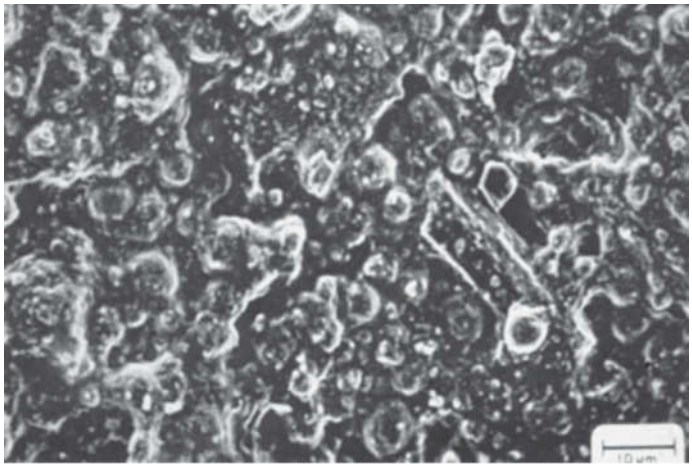


FIGURE 6.55: SEM photograph (surface view) of a weathered solvent-based IOZ coating. Note the dense structure of the coating.

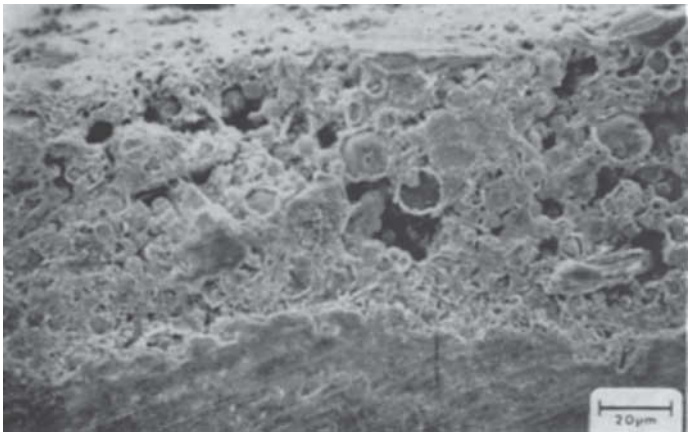


FIGURE 6.56: SEM photograph of a cross section of newly applied solvent-based IOZ coating. Note the porosity, the coating surface, and the intimate contact with the sand-blasted steel.

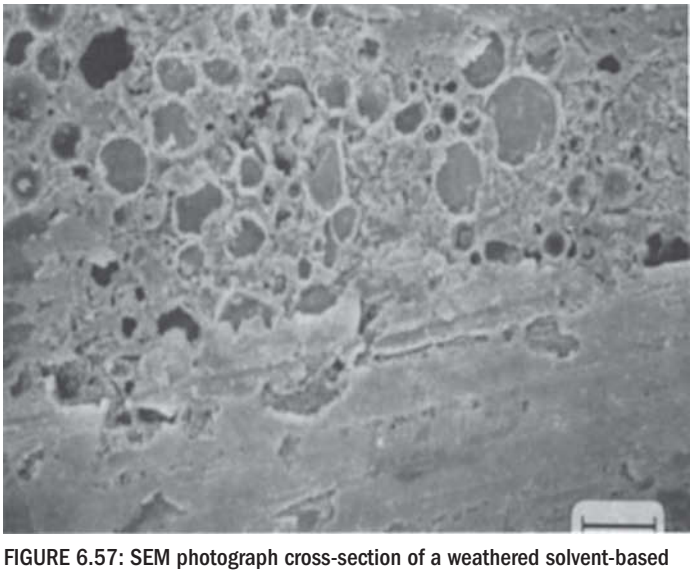


FIGURE 6.57: SEM photograph cross-section of a weathered solvent-based IOZ coating. Note the coating density, the zinc reaction products surrounding the zinc particles, and the excellent contact with the sandblasted steel.

Immersion

Marine atmospheres have proven to be an excellent exposure for IOZ coatings. Marine immersion, however, is quite a different condition. Inorganic coatings are seldom used alone when in direct contact with seawater. However, it has been shown that excellent galvanic protection of the underlying steel can be obtained for periods of time up to two years or more. Not only will the coating provide full corrosion protection, but it will be antifouling as well. The two properties go hand in hand; as long as the zinc provides corrosion protection, it also will provide protection from marine fouling. The zinc ions are responsible for both reactions.

This condition, however, tends to change with time, and at some period from 18 months to beyond two years, the coating ceases to provide CP and becomes inert. At this time, the coating also will start to allow growth of marine organisms. This inerting reaction of the coating reverses its polarity so that instead of being anodic, it becomes cathodic. This phenomenon also has been noted in the literature by M.O.P. Velsboe, who states,

> A current will start to flow if a steel panel coated with zinc paint. is connected to a bare steel panel. The current can be measured on the meter. The current will drop as time goes by and so, when measured against a reference electrode, the current will become zero after some time telling us that the galvanically active period of the paint is over. But no rust will be visible on the coated panel even if it is left for months in water. This means that the film protects the steel from rusting even if it is no longer galvanically active. The pores have been blocked completely. If the paint on the panel is then scraped down to the steel, the current will start to flow again because there is still excess metallic zinc in the paint film.[32]

Figure 6.58 is a good example of this. These panels were fully immersed in seawater approximately one foot below the surface for 11 years. Note the corrosion along the edges of the panels where fouling made a break in the coating. Even where the oysters were tightly attached to the center portion of the coating, it is completely intact and completely protecting the steel.

Figure 6.59 shows the coating surface that existed beneath one of the tightly adherent oyster shells. Some of the coating was broken away when the oyster was removed, but the zinc particles continue to exist along with the dense in- organic structure surrounding the zinc particles. The surface of the coating had become completely inert and the coating was acting as an inert coating over the surface of the steel, fully protecting the metal by its inert film rather than by cathodic protection. Uhlig recognized the same reaction.[38]

At room temperature, in water or dilute NaCl, the current output of zinc as an anode decreases gradually because of insulating corrosion products which form on its surface. In one series of tests, the current between a couple of Zn and Fe decreased to zero after 60 to 80 days and a slight reversal of polarity was reported.

In this case, the zinc referred to is metallic zinc or galvanizing. It also is interesting to note that the same reversal of polarity does

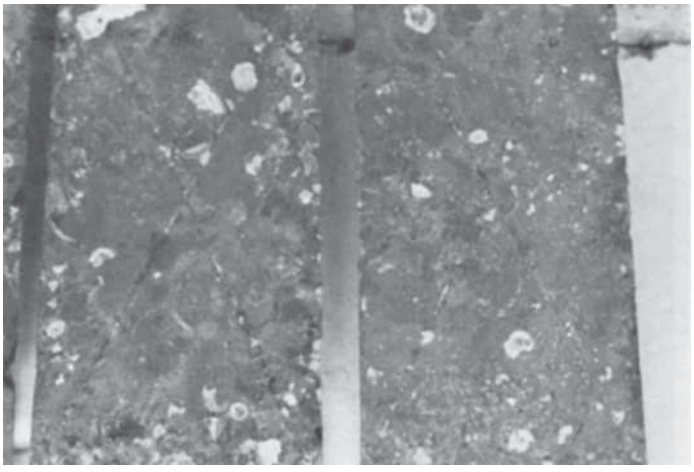


FIGURE 6.58: Water based IOZ coated panels immersed in seawater for 11 years. Note the excellent corrosion protection (except at edges), even at the scribes.

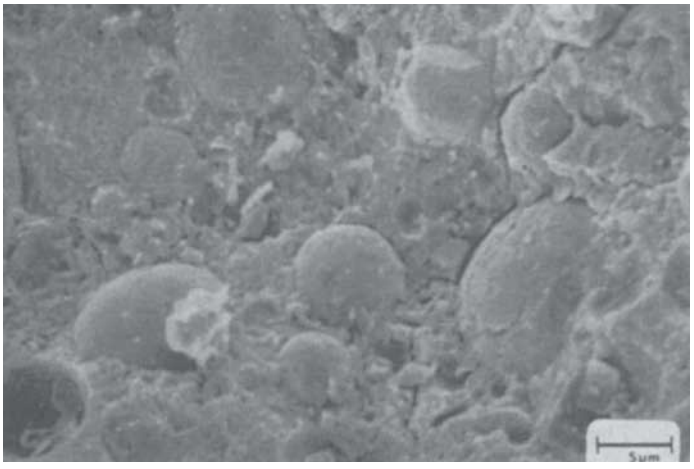


FIGURE 6.59: SEM photograph of the surface of the coating in Figure 6.56 after removal of a large oyster. Note the dense coating and encapsulated zinc particles.

not take place in the tidal area where the coating will continue to protect for much longer periods than where the coating is in full immersion.

The initial reactions that occur on zinc coatings in a marine environment are all similar to those previously shown for a rural atmosphere. The one substantial difference is the presence of the seawater salts, which create a highly conductive solution on the coating (Table 6.14).

It has been indicated by Pourbaix that zinc is thermo-dynamically unstable in the presence of water and aqueous solutions and tends to dissolve with the evolution of hydrogen in acid, neutral, or very alkaline solutions. Pourbaix also indicates that zinc in the presence of moderately alkaline solutions of pH between 8.5 and 10.5 can cover itself with a film of zinc hydroxide.39 When CO^2 is present, this pH range is extended from approximately 7 to 10.5. This is the pH range where the corrosion rate of zinc is at a minimum due to passivation by the hydroxide film.

The presence of insoluble zinc hydroxide on and within the coating is believed to inert or passivate the zinc coatings when immersed in seawater. Seawater has a pH of approximately 8. It also contains a substantial amount of bicarbonate so that conditions appear proper for the formation of zinc hydroxide as the principal corrosion product.

The reaction of metallic zinc, ionizing and forming an insoluble hydroxide film, is a slow process in the presence of other sea salts such as chlorides and sulfates. This accounts for the period of 18 months to two years that zinc coatings protect the steel over which they are applied.

Enough time is required for the zinc hydroxide to form in all of the pores of the coating and on the surface to prevent any additional zinc ions from forming. When this occurs, the coating surface becomes inert and thus cathodic to the iron substrate. If there are no breaks in the coating, it fully protects the surface; however, if a break does occur, it creates a condition of a very large cathode and a relatively small anode. Such a condition makes for rapid pitting at the break, which is what occurs. This phenomenon takes place irrespective of the type of zinc coating (i.e., galvanizing, IOZ coatings of all types, and even organic zinc-rich coatings (Figure 6.60).

The passivation of the zinc coating by the hydroxide deposit is also the reason for fouling organisms to deposit on the surface. As long as the heavy metal zinc ions are available, it makes an unsatisfactory surface for fouling attachment. As soon as the surface ceases to provide the soluble metal ions, the marine organisms no longer find it objectionable.

Most zinc coatings, because of the above type of reaction, are not generally recommended for use alone for seawater immersion conditions. They have been used effectively as a basic primer on steel surfaces for marine uses, ship bottoms, offshore platforms, and similar structures where the zinc coating has been overcoated with coatings such as vinyls, epoxies, and coal tar epoxy coatings.

The pH of a solution has a substantial influence on the solution rate of zinc. It is believed that the same essential reaction takes place

TABLE 6.14: Composition of Seawater and Ionic Constituents

	G/Kg of Water of		
Constituent	Salinity, 35 %	Cations %	Anions %
Chloride	19.353	Na^{+} 1.056	CL-1.898
Sodium	10.76	Mg^{++} 0.127	SO4 0.265
Sulfate	2.712	Ca^{++} 0.040	HCO3 0.014
Magnesium	1.294	K^{+} 0.038	Br^{++} 0.0065
Calcium	0..413	Sr^{++} 0.001	F^{-} 0.001
Potassium	0.387	_____	_____
Bicarbonate	0.142	Total 1.263	Total 2.184
Fluoride	0.001		

Source: J. Lyman, R.B. Abel, "Chemical Aspects of Physical Oceanography," *J. Chem. Education* 35 (1958): pp. 113–115.

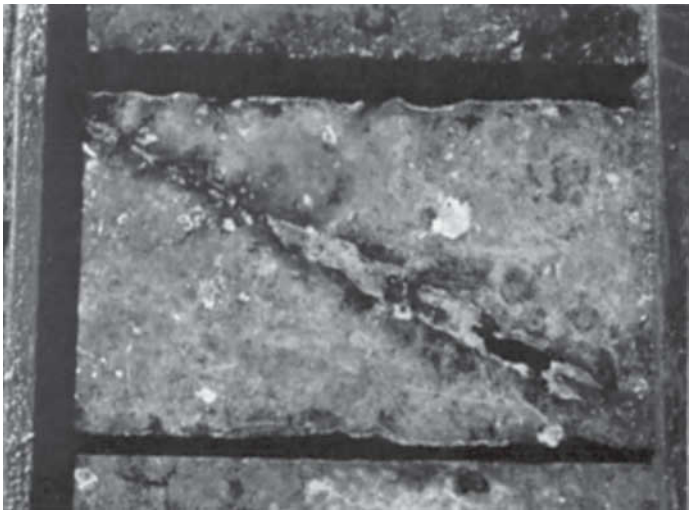


FIGURE 6.60: Corrosion anodes formed along scribe and on edges of panel coated with IOZ coating immersed in seawater. Note perforation of panel in lower anode area.



FIGURE 6.61: A white powdery deposit has penetrated the coating surface of some galvanized deck piping. The deposit formed beneath the coating has pushed the coating from the surface.

as was indicated for immersed zinc, except that during the rise and fall of the tide, carbon dioxide from the air tends to lower the pH slightly and the reaction product may be zinc carbonate in place of zinc hydroxide.

As indicated in Table 6.15, the solubility of zinc carbonate is substantially higher than for zinc hydroxide. As the zinc carbonate is slowly dissolved, the tidal surface is kept active, with the zinc coating continuing to provide CP.

There also is an interesting environmental reaction on zinc coatings in marine atmospheres. This is a reaction that takes place when zinc coatings, galvanizing, or in organic zinc, are coated with a relatively thin porous coating.

The coating in this case must be sufficiently porous to allow sodium and chloride ions to contact the zinc. In this case, the metallic zinc and sodium chloride react together in the presence of moisture to form a zinc oxychloride compound and sodium hydroxide. The reaction is as follows.

$$2Zn + 2NaCl + 3H_2O \rightarrow ZnOZnCl_2 + 2NaOH + H_2 \qquad (6.7)$$

It is interesting that above the pH of approximately 10.5, zinc reacts rapidly to form soluble zincates. As the sodium and chlorine ions penetrate the thin organic topcoat, they are held within and under the coating, causing a buildup of pH from the NaOH formed from Equation (6.7). The zinc oxychloride is insoluble, and with continuing contact with moisture, salt, and carbon dioxide, voluminous white salts are formed, which penetrate the porosity of the top-coating, forming a heavy, white precipitate on the exterior, as well as building up underneath and disrupting the coating. Such a reaction is not uncommon aboard ship or on offshore structures and has created conditions whereby both the zinc coating and the topcoat have been severely damaged. This reaction consumes substantial amounts of zinc, with the underlying zinc coating being rapidly depleted so that the entire coating system must be removed and replaced (Figure 6.61).

Fortunately, such a condition can be overcome at the time that either the galvanizing or the IOZ coating are originally topcoated. The topcoat, under these conditions, should be adherent, inert, impervious, and above all, thick enough to provide a completely nonporous film through which ions, such as sodium chloride, cannot penetrate. Thin vinyl, epoxy, and other coatings have shown the above reaction; on the other hand, when these materials have been properly applied and applied in proper thickness, no evidence of such a reaction takes place.

When only a cosmetic coat is to be applied, under conditions where sodium chloride ions are available, it may be better to leave the zinc coating bare rather than to put a coating of improper thickness or porosity over it.

As indicated by the various exposures for zinc and inorganic coatings, the environment has an important effect on these coatings. It is responsible for conditions whereby the coating is much more resistant and long lasting, as well as conditions which can lead to its breakdown. Fortunately, the reactions to the environment are such that the majority of zinc-coated surfaces, either galvanized or inorganic zinc, have provided protection to steel surfaces that is not possible by any other form of protective coating.

TABLE 6.15: Solubility of Zinc Topcoats

Porous Topcoating	Solubility in Cold Water
Zinc Carbonate	0.001 gr/100 m.l.
Zinc Oxide	0.00016 gr/100 m.l.
Zinc Hydroxide	0.00000026 gr/100 m.l.

Source: *Handbook of Chemistry and Physics,* 47th Ed., Chemical Rubber Co., Cleveland, OH.)

The use of IOZ coatings for actual immersion service has long been an area of debate. Many coating and corrosion engineers claim they should be used for atmospheric purposes only, while others recommend immersion when properly topcoated. This "properly topcoated" criteria seems to be the key to immersion resistance, particularly in water and saltwater, and the organic primer applied directly over the inorganic zinc is the key to its success. One very effective immersion coating system consists of:

1. One coat solvent-base IOZ
2. One coat epoxy polyamide primer
3. Two coats epoxy coal tar
4. A total thickness (complete system) of 500 μm (20 mils)

This has been an effective system for ship bottoms and ballast and ballast crude oil cargo tanks. Another system, which originally was used for ship bottoms and boottopping areas but which has declined in use due to VOC restrictions, has been:

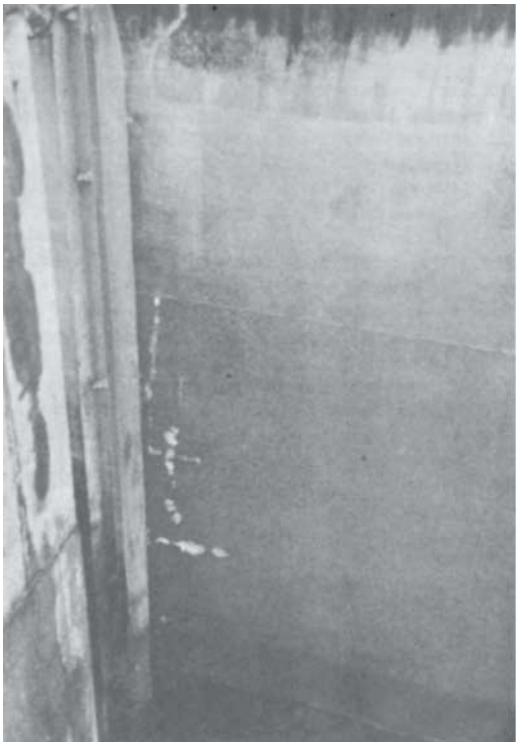


FIGURE 6.62: Close-up view of boot-topping (right) on a VLCC after five years of exposure. Note the smooth, corrosion-free surface. The boot-topping is immersed, except when the ship is light (without cargo or ballast). Note severe abrasion from dock bumpers (left).



FIGURE 6.63: View of boot-topping and topside coating after five years of service. Inorganic base coat-vinyl topcoat system. Note the corrosion-free surface.

1. One coat IOZ
2. One coat vinyl primer
3. Two coats vinyl topcoat
4. A total thickness (complete system) of 200 to 250 μm (8 to 10 mils)

Both solvent-based IOZ and post-cured water-based IOZ are suitable for topcoating and use in water immersion service. The self-cure water based IOZ with topcoats tends to result in reduced topcoat adhesion to the water based inorganic zinc and blistering in water immersion service.

Figures 6.62 and 6.63 show the boottopping on a very large crude carrier (VLCC) after five years of continuous service. Even with the extreme abrasion caused by the dock shoes, there is no corrosion or other coating failure in evidence. The ship utilized the same coating system on the bottom, and it was equally effective.

Topcoating of Inorganic Zinc Coatings

Millions of square feet of surface have proven that IOZ coatings are very effective when used alone and not topcoated. However, topcoating to improve chemical resistance, general corrosion resistance, or appearance is the more common practice. Most inorganic coatings are a nondescript grey and may become mottled by weather exposure. This in no way changes their corrosion resistance; in fact under some conditions the uncoated inorganic may perform better than one that is poorly topcoated (e.g., voluminous white deposit buildup). Topcoating has become the rule with IOZ coatings rather than the exception, and most of the high performance coatings not only adhere well to the IOZ, but the lives of the topcoats are multiplied several times due to lack of undercutting. The IOZ, organic topcoat system provides maximum corrosion resistance and life for coatings in difficult corrosion areas.

While topcoating is a preferred coating method, it also can create a serious problem under many conditions. If an organic topcoat is applied over an IOZ-based coat prior to its advanced stage of cure, immediate blistering of the topcoat occurs while the coating is still wet. These blisters may break, leaving a pinhole within the film, or the organic coating may be sufficiently strong so that the blister forms and stays in the film. Often times, as the coating dries, the blister falls back and flattens out in the surface. The areas under the blister will have no adhesion. This problem is due to the volatile materials or solvents evaporating into the porous zinc coating as the organic coating dries. If the surface of the organic dries rapidly and forms a skin, the vapor pressure from the volatile solvents within the zinc coating exert sufficient pressure to push up underneath the topcoating and form blisters (Figure 6.64).

If the surface is warm, the solvent evaporation is more rapid, the vapor pressure is greater, and the blistering is exaggerated. The opposite is, of course, true for cooler surfaces. There are several approaches to overcoming the problem.

1. A non-solvent topcoating may be used. In this case (there are a number of non-solvent or very low solvent topcoatings available), there is little or no solvent to evaporate. As the coating is applied, it flows into the pores and dries in place, sealing the surface of the inorganic zinc coating. This is the best approach to the problem of blistering.
2. A coating containing a high boiling or slow evaporating solvent may be used. This acts in many ways like the non-solvent coat-

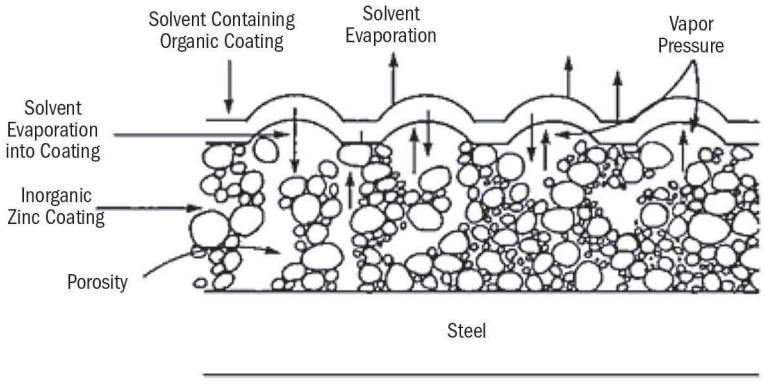


FIGURE 6.66: An IOZ topcoat blistered from the vapor pressure created by a rapidly drying surface.

ing. With the high boiling, low volatility solvents, the coating can penetrate and flow on the surface without any buildup of vapor pressure. This reduces the blister problem. Care should be exercised, however, on warm or hot surfaces such as tank tops.

3. Some applicators and coating manufacturers recommend the application of a thin flash or mist coat followed, within minutes, with a full coat of the organic topcoat. The solvent flashes off of the thin membranes and semi-seals the IOZ surfaces. This process is less than foolproof since the zinc coating is still porous, solvents can penetrate, and blisters still form. It does help on cool and on vertical surfaces that are not warm, but it is not completely effective on surfaces warm from the sun.
4. Water-based topcoats also are used. In this case, the vehicle is a water emulsion, and the topcoat acts in many ways like the coatings with a slow evaporating solvent. Water evaporates slowly and allows the coating to flow without building up much vapor pressure. Also, and this may be more important, the vehicle is a dispersion (emulsion) and forms a film in a manner different from that of a solvent-based coating. The emulsion is a series of discrete particles until almost all of the water has evaporated. At that time, the particles coalesce into a film; while prior to that time, the coating is porous to water and water vapor. Thus, if a thin water-based emulsion is applied for cosmetic purposes and the structure is in a humid area where sodium chloride or other chemical salts are present, the porous top- coat could cause the zinc coating to self-destruct by forming voluminous white salts on the surface, as was previously described. Industrial grade water borne acrylic topcoats have performed very well applied directly over IOZ primers.

This does not mean, however, that all IOZ coatings will cause topcoats to blister, or even that this problem occurs in most inorganic topcoat systems. In fact, coatings which have cured from a few days to several months, depending on the area and weather conditions, usually do not cause blistering. Post-cured inorganics are normally free of or have significantly reduced incidence of blistering problems, since the post-cure seals the surface with insoluble salts during the curing process. There is little chance that the thin preconstruction primers will cause blistering either. This type of coating is sufficiently thin so that little porosity exists. The organic modified IOZ coatings also have been used to help eliminate this problem. In this case, the organic modifier in the film helps in terms of volume to reduce the coating porosity.

All in all, the blistering of topcoats over inorganic zinc can be a frustrating problem. On the other hand, advance planning and timing of the topcoat application during cool conditions and the use of one or more of the previously described approaches can prevent this application difficulty.

Rapid Topcoating of Inorganic Zinc Coating

Historically, under most application conditions, IOZ coatings have undergone considerable exposure times so that the initial cure is complete before they are overcoated. This had always been considered necessary. This is no longer the case, as rising costs of fabrication and construction have created pressures to finish projects on time and on budget, leaving precious little time for optimum curing of inorganic zinc coatings prior to topcoating. Special formulations of solvent-based inorganics have been created for this purpose by the addition of low molecular weight reactive additives and faster reacting solvents. By increasing the degree of pre-hydrolysis of the silicate polymer in solvent-based IOZ primers, the amount of moisture needed from the air is reduced to a minimum for a complete cure. Since organic films have a definite moisture transfer rate, the cure can be completed after the topcoat has been applied. Daniel H. Gelfer, in a paper, "Rapid Topcoating of Inorganic Zinc Rich Primers," explained this mechanism.

Mechanism of Curing Under Topcoats

In an attempt to explain these results, the following hypothesis was evolved:

1. The silicate binder in the primer film at the moment of topcoating is at the same degree of prehydolysis and inorganic polymer formation as formulated in the wet package condition.
   (a) The brief time interval between primer application and topcoat application is not sufficient for any moisture uptake from the atmosphere.
2. During the saturated humidity exposure period, moisture vapor permeates through the topcoat, in an amount deter mined by the moisture vapor permeability of the topcoat.
3. Depending upon the moisture vapor permeability of the topcoat, sufficient water will permeate to and be made available to the silicate vehicle of the primer and will react with and complete the hydrolysis of the vehicle.
4. The volatile byproduct of the hydrolysis reaction, ethyl alcohol or other alcohol, permeates the organic topcoat in the opposite direction, without disrupting the topcoat, and escapes into the external atmosphere.[40]

Differences in the moisture vapor permeability characteristic of the organic topcoat were reviewed to see how they would affect the 72-hour test results obtained above. The permeance of these topcoats, plus other candidate topcoats, is recorded in Table 6.16.

Since Table 6.17 consists only of laboratory tests, additional tests and field trials have established that the rapid overcoating of certain IOZ primers can be applied successfully. Touch dry times can be as quick as 10 minutes, hard dry 60 minutes and minimum recoat time as low as 4.5 h. It should be remembered, however, that topcoating of self-curing IOZ films in the first 24 h after application of the zinc is problematic, dependent on the rate of cure of the IOZ film, ambient temperature, and the relative humidity; there can be a resultant decrease in porosity of the applied film. One item needs to be kept in mind when rapid topcoating the IOZ coatings, the coating system will be more sensitive to mechanical damage than when the inorganic zinc coating is allowed to cure for a longer period of time before topcoating.

TABLE 6.16: Permeance of Organic Topcoats

Topcoat Type	Permeance-Metric Perms (ASTM E96) (Gm/24 h. Sqm. mm Mercury)
High-Build Polyamide Epoxy	0.35
High-Build Fast-Drying Epoxy	0.30
Epoxy/Urethane	0.105
Coal Tar Epoxy	0.042
High-Build Vinyl	0.092
Vinyl-Acrylic	0.115
Chlorinated Rubber	0.089

Note: Comparing these permeance values with onset of primer hardness reveals a correlation between rapid development of primer hardness and the higher permeance values of the topcoat.

Source: "Organic and Inorganic Zinc-Filled Coatings for Atmospheric Service," Report 6B173 (Houston, TX: NACE, 1973).

TABLE 6.17: Immersion Performance: Single-Package Inorganic Zinc Topcoat Systems 5500 Hour Synthetic Seawater Immersion After 1200 Cleveland Humidity Chamber Exposure

Topcoat Type	Primer Dry Time (Hours)	Adhesion to Steel	Intercoat Adhesion	Blistering (ASTM D-714)	Scribe Corrosion (ASTM D-1654)
High-Build Polyamide	1	Good	Good	None	Nonee
Epoxy	4	Good	Good	None	None
	7	Good	Good	None	None
	16	Good	Good	None	None
Fast-Drying Epoxy	1	Fair	Good	None	None
	4	Good	Good	None	None
	7	Good	Good	None	None
	16	Good	Good	None	None
Coal Tar Epoxy	1	Poor-Fair	Poor-Fair	None	None
(16 mils)	4	Poor-Fair	Poor-Fair	None	None
	7	Poor-Fair	Poor-Fair	None	None
	16	Poor-Fair	Poor-Fair	None	None
Epoxy Tiecoat/Urethane	1	Satisfactory	Satisfactory	Few No. 8	None
Topcoat	4	Satisfactory	Satisfactory	Few No. 8	None
	7	Good	Good	Few No. 8	None
	16	Good	Good	None	None
Chlorinated Rubber	1	Good	Good	None	None
	4	Good	Good	None	None
	7	Good	Good	None	None
	16	Good	Good	None	None
High-Build Vinyl	1	Satisfactory	Satisfactory	Dense No. 8	None
	4	Good	Good	Dense No. 8	None
	7	Good	Good	Dense No. 8	None
	16	Good	Good	Dense No. 8	None
Vinyl Tiecoat/Vinyl Topcoat	1	Satisfactory	Satisfactory	Few No. 6	None
	4	Good	Good	None	None
	7	Good	Good	None	None
	16	Good	Good	Few No. 8	None
Vinyl Tiecoat/Vinyl-Acrylic	1	Fair	Fair	Dense No. 8	None
Topcoat	4	Good	Good	Dense No. 8	None
	7	Good	Good	Few No. 8	None
	16	Good	Good	Dense No. 8	None

Source: D.H. Gelfer, "Rapid Topcoating of Inorganic Zinc-Rich Primers—A Case for Improved Productivity," CORROSION/80 (Houston, TX: NACE, 1980).

Comparison Summary

As an indication of the effectiveness of various zinc-rich coatings, Table 6.18 provides some results of actual full-scale applications after several years of service. Both the coatings and the service conditions are compared. Zinc-rich coatings, both alone and overcoated, are represented, with the results indicating the excellent corrosion protection provided by most zinc-rich products. Generally, the IOZ coatings provide longer continuous service than do the organic zinc-rich products.

Tables 6.19 and 6.20 give a direct comparison of general resistance and physical properties of both organic and IOZ-rich coatings. Such tables summarize the difference between the two systems and provide general information about the two coating types. The information is not specific for any individual coating.

IOZ coatings have come a long way since they were first conceived by Victor Nightingall. Their use is expressed in acres rather than in square feet, and they have proven effective in hundreds of areas of severe corrosion. They have provided revolutionary corrosion control irrespective of the size, complexity, or location of the structure, and in one coat, they have reduced both initial capital cost and the continuing cost of maintenance. Even with such extensive use and service, however, many believe that their development is still incomplete. These inorganic-based materials may one day provide the means by which all metal surfaces are both protected and decorated. Their outstanding qualities have been proven, it requires only imagination and research to match them with the work to be done.

TABLE 6.18: Experience Records on Various Zinc-Filled Coatings

Binder Type	Type of Surface	Geographic Location	Exposure	Surface Preparation	Coating System	Performance
Inorganic silicate, post-cure	Structural steel in a chemical plant	Los Angeles, CA	High humidity, salt air, industrial fumes	Sandblast Near White NACE No. 2	1 coat zinc silicate 1 coat tiecoat 2 coats vinyl Total thickness 14 mils	10 yr maintenance-free service and still offering excellent protection
Inorganic silicate, post cure	Steel piping on cooling tower	Lake Charles, LA	High humidity	Sandblast Near White NACE No. 2	1 coat 3 mils	12 yr continuous service
Inorganic silicate, self-cure	Structural steel	Cape Kennedy, FL	High humidity, salt air	Sandblast Near White NACE No. 2	1 coat zinc silicate 1 coat vinyl tiecoat 2 coats vinyl	Applied in 1959, touch-up of topcoat, primer still intact and in service (1967)
Inorganic silicate, self-cure	Structural steel	Texas Gulf Coast	High humidity, industrial fumes	Sandblast Near White NACE No. 2	1 coat zinc silicate 2-3 mils	5 yr service (1967)
Inorganic, phosphate	Tank exterior	Texas Gulf Coast	Coastal industrial atmosphere	Sandblast Near White NACE No. 2	1 coat zinc primer, 3 mils 1 coat vinyl, 5 mils	In excellent condition after 8 yr service
Organic Epoxy Ester	Unitized automobile body, blind fenders, box sections	Detroit, MI	High humidity, road salts	Pickled and/or phospated steel	1 coat, 2-3 mils	Prevented corroding of car body for 8 yrs
Organic Chlorinated rubber	Structural Steel	Chicago, IL	Industrial fumes	Sandblast Near White NACE No. 2	1 coat chlorinated rubber zinc 1 coat chlorinated rubber finish 5 mils	6 yrs condition perfect
Organic Phenoxy	Structural steel, paper mill	Charleston, SC	Coastal area, acid fumes	Shop blasted	1 coat zinc primer 2 coats epoxy 2 component 8-10 mils total dry film	6 yr service, no touchup or repaint to date
Organic epoxy, two-component	Structural steel	New Jersey	Industrial fumes, coastal atmosphere	Sandblast Commercial Blast NACE No. 3	1 coat epoxy zinc primer 1 coat epoxy topcoat	After 5 yr topcat has weathered to expose primer Complete topcoat recommended.
Organic polystyrene	Galvanized structural steel	Philadelphia, PA	Rural and mild industrial	Repair of damaged galvanized steel, field repair	1 coat	Requires touch-up in 4-5 yrs. Pinhole rusting observed

Source: "Organic and Inorganic Zinc-Filled Coatings for Atmospheric Service," 6B173 (Houston, TX: NACE, 1973).

TABLE 6.19: Resistance of Zinc-Filled Coatings in Various Environments

Organic	Inorganic
Water and Moisture	
Excellent resistance to high humidity, splash, and spray conditions in both fresh and saltwater atmospheres.	Excellent resistance to high humidity, splash, and spray conditions in both fresh and saltwater atmospheres. The inorganics in single coat applications have a long history of excellent service in humid environments.
Inorganic Acids, Oxidizing Agents, Organic Acids	
Not recommended for direct splash, spillage, or fume from inorganic acids, oxidizing agents, and organic acids.	
Alkalies	
Will tolerate mild alkaline atmospheres. Alkyd vehicles are not recommended for alkaline service.	Not recommended for prolonged exposure to alkaline atmospheres. Silicate binders are attacked by dilute alkalies.
Salt Solution	
Excellent resistance to splash, spillage, and fog of neutral salt solutions. Resistance to acid and basic	Excellent resistance to splash, spillage, and fog of neutral salt solutions.
Solvents	
Very limited resistance to solvents. Epoxy, two-components, alkyds, and epoxy esters can be used aliphatic hydrocarbon service.	Excellent resistance to aliphatic, aromatic and dry hydrocarbons, petroleum, products, esters, and ketones.
Oils and Fats	
No information available.	Limited information indicates satisfactory performance. Not satisfactory in fatty acids or oil iwth high acid number.
Gases	
Coatings are permeable and will be attacked by wet acidic gases such as SO_2, SO_3, Cl_2, and also by alkaline gases such as NH_3.	

Source: "Organic and Inorganic Zinc-Filled Coatings for Atmospheric Service," 6B173 (Houston, TX: NACE, 1973).

TABLE 6.20: Physical Properties of Applied Zinc-Filled Coatings

Organic	Inorganic
Temperature Limitations	
Maximum dry service temperature at which a coating can be used is determined by the type of binder. The normal maximum temperature limits of the various binders are listed. These same binders, when loaded with zinc dust may yield films with different service temperature. Chlorinated Rubber 71 °C (160 °F) Styrene-Butadiene 71 °C (160 °F) Polystyrene 71 °C (160 °F) Epoxy Ester 107 °C (225 °F) Phenoxy 120 °C (250 °F) Epoxy, 2-Component 120 °C (250 °F) Silicone Alkyd 232 °C (450 °F) Silicone 400 °C (750 °F)	Provide protection at a maximum service temperature of 315 C° (600 °F). Some have been reported to withstand intermittent temperature service 50 593 C (1,100 °F) when topcoated with silicone aluminum. The latter temperature is above the melting point of zinc (420 °C) 788 °F.
Abrasion and Impact Resistance	
Epoxy, esters, thermoset epoxies, and thermoplastic epoxies have good abrasion resistance. Chlorinated Rubber and styrene binders lack this resistance initially. As organic films age, their abrasive resistance increases but never reaches that of the inorganics.	Possess outstanding impact and abrasion resistance when thoroughly cured.
Weathering	
Excellent resistance to atmospheric weathering when when applied in 2- to 3-mil dry film thickness. Typical matte gray appearance will lighten on exposure. White rust common to galvanized steel can form can form on zinc-filled coatings. Optimum performance is obtained from multiple coats of zinc paint or when topcoated with appropriate finish coat.	Excellent resistance to atmospheric weathering in one coat. Typical matte gray appearance will lighten on exposure. White rust common to galvanized steel can form on zinc filled coating.
Toxicity	
In general, the cured films are considered nontoxic. The use of extender pigments, plasticizers, and resin modifiers may change the nontoxic status significantly.	Cured films using zinc dust as the only pigment are considered nontoxic and have been used as a container lining for dry food products. The use of certain extender pigments, particularly lead compounds, will influence the toxicity rating
Weight of Applied Coatings	
Dry film specific gravity normally ranges from 4.5 to 5.5, which will yield films varying in weight from 0.02 to 0.03 pounds per square foot per mil.	
Electrical Properties	
Should be considered electrically conductive coatings. The degree of conductivity will depend upon zinc content, binder type, as well as the amount and type of extender pigment.	
Adhesion	
Excellent adhesion to sandblasted and acid-pickled steel. Polystyrene, phenoxy, and chlorinated rubber coatings are applied also over galvanized steel, aluminum, and copper surfaces with excellent results.	Excellent adhesion to properly sandblasted steel surfaces. Adhesion to sandblasted aluminum is good.
Appearance	
Organic and inorganic zinc-filled coatings are flat. Color may not be uniform.	

Source: "Organic and Inorganic Zinc-Filled Coatings for Atmospheric Service," 6B173 (Houston, TX: NACE, 1973).

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ANNEX 6A

A Short History of Water-Based High-Ratio Potassium Silicate Inorganic Zinc Coatings

One of the most controversial coatings ever developed has been water-based high-ratio potassium silicate inorganic zinc (WBHRZ).

The origin of this technology is the original NASA patent #3,620,784 issued on November 16, 1971. The mole ratio of silicate to alkali metal was 5.3:1. On November 20, 1997, patent #WO1997043350 A1 was issued for a corrosion-resistant, weldable coating composition having a molar ratio of silicate to potassium of 4.2 to 6.0. The formula included iron phosphide as well as zinc and potassium silicate. Another patent, U.S. 4162169A, was issued July 24, 1979, for a paint binder utilizing either potassium or a sodium silicate dispersion having a silicon dioxide to alkali metal oxide mole ratio of from 4.8:1 to 6.0:1. This patent utilizes a silicon dioxide hydrogel.



Figure 6A.1: Underside of bridge after 17 years of exposure (no apparent rusting). Source: Polyset Co.

Early History

The earliest tests and applications under the various U.S. Government programs and locations established the excellent corrosion prevention properties of the original NASA patents. Commercialization of the technology did not achieve any significance until the licensing of the technology to Inorganic Coatings, Inc. in 1985. The Polyset Co. manufactured the silicate portion of the product (IC531) (Figure 6A.1). It had a mole ratio of silicate to alkali metal of 5.3:1. The inorganic zinc (IOZ) pigment was purchased on the open market. The product featured a very fast cure.

Despite the tendency of the product to plug up the conventional spray guns recommended for its application, the company made significant inroads into the government facilities, bridges, and marine decks and chain lockers. Dry film thickness of up to 200 µm was achieved without mud cracking and the decks of a number of ships were reported to be in excellent condition after 10 years of service.[1] Unfortunately, sometime in 1991/1992, Inorganic Zinc, Inc. changed its source of supply for the potassium silicate solution with disastrous results. IC531 applied to decks of ships by the same crew that had such great success previously suddenly disappeared during the first rain.[1]

After the original patents expired, several major global scale coatings manufacturers introduced water-based high-ratio IOZs with modification of their own (including modification with lithium silicate), but market share continued to dwindle. Technically, any water-based potassium silicate IOZ with a mole ratio above 3.2:1 can be considered to be high-ratio IOZ. However, the lower ratio water-based inorganic potassium silicate IOZ will not have the same cure mechanism as the NASA patented 5.3:1 IOZ.

TABLE 1: Life to first maintenance in years of IOZ and hot dip galvanizing coatings from AS/NZS 2312 1994 and 2002 versions.

System	Designation	ISO Environment				
		C3	C4	C5-I	C5M	Tropical
Sa 2½/75µm IZS-SB	1994 MP1A 2004 IZS1	5-10 10-15	NR 5-10	NR 2-5	NR 2-10	NR 10-15
Sa 2½/75µm IZS-WB (not in 1994 version)	2002 IZS2	25 +	15-25	2-5	10-15	25 +
Sa 2½/ 125µm IZS-WB	1994 LP3 2002 IZS3	10-20 25 +	10-20 25+	NR 5-10	10-20 15-25	10-20 25 +
Hot Dip Galvanize	1994 GZ 2002 HDG 600	10-20 25 +	5-10 15-25	2-5 2-5	NR 5-15	10-20 25 +

NR: Not Recommended, SB: Solvent Borne, WB: Waterborne, IZS: Inorganic Zinc Silicate



FIGURE 6A.2: Corrosion Test Panels Next to seashore in Australia after 30 years exposure.



Figure 6A3: WBHRZ on deck plate offshore after 13 years of service.



Figure 6A.4: WBHRZ Under lower deck offshore after 13 years of service.

In Southeast Asia, the standard that specifies performance and formulation requirements for IOZ silicate coatings is AS/NZS 3750[2] Part 15. This standard describes six types of which Type 3 (WB), Type 4 (SB), and Type 6 (WB High Ratio) are currently used as single coat systems and primers. It should be noted that Type 6 zincs contain a mole ratio of 4.7:1 silica to alkali metal as defining "high ratio."[3]

Self-cured alkali silicates cure initially by the evaporation of water from the coating. This concentrates the water-soluble silicate binder leading to condensation and precipitation of the basic zinc silicate and polymerized silica matrix. Ultimate hardness is achieved with ongoing polymerization of silicate particles with time. A consideration during this process is the formation of an alkali metal hydroxide as the zinc replaces the alkali metal on the silicate. If water ponding or dew occurs on the coating during this period the silica matrix can be re-dissolved and leached from the coating with the highly alkaline solution. Under normal cure conditions the hydroxide reacts with carboxilic acid as carbon dioxide (CO_2) is absorbed from the air and a neutral surface is achieved.

A driving force in the use of waterborne zinc silicates in Australasia has been the life expectancies attributed to them in AS/NZS 2312[4] as in Table 1:

A widely reported successful application of WBHRZ has been the work of Alex Szokolik on platforms in the Bass Strait offshore Australia. Some of his original test panels exposed just a few meters from the seashore are shown in Figure 6A.2. The bottom four panels on the left side are all WBHRZ; the others on the right are multi-coat systems of various types.

Figure 6A.3 and 6A.4 shows the condition of deck plate and under deck areas of one offshore platform coated with water based high ratio potassium silicate IOZ after 13 years of service.

Beginning in October 2010 the Polyset Co. began to reintroduce the 5.3:1 ratio water-based potassium silicate IOZ product to the market as based on its original silicate formula used in the NASA patents. It uses 98% pure zinc pigment that meets the standard of ASTM D520,[5] Type III. To mitigate the gun-plugging tendency of the fast curing formula the company has used unique conventional spray guns made by 3M and Devilbiss. The internal parts are composed of Delrin polymer to isolate the silicate mixture from contact with the metal body of the guns.

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7 Structural Design for Coating Use

Design is a key word in our culture. It not only dictates fashion styles, but influences the wide world of industrial products and plants, offshore structures, ships, aircraft, household equipment, and consumer products as well. Design and engineering are as important to our complex, mechanical society as raw materials, for without the ability to visualize an end product and the skills to realize that vision, most basic materials would be useless.

Even the formulation of protective coatings involves designing. Formulation, in fact, is the design of a coating for a specific job, for the results of improper selection and combination of materials to form a coating could be much worse than having no coating at all. Coatings in themselves, however, cannot be designed as end products. Since a coating must be applied and formed in place before it can perform the role for which it was designed, it is part of a much larger design (e.g., that of a structure, a piece of equipment, or an entire plant). The design and construction of a coated structure under corrosive conditions are the keys to its life span and ultimate effectiveness. Thus, a large part of expensive service failures due to corrosion would not occur if proper precautions were taken during the design stage.



FIGURE 7.1: Typical bridge construction where design for coating and corrosion protection has been overlooked. Note the angles, corners, edges, and open box sections.

One factor in the proper design of a coating is its acceptability for application to the plant or structure for which it was intended. On the other hand, the structure or object to which the coating is to be applied must be designed in such a way that it can easily accept the coating and provide a proper base for it. This is an important concept for the architect or engineer who is responsible for the design of a building or plant. Many of them do not understand that if a structure is not properly designed to accept a coating and allow it to form a continuous film of even thickness, it is difficult to keep the structure free of corrosion.

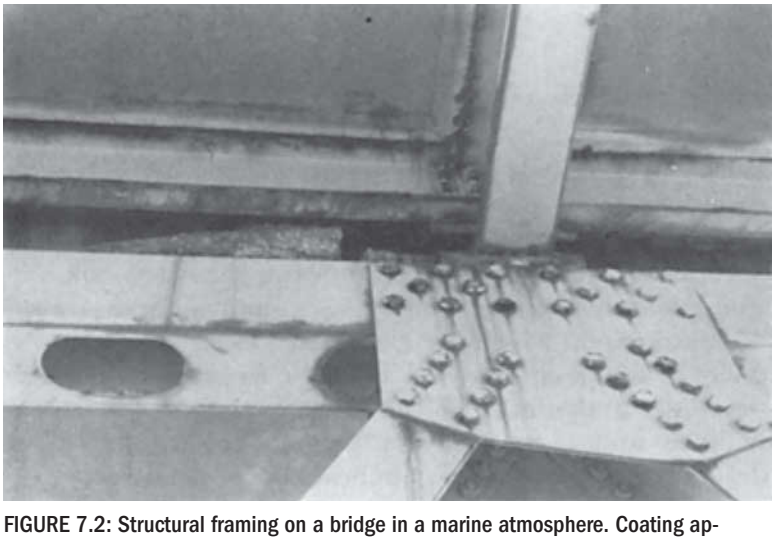


FIGURE 7.2: Structural framing on a bridge in a marine atmosphere. Coating application is approximately two years old. Note the heavy scale (left center) that has dropped from the back of the channel above where coating access was impossible. Note also the rusting of edges, bolt heads, and overlapping steel sections.

Bridges are often a good example of this, since many of them have been built with open box beams, hidden recesses, rivets, bolts, overlapping joints, and many other untenable problems from a coating and corrosion standpoint (Figure 7.1). Figure 7.2 is a closer view of the junction of several key bridge members showing the open box section, the overlapping bolted plates, and hidden and inaccessible areas, which are all exposed to a marine atmosphere. Such design may be adequate from a strictly engineering standpoint, but can soon lead to costly maintenance and even steel replacement because of poor design for proper coating application. Fortunately, today's bridge designers are focusing more on eliminating built-in corrosion traps by emphasizing smoothness of detail and aesthetics.



FIGURE 7.3: Perforation of the web of an H beam on a corroded offshore platform occurred after only a few years of service in the Gulf of Mexico.

Plants of all types, from those for food processing to refineries, may be designed in the same way, (i.e., with little regard for corrosion resistance). This lesson of design for coating application and corrosion resistance was soon learned by the offshore engineers, who quickly changed from structural shapes to pipe or cylinders in order to reduce the surface area and eliminate as many corners, edges, and discontinuous areas as possible, forming a smooth structure with as many plain or rounded surfaces as was practical. Figure 7.3 is a good example of the original design used in offshore construction with its angles, channels, and H-beams. This section of the offshore platform, however, was removed as being unsafe due to corrosion.

Figure 7.4 shows an offshore platform using the more modern design with rounded smooth surfaces. There is no question about the severity of the exposure, yet this photograph was taken after 14 years of service with only one coat of inorganic zinc (IOZ) coating. The corroded areas in the lower region are open work gratings, which were galvanized. Of all structural forms, open work grating is the most difficult to coat and properly protect. As a result, there is a growing trend toward pultruded reinforced plastic gratings wherever they can meet the load ratings.

Figure 7.5 is a closer view of the pipe design showing the smooth, uninterrupted surface; even where one section joins another. Such design provides the best possible surface for coating and obtaining maximum corrosion protection. The entire surface, including the welds, is freely available for proper surface preparation and coating application. This offshore design was quickly adopted for a number of reasons: (1) because of the severe continuous corrosion encountered; (2) because the use of steel as the basis of a structure was the only practical material, both from an ease of workability and a cost standpoint; (3) coatings are the only practical corrosion control method for large complex structures subject to continuous severe corrosion; (4) the most effective coating is one applied to a plain, smooth surface with a minimum of discontinuities; and (5) the combination of a steel structure and high-performance coatings provides the most economical method of construction for large, complicated corrosion-resistant structures.



FIGURE 7.4: This coated, smooth pipe construction is free from extensive corrosion after 14 years of exposure due to its plane surface and the absence of corners, edges, and inaccessible areas.



FIGURE 7.5: Close-up of pipe section design showing the smooth flow of one section into another area where they are joined.

Principle of Design for Coating Use

The basic principle underlying design for the use of coatings on corrosion-resistant structures is to keep the structure as simple as possible and to reduce the surface area to be coated to the smallest area practical. This includes the deliberate reduction of complicated areas (i.e., those inaccessible to proper coating application); the elimination of all overlaps and riveted or bolted points wherever possible; and the reduction of sharp edges, corners, and rough areas.

These considerations must then be balanced with the necessary engineering requirements for a safe and effective structure able to perform the service for which it was intended. While this may not be an easy task, it is much more effective than adhering to conventional design methods, which ignore the need for a good coating base. Rudolf gives examples of this more effective design approach in an early paper on design.

> A 4 × 5 inch T can be used to replace two 3 × 3 inch angles with the following design figures. Two 3 × 3 ×1 inch angles weigh 9.8 pounds per foot of run, a 4 × 5 inch T weighs 8.5 lbs. Two 3 × 3 inch angles have a radius of gyration in x direction of 0.93 and the 4 × 5 inch T is about equivalent. The total exposed area of the two 3 × 3 inch angles is about two square feet per foot of run, of the 4 × 5 inch T, about one and one half. Of much greater importance is the fact that the area between the backs of the angles, 25 percent of the total, is a foul area which cannot be cleaned or coated adequately and which is a source of maintenance trouble all its life. The T on the other hand has no foul area, is readily cleaned and coated, does not harbor corrosion and presents even less area to clean and coat than the shape it replaces.
>
> A comparative newcomer to this field of substitution of simple shapes for a combination of shapes is the welded hollow tube, sealed at both ends. The most familiar and striking example of this is the water tower leg made from rolled plate and welded. With this substitution surface is not only decreased, but half the total surface

is removed from corrosive influence altogether. Consider the perimeter of a standard combination of shapes; a tower leg made up of two channels, plate riveted to the channels for a third side and the fourth side a lattice of bars riveted to the channels. If 12-inch channels had been used, the total exposure to corrosion per foot of run of such a column could scarcely be less than ten square feet. Whereas a 12-inch diameter pipe sealed at the ends has a total corrosion exposed area of three square feet per foot of run (Figure 7.6).[1]

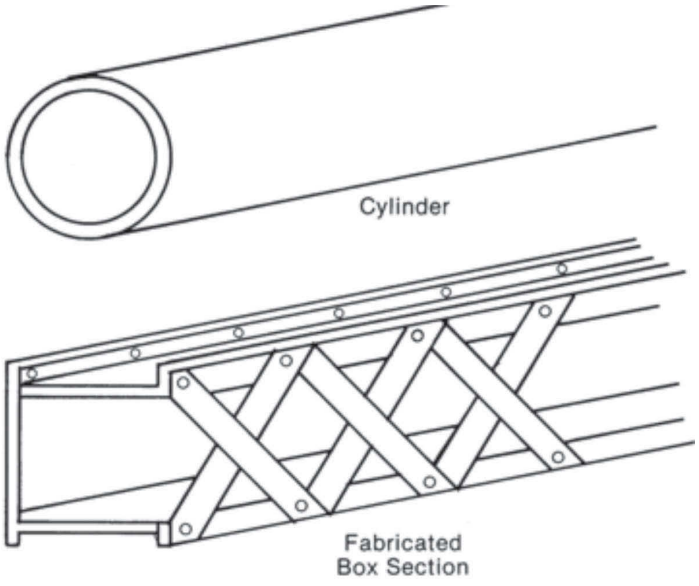


FIGURE 7.6: The comparative simplicity of essentially equivalent structural designs. Note the greatly reduced surface area of the cylinder.

It should be noted that in addition to reducing the exposed area (pipe vs. made-up beam), the use of the pipe for construction also eliminates numerous angles, corners, overlaps, and rivets, all of which are difficult to coat properly as well as being focal points for corrosion.

The previous examples not only influence the effectiveness of the coating and the corrosion resistance of the structure, but they also influence effective coating application. Pipe is by far the easiest structural section to coat, while the made-up box section cannot be properly coated by any practical means. If the structure cannot be properly coated, and there are literally hundreds of areas in presently designed structures where this is the case, the structure cannot be made even reasonably corrosion-resistant. The basic design, then, controls the effectiveness of the coating application and thus definitely influences the corrosion resistance of the structure.

The selection of materials and structural forms solely for their functional use may not be the best answer to all design problems. Many such designs have proven unreliable, unsafe, expensive, and very corrosion prone. The designer, therefore, must look beyond the functional aspects of his or her design and also consider the life of the structure under the environmental conditions in which it is placed. In the practice of responsible engineering, corrosion control cannot remain subordinate to any other portion of the design work any more than weight, wind loads, or earthquake stresses can be overlooked.



FIGURE 7.7: A bolted steel production tank used for the storage of sour crude. The tank was completely corroded from both the interior and exterior in two years.

Interior and Exterior Design

There are two distinct areas where design for the use of coatings is quite different: (1) the interior of containers for use in processing materials; and (2) the exterior of structures subject primarily to atmospheric conditions. When dealing with the interior of tanks or similar structures, design for coatings and linings has generally followed the basic principal outlined previously, that is, reduction of the area exposed to any corrosive substance.

The interior of a tank using dished heads is a good example. The entire interior surface is a perfectly smooth, continuous surface. The only breaks in the surface are at welds, at the manhole, and at inlets or outlets to the tank. Thus, the welds are generally ground smooth and the outlets in the tank, including the manhole, are ground around the perimeter of the opening in order to provide a smooth radius rather than a sharp corner or edge. In other words, the interior is designed to accept the coating or lining in order to gain their full effectiveness. All welded tanks, no matter what size, generally follow this design principle.

Large storage tanks may have a roof problem, where structural supports are required to support the roof. Many of them use a central column or series of columns throughout the tank to support the roof. If the material to be contained is particularly corrosive, all supports, trusses, and beams other than the columns can be placed on the exterior rather than the interior, and all columns can be made from pipe. This type of construction maintains the smooth interior surface throughout, thus making for the best possible coating application.

Bolted tanks, which are a common design option, generally are used for temporary storage where tanks can be moved from one place to another. Unfortunately, the temporary storage often becomes permanent storage and the bolted design then presents a problem if a coating is required to protect the interior from serious corrosion.

The storage of sour crude is a good example of the type of product that can cause considerable corrosion damage. Figure 7.7 indicates the extensive corrosion that may occur with improperly designed and coated tanks used for the storage of sour crude. The complete destruction of this tank required less than two years. An all-welded tank, properly coated, would have eliminated this problem. Much larger tanks in the same area, which were properly designed and coated, are performing satisfactorily.

Generally, interior surfaces subject to corrosion are more likely to be designed with coatings in mind than are exterior structural surfaces. Many modern plants are not fully enclosed, so that the exterior of all the surfaces are subject to whatever atmosphere may be in contact with the structure. This type of design is particularly true of chemical plants and refineries where much, if not all, of the processing equipment and pipe is subject to the plant atmosphere.

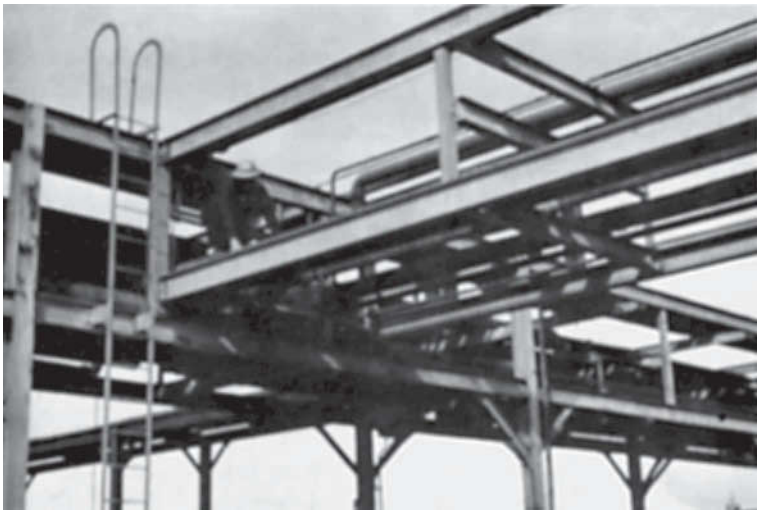


FIGURE 7.8: A design showing hundreds of linear feet of edges, as well as overlapped bolted joints. Such a design is difficult to both properly coat and maintain.

Figure 7.8 shows a pipe rack in a typical chemical plant fabricated from a standard structural shape. Joints are overlapped and bolted, increasing the surface area and providing additional edges, corners, cracks, and crevices where corrosion can initiate and continue. The exterior design of such structures could vastly improve the corrosion resistance of the unit. Structures that have been designed for the acceptance of a coating (i.e., those with flat, cylindrical, and smooth surfaces, as well as surfaces joined by continuous welding with a minimum of overlapping joints) are much more easily maintained and coated.

The cost of maintaining a structure also is directly related to its design. A structure with a minimum of edges, corners, crevices, and so forth, can be much more easily maintained and will have a much longer useful life under corrosive conditions than one that is designed without regard to the structural requirements of coatings.

Coating Problems Related to Design

Structural Steel Shapes

Structural steel shapes almost always pose coating problems, particularly those in smaller areas. Unfortunately, they represent a basic building material and therefore, in many cases, must be used regardless of the coating difficulties they create. These basic structural shapes consist of the angle, channel, H-beam, and I-beam (Figure 7.9).

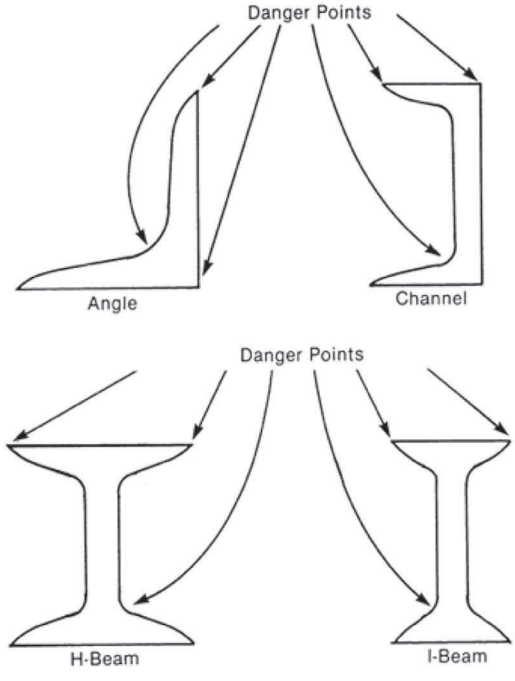


FIGURE 7.9: Basic types of structural shapes.

The angle contains the most problem areas. The outside of an angle forms a continuous right angle edge and is a danger area where coatings are generally thin. Thus, the area is subject to considerable corrosion damage because of its location. The same holds true for the arm ends of an angle since the edges and exterior corners are more vulnerable to coating failure than the flat portion of the angle. Most high-performance coatings, with the exception of the inorganics, exhibit considerable surface tension upon drying, which causes the coating to pull away from edges and exterior corners, making it much thinner in these areas than on the flat section. Where a coating is applied to an area making a sharp change in direction (Figure 7.10), the internal forces in the coating draw it away from the edge, leaving it either exposed or only minimally covered. In general, the higher the volume solids of the coating the lesser the shrinkage from the edge, however, all coatings shrink away from edges to some extent.

The interior corner is also an area of difficulty and a danger point. During surface preparation, considerable dust or other contaminants can build up in this area where removal of these materials is much more difficult than on a flat surface. From a maintenance standpoint, it is an area where dirt accumulates, particularly if the angle is in a horizontal upright position. It also accumulates moisture, which can quickly create areas of coating failure. Interior corners are also difficult to reach by either spray or brush, and therefore they make it difficult to maintain a constant coating thickness. Air spray tends to bounce out of a corner, while airless spray may apply much too great a volume of coating in that area.

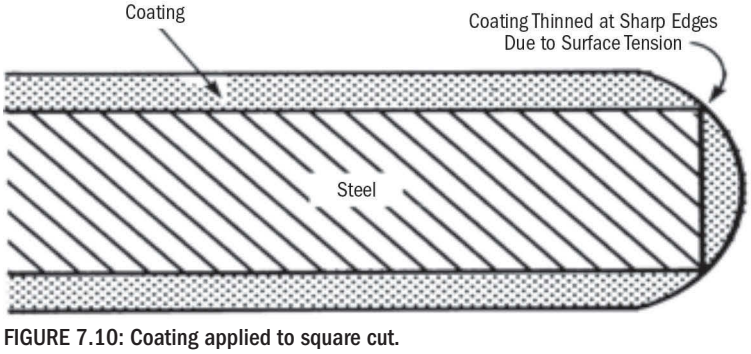


FIGURE 7.10: Coating applied to square cut.

In many cases, the high-strength organic coatings tend to shrink somewhat upon drying, due to both surface tension and decrease in volume because of solvent evaporation. If there is dust on the surface prior to coating, which then prevents proper wetting of the interior corner area, the high-tensile film may tend to bridge over the inside angle, causing an air space to form between the coating and the metal (Figure 7.11). This coating reaction becomes a focal point for corrosion in any corrosive environment.

Channels cause a problem similar to those of angles, with the exception that the problem areas on channels are double that of the angle. I-beams and H-beams also have similar danger points to angles and channels except for the sharp right angle exterior corner. They are perhaps somewhat less of a problem than the other two shapes since their dimensions are often greater, thus allowing a greater proportion of flat area, which can be properly coated as compared with the area of coated corners and edges. Thus, wherever coatings are involved, structural shapes should be regarded with additional care in surface preparation and coating application so that a continuous, smooth, even coating thickness is created over the entire surface.

In order to reduce surface preparation costs, many coating systems are applied either in part (e.g., primer or base coat only) or in full to sections of the structure prior to erection. Applying the coating "on the ground" where there is ready access and easy movement around the section, makes for better surface preparation and better application as compared with the same structure coated upon completion hundreds of feet off the ground. Similarly, many block sections of ships are pre-coated before erection because of greater access to the surface, better visibility, better ventilation, and better overall coating application conditions. Where structural shapes are used, such prefabrication and design, with coating before erection, increases the probability of a good corrosion-resistant structure. This is particularly the case where IOZ coatings are applied as a base coat, since they are relatively unaffected by handling after coating because of their excellent abrasion resistance.

One problem with pre-coating a prefabricated section before erection lies with the construction joints. Where structural steel is erected using high-strength bolts or rivets, the overlapping surface can create a corrosion problem, particularly where it is left bare of coating prior to joining. Since IOZ coatings have a good coefficient of friction, they can be applied to faying surfaces prior to erection. Coating the faying surfaces in this way reduces the possibility of corrosion at the steel joints.

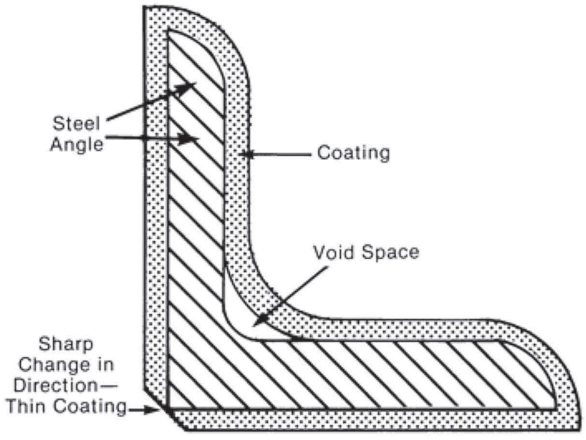


FIGURE 7.11: A coating danger point is created where the coating bridges over an inside angle, causing an airspace form between the coating and the metal.

In large fabricated sections, such as the block sections in the construction of a ship, the joining welds are always a problem. Again, a base coat of IOZ can be used on the block sections and junction welds made with very little burn back of the coating. After installation and prior to coating application, the welds must be smooth and thoroughly prepared. There are many instances of block section designs where the body of the coating on the block section is in excellent condition, yet all of the construction welds have failed within a short period of time due to poor surface preparation and lack of care during coating application.

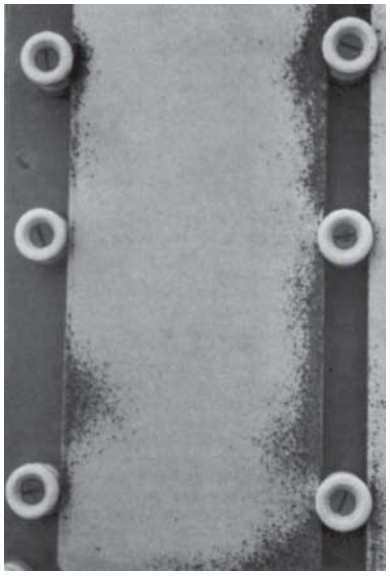


FIGURE 7.12: Corrosion beginning at the edges of a panel.

Sharp Edges

Sharp edges of steel on overlapping plate, or edges left by shearing or cutting, can present serious coating problems. Coatings will fail first in areas with sharp edges almost without exception. This is demonstrated in Figure 7.12, where an exposure panel was placed in a marine atmosphere. The panel was a cold-rolled panel sheared to shape, and then sandblasted and coated. Extra care was even taken in coating the edges to prevent edge corrosion, but nonetheless, when the coating started to fail, it first failed at the square cut edges rather than in the smooth area of the panel.

While square-cut edges are the most vulnerable to failure, the same principle holds true to the smoother edges of most structural steel, which come to a small radius and are still much more difficult to coat than plain surfaces. Not only does the surface tension tend to pull the coating away from these areas, but also more often than not, the application of the coating is tangent to the edges, rather than direct, thus creating a thin area of coating along the edge. This is further aggravated wherever there are corrosive dusts or the precipitation of corrosive fumes or mists. These accumulate on the flanges of structural steel, since corrosive products tend to concentrate at the edges of any horizontal shape (Figure 7.13).

In order to provide coating protection for edges, it is necessary to apply coating directly to the edge before each complete application and then apply the normal coating layers out over the edge in order to develop an equivalent coating thickness in those areas. In many cases, the best protection is achieved by actually increasing the thickness on edge areas, if at all possible.

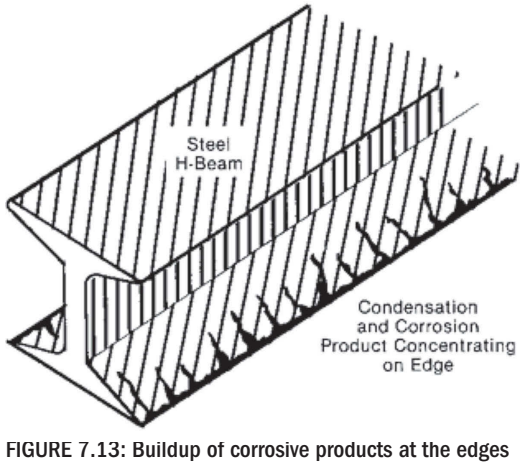


FIGURE 7.13: Buildup of corrosive products at the edges of a horizontal shape.

Rivets and Bolts

Rivets and bolts, used for connecting steel sections in a structure, represent another area where the coating will preferentially fail. This is due to the increased surface area as well as the increased edge area where this type of construction is used. Each of these methods increases the chance of crevices and similar surface discontinuities around the edges of the bolts or rivets.

There are three common types of rivets: round, pointed (conical), and countersunk (Figure 7.14). The counter sunk rivet is the easiest to coat since the finished rivet is almost level with the bare steel, leaving only a small line around the edge of the rivet, which requires attention from a coating standpoint. Round rivets are the most common. They have an almost hemispherical head and fit tightly to the surface when properly installed. Conical rivets are becoming less and less common. They used to be a standard material in riveted tanks and riveted tank cars. They create more of a coating problem than the other two types, however, because of the conical shape of the rivet, which comes to a relative, though not sharp point at the top. It thus creates an area which can easily be damaged and one from which the coating tends to pull away and form a thin, vulnerable area.

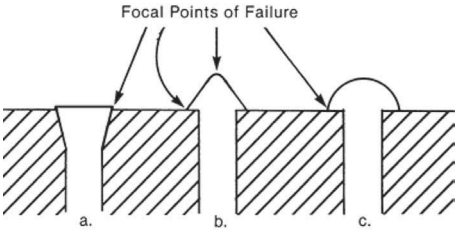


FIGURE 7.14: Coating applied to square cut.

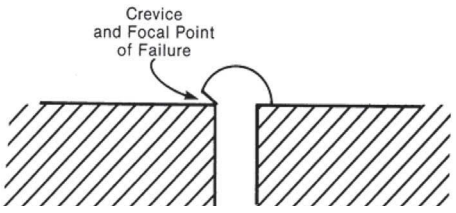


FIGURE 7.15: Coating applied to square cut.

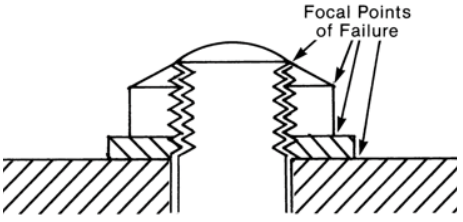
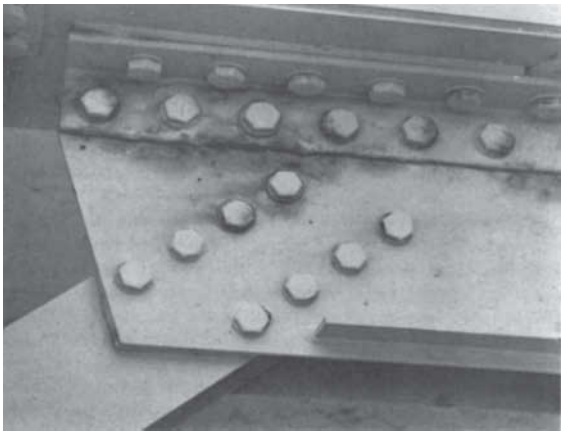
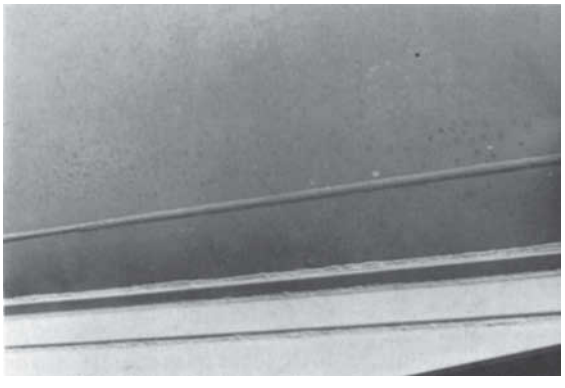
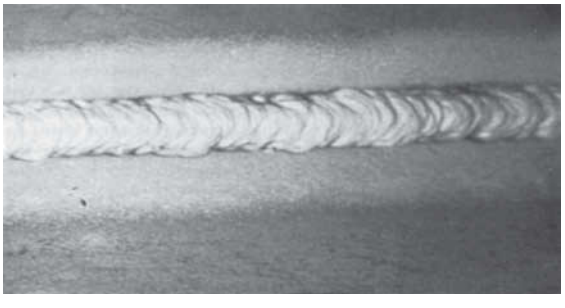


FIGURE 7.16: Points of failure on a steel bolted joint.


FIGURE 7.17: Bolted steel sections exposed to a marine atmosphere. Note the corrosion at the overlapping joints on and around the bolt head.


FIGURE 7.18: Typical machine (top) and hand (bottom) welds.


FIGURE 7.19: Typical machine (top) and hand (bottom) welds.

One of the problems in using the last two types of rivets, round and conical, is that of a cocked rivet. This occurs where one side of the rivet is driven tight while the other side is cocked away from the surface, causing a crevice between the rivet and the surface (Figure 7.15). This is an extremely difficult area to properly coat and thus is an area where corrosion can easily take place. All rivets used in corrosive areas should be caulked tight, which involves going around the edge of the rivet with an impact gun and caulking tool, driving the edge of the rivet against the surface to make tight contact so that no crevice areas exist.

Riveted joints between steel sheets represent another area to watch. The overlapping plate, unless thoroughly caulked tight, will provide a crevice area containing air and one in which moisture and chemical solutions can easily penetrate. It is also an area that is almost impossible to cover with a coating, and thus serves as a focal point for corrosion.

All hot driven rivets have an oxide scale on the exterior. Therefore, they must be thoroughly blasted in order to remove the black iron oxide, which is strongly cathodic to steel and thus an aggravation to corrosion in any crevices that may exist.

In order to obtain proper coating protection on a riveted structure, it is necessary to double coat all riveted areas in the same manner as described for a sharp edge. It is preferable to brush the first coat around each rivet in order to ensure full adhesion and coverage. Since rivets are always a focal point for corrosion, it is preferable to use welded construction rather than rivets or bolts to join steel sections in any area where corrosion is a factor.

Bolted Joints

Bolted joints are more difficult to coat than riveted joints, and many modern steel structures are installed with high-strength bolts. Not only do they consist of many sharp edges, including the threads on the bolt and the sharp edges on the hex nut but also washers are usually used, which create an additional area for crevices (Figure 7.16). In order to properly coat bolted areas, essentially the same procedure should be used as that for rivets. The first coat (primer) should be thoroughly brushed around each bolt head, which is difficult because of the many edges and crevices that are possible. When spraying subsequent coats, it is necessary to spray completely around each bolt head to properly cover each surface along with the many edges.

In Figure 7.17, the overlapping steel bolted joint shows active corrosion beginning at the joint as well as around several of the individual bolts. While situations such as this often are blamed either on poor coating application or a poor coating, the actual difficulty is the conventional design of the structure, which was not suited for a corrosive atmosphere.

Welds

The majority of modern steel construction uses welding to join steel sections. The process has become extremely sophisticated with automatic machines making most of the welds. Figure 7.18 shows the exterior of the hull of a ship and demonstrates two types of welds. The upper weld on the smooth hull is an automatic weld joining two hull plates. It is smooth and continuous, with no undercutting along the edges. The three welds made below the machine weld involve the stabilizer fin, which is attached to the hull. These are considered very good hand welds. Notice, however, that they are somewhat rough and are thus more vulnerable to coating application problems and possible corrosion failure than are the machine welds. Thus, machine welds are preferable and made on a structure wherever possible.

Even in shipbuilding, however, where much of the welding is done by machine, a large part of welding footage is still done by hand. Figure 7.19 shows a hand weld between two plates, which were sandblasted to emphasize the details. Notice the roughness of the weld, which is created by the manual application. Note also that along the edges there are some minor undercuts and shallow crevices, which pose difficulties in coating. This particularly is true when using organic coatings that often bridge such areas. IOZ coatings, however,

which do not shrink on curing, would wet and remain in these irregular areas without difficulty. Weld areas also should be thoroughly blasted to remove scale and weld slag. It is preferable to brush organic primers over a weld to work the coating into all rough and uneven spots.

From a design standpoint, a welded joint is highly preferable to a bolted or riveted joint and both from a corrosion protection and a coating application standpoint. Unfortunately, hand welds are only as poor or as good as the welder who makes them.

Although rough welding is not designed into a structure, specifications should be written in such a way that rough welds are eliminated from any installation where corrosion is a factor. If they do exist in critical areas, they should be ground smooth and special care taken in coating the areas to ensure full coating thickness and continuity. The best protection for rough welds is an IOZ base coat (Figure 7.20).

Figure 7.21 shows the results of a rough weld on an otherwise well-coated bulkhead. The rough weld and its location close to a reinforcing member caused a porous coating over the weld and therefore early corrosion. Care in the treatment of the weld and in the coating application over the weld could have prevented this costly corrosion problem.

One of the major difficulties along welds occurs because of the weld spatter. These are small adherent balls of metal, which fly away from the hand weld and stick to the adjacent metal surface. These small, adherent balls of metal provide points from which the coating flows away and becomes thin. Small crevices also develop in and around the base of the metal ball, which creates an area where coatings do not tend to penetrate well (Figure 7.22). These rough areas of weld spatter should therefore be removed before the surface is prepared for coating.

Figure 7.23 shows a weld with some weld spatter made in a design, which can only cause difficulty. Corrosion is already starting around the weld and in the crevice between the two pieces of metal. Note also the coating break in the middle of the weld caused by the weld slag that was allowed to remain on the surface and was then coated over.

Seal Welds

Smooth seal welds should be used along seams between two metal pieces to seal them against penetration of moisture and other corrosive elements. Seal welding differs from the standard forms of welding. Its primary purpose is to provide a metallic seal between two surfaces to prevent penetration of gases or fluids into the crevice and to provide a continuous metal surface over which to apply coating. The secondary purpose of the seal weld is to provide a fastening between the two surfaces.

Weld flux is necessary for the proper welding of the metal. It prevents oxidation of the molten metal and allows it to flow together to make a completely fused joint. On the other hand, especially where there are hand welds, it can be retained in rough areas, particularly along the edges of the weld and even where the weld is blasted. Care in both blasting and coating is necessary, as slag is difficult to remove and its strongly alkaline hydroscopic nature creates a spot where early coating failure will occur. See spot failure in Figure 7.23.

Although welding is one of the best methods for joining two steel surfaces, there are problems involved in its use that must be taken into consideration wherever coatings are to be applied.

Numerous types of brackets, hold-downs, permanent scaffolding, and other fabricating aids are used in the construction of steel structures and are welded to the steel surface. These may or may not be designed into the structure, but are oftentimes necessary for the construction of the unit. As long as they do not pose any mechanical problems in terms of the finished structure, they are often left in place. Otherwise, they are either cut from the surface with acetylene torches or merely broken away with a hammer (Figure 7.23). The rough metal left from such an installation, however, causes a focal point for coating breakdown and therefore, serious corrosion. This should be considered in the design specifications, which should call for the complete removal of the units and grinding down of the steel to create a smooth surface. NACE SP0178 (2007),[2] "Design, Fabrication, and Surface Finish Practices for Tanks and Vessels to be Lined for Immersion Service," has an excellent replica of the various levels of smoothness of welds that may be used by the specification writer to improve the acceptance of coatings on these difficult-to-coat areas. Proper

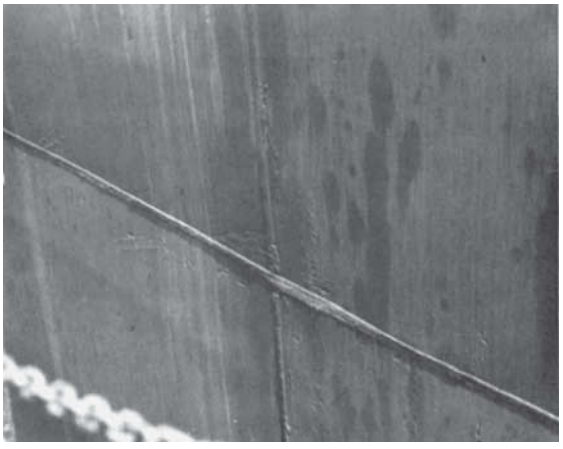


FIGURE 7.20: Rough hand welds showing areas where metal brackets have been cut from the surface. Inorganic zinc protects poor workmanship.

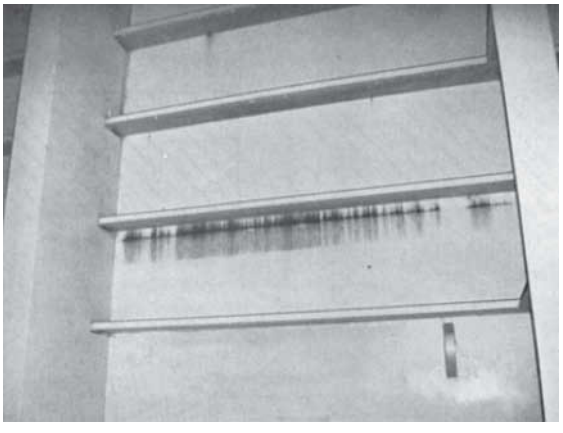


FIGURE 7.21: Rough welded seam that creates a corrosion problem.

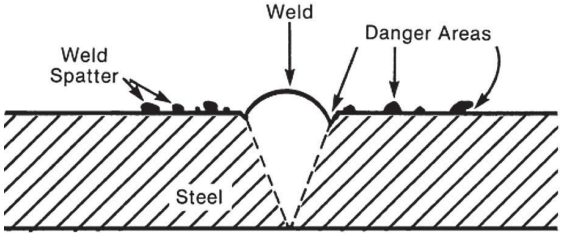


FIGURE 7.22: Schematic showing a weld with some weld spatter.

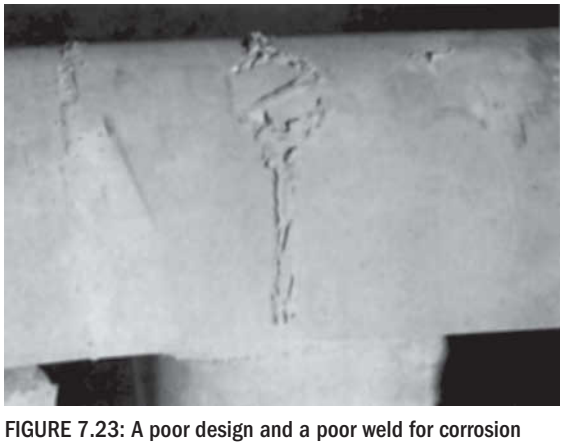


FIGURE 7.23: A poor design and a poor weld for corrosion protection. Note the weld splatter and the crevice between the two metal sections. Rough steel remaining after a construction bracket was cut from the surface. Note the rough metal and sharp undercuts, all of which create coating problems.

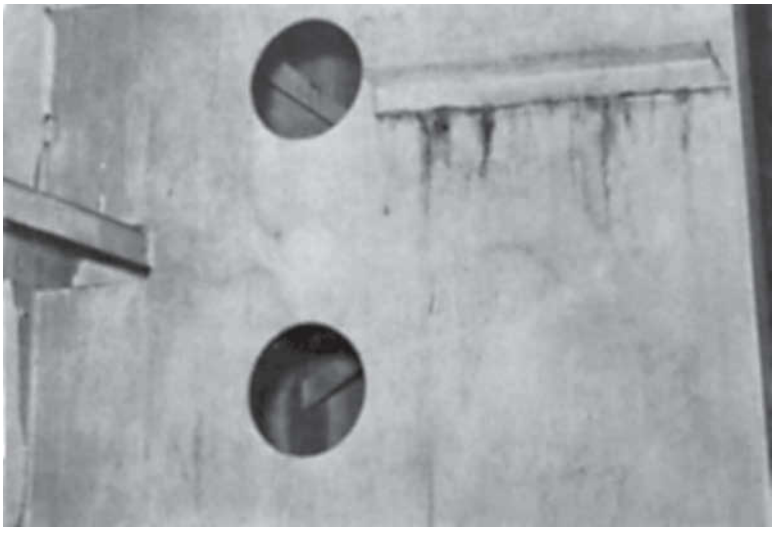


FIGURE 7.24: Scaffold bracket remaining in a coated tank showing corrosion underneath the bracket. Such permanent brackets should be seal welded to allow for proper coating.

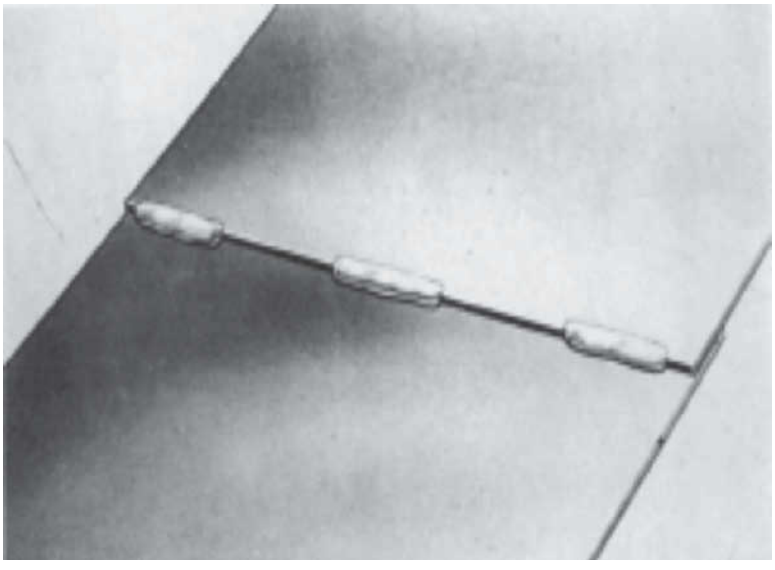


FIGURE 7.25: Skip welding.

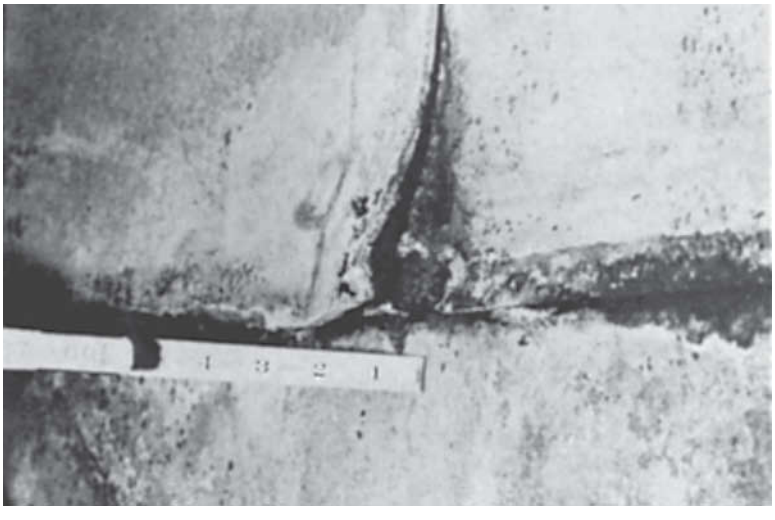


FIGURE 7.26: A lap welded seam on a tank interior showing corrosion between the overlapped plates.

specifications also should call for the seal welding of any brackets left permanently attached to the structure, since corrosion can occur rapidly underneath the overlapping steel (Figure 7.24).

Skip Welds

It is a common design practice to call for the use of a skip welding technique in the construction of many structures. Skip welding is a process of welding two or three inches, skipping several inches, and then applying additional welds of a similar length, until the designated area is covered. It is used mainly for reinforcing purposes where it is not considered necessary to provide a continuous weld (Figure 7.25). Skip welding is commonly used for the reinforcing ring around the top of an open-top tank. It also may be used on roof structures; some areas of trusses, machinery, or tank bases; and many other similar areas.

Skip welding, however, creates several problems since corrosion easily penetrates the area between the welds and is thus a constant source of difficulty. It also makes coating application difficult since shortly after welding, air and moisture accumulate in the openings between the welds (Figure 7.25). Buildings or structures that are exposed to moist, corrosive atmospheres should therefore have continuous seal welds in between the heavier skip welding. The seam should be sealed to prevent corrosive materials from accumulating and to provide a continuous surface over which to apply a coating. Without the continuous seam weld, skip welding not only creates all of the welding difficulties that we have previously covered, but it leaves a deep crevice, which is impossible to fill with a coating. In any design for corrosion service, seal welds should be used to augment skip welds. If this is not possible, the next best alternative is to caulk the areas between the skip welds with industrial caulking that is compatible with the coating system being applied.

Lap Welding

In some tank construction and often in tank roofs, a lap welding technique is used. This is the welding of steel continuously on the exterior of the tank or roof while leaving the plate merely lapped on the interior. This provides good weather resistance and makes a tight tank. On the other hand, it also creates a crevice on the interior into which moisture, corrosive gases, or corrosive liquids can penetrate and accumulate (Figure 7.26).

If such an overlapping technique is called for in a design, the only possible answer to overcoming the corrosion problems it creates is to seal weld the interior of the lapped steel continuously in order to close off the area and to provide a smooth area on which to apply the coating. A much preferable design, however, is to butt-weld the tank plates and roof sheets. This immediately eliminates the problem with little or no additional cost. A common design in the construction of steel truss buildings is to use the back-to-back angle technique to form the trusses. Such angles are ordinarily separated by washers and then riveted or bolted together so that the two back-to-back angles form a T. Part of the design is to join other members to the truss by using the area between the back-to-back angles and bolting the third member between the two angles. Usually, there is a space of 1/8 to 3/8 in (3.18 to 9.53 mm) wide left in between the two angles. This space is then left completely unprotected from any corrosive dust, fumes, or moisture (Figure 7.27). This type of truss construction is almost impossible to protect properly (Figure 7.28).

The space between two angles is impossible to properly clean and there is no way of satisfactorily applying a coating into such a deep crevice. There are, however, several design alternatives. One is to use a T shape and thus eliminate the back-to-back angle construction. A cylindrical pipe shape also can be used in place of the back-to-back angles. If the structure already exists and coatings are required, such areas can be sealed by the use of heavy mastics applied in and along the seam between the two angles.

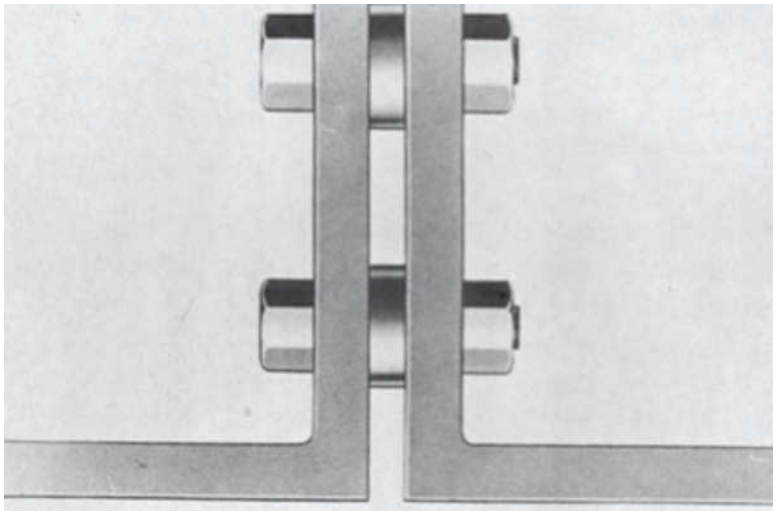


FIGURE 7.27: Typical back-to-back angle design with a deep crevice between the angles.

Box Beams

Box beams are a relatively common type of construction in areas where the box cross-section provides the strength, and where some of the steel can be eliminated to reduce weight. There are a number of box designs. Some are completely sealed and are not responsible for any particular corrosion problems (Figure 7.6).

Another box beam design involves the periodic removal of steel to reduce weight (Figure 7.29). These open box designs should never be considered where corrosion problems are involved. With periodic openings, the interior of such a box beam is impossible to properly protect against corrosion. Heavy rust, corrosion, and scale build up on the interior most often cause failure of the structure. In the bridge shown in Figure 7.29, there were several thousand linear feet of such beams, and heavy scale corrosion had built up on the interior of the boxes within a matter of only two to three years.

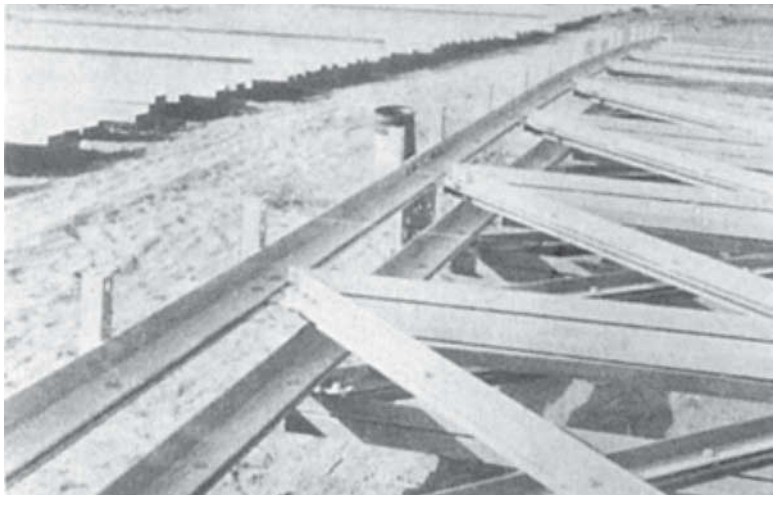


FIGURE 7.28: Back-to-back angle trusses before installation.

Some box sections are designed to be almost entirely closed. Even though the openings are small, however, the atmospheric heating and cooling of the box will make it breath, causing condensation and even salt buildup. Corrosion then takes place on the interior where it goes unnoticed until the structure fails. Such hidden areas are a real safety hazard to any critical section of a structure such as the beams shown in Figure 7.29. To prevent such corrosion, box sections, or other enclosed spaces where proper maintenance is impossible, should be seal welded with installed fittings for pressure testing. Low-pressure air tests will reveal openings or pinholes that would allow breathing with consequent internal corrosion.

If a void area can retain 5-psi air pressure, it is an indication that the void space or box section is tight enough to prevent breathing of moist air into the void. Pipe sections used in a similar manner for support or columns, should be seal welded closed and pressure tested in a similar manner in order to ensure a corrosion-resistant structure. The exterior of such fully closed box beams or pipe columns can be easily maintained and protected by proper coating application.

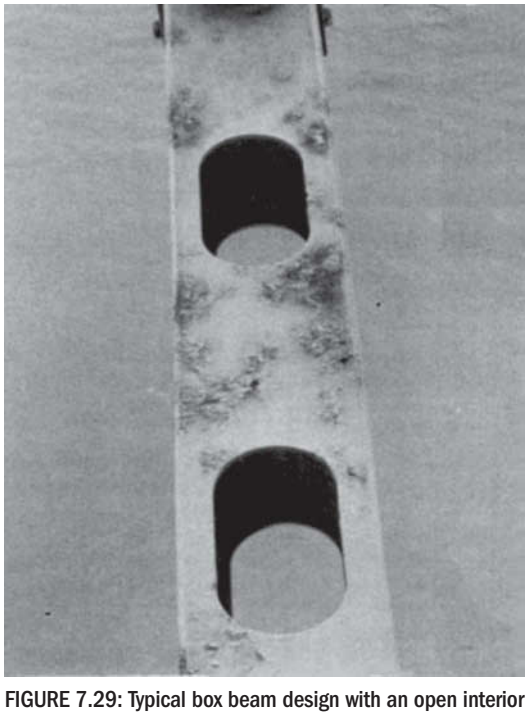


FIGURE 7.29: Typical box beam design with an open interior where both proper surface preparation and coating are impossible.

Tank Construction

Many tanks are constructed with a cone roof and an umbrella-type roof construction. This design usually calls for a center pole with I-beam rafters extending from the center to the outer edge of the tank. The rafters may be simple I-beams or they may be reinforced by internal truss members to provide the proper strength. The steel roof plates are then laid directly on top of the rafters, completing the roof construction. In any such tank, regardless of the liquid it contains, the cone roof area is subjected to constant high humidity and fumes, with condensation taking place on the underside of the roof, particularly during the cooler night hours. The entire area of the tank above the liquid level is subject to constant oxidation and continual wet, corrosive conditions. The underside of the roof, the rafters, and the trusses must withstand such conditions (Figure 7.30).

There are two extremely difficult areas to protect with coatings in this construction. The first is the area between the I-beam rafters and the steel plate roof. The steel plate roofs are not ordinarily welded to the rafters because of the continuous expansion and contraction of the roof plate. Thus, there is an area between the roof plate and the rafter that provides a crevice that is extremely difficult to pro-

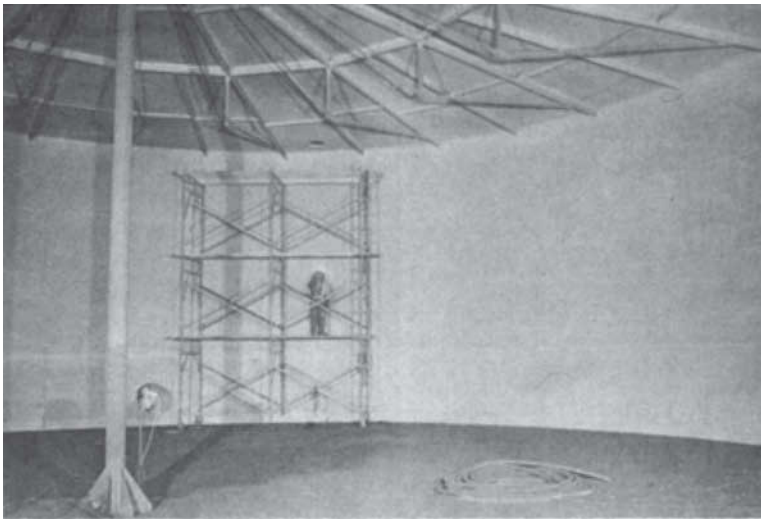


FIGURE 7.30: Typical umbrella-type storage tank with complex rafter design.

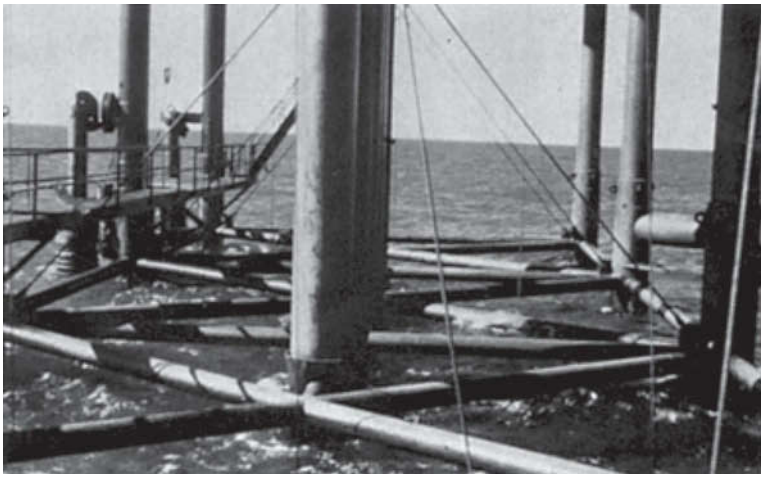


FIGURE 7.31: A typical design for an offshore drilling structure in the Gulf of Mexico. Excellent protection was provided by the coating even after several years of exposure.

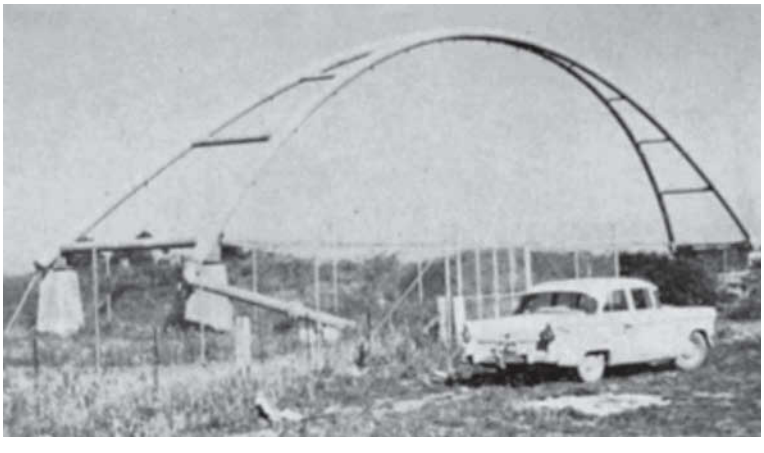


FIGURE 7.32: Pipe bridge with a simple but effective design for corrosion resistance.

tect. If a coating is the only corrosion protection to be used, the rafters and the underside of the roof should be coated prior to installation, thus allowing proper application. If the coating is applied after construction, it is necessary for the roof plate to be raised by wedges or other means and coated by whatever means is possible. The coating must be applied to both the underside of the roof plate and to the top of the I-beam rafter to provide good protection. Coating of such areas is difficult at best and generally requires continuous maintenance in order to prevent internal corrosion of the roof to the point where leaks occur.

The second area is caused by the overlapping of the steel roof plates, creating a shingle effect from one plate to another. This provides a lapped joint, and the crevice between the lapped roof plates provides a reservoir for corrosive solutions, moisture, and condensation, and corrosion takes place very rapidly. Most often, the roof plates are welded on the exterior to provide a continuous roof structure, while the interior of the lap is left open. Where this type of construction is necessary, a seal weld should be used on the inside of the lapped joint in order to provide a continuous surface for proper coating. Preferable construction is the use of butt-welded roof plates. Also, since the roof plates have a tendency to expand and contract, a rubber or a plastic cushion should be applied, where possible, to the top of a rafter in order to prevent abrasion between the roof and the rafter caused by the metal movement. Such a rubber or plastic strip, with the proper adhesive, will adhere to the rafter and protect it against corrosion.

A completely different type of tank design is used for process vessels. Since most vessels are designed for a lining, the interior is smooth, the tank heads are dished, and all welds are ground level with the tank steel. This provides a continuous surface for the coating or lining. If such tanks are to receive baked coatings, however, such as a high-baked phenolic, a coating problem can develop that may have not been anticipated in the original design. Tank supports, reinforcing, tank outlets, and similar areas on the tank exterior act as heat sinks and may remain at temperatures below the curing temperature of the baked lining during the heating process. This creates areas of coating in these spots that are uncured and are thus focal points for coating breakdown. Such exterior heat sinks require heavy insulation during the baking process, and the heating of the tank should be continued for a sufficient time for the heat sinks to reach the same temperature as the body of the tank in order to prevent serious coating failure.

Pipe or Cylindrical Construction

As discussed previously, pipe or cylinders provide the smallest amount of surface area subject to corrosion compared to ordinary structural shapes. They also have no angles, corners, edges, or other surface configurations that can cause coating problems. The offshore industry, because of the corrosion problems involved with other structural shapes, have gone to cylindrical members for most all of their critical strength areas in order to reduce the possibility of coating failure and corrosion (Figure 7.31).

This structural use of pipe, however, is not without some problems. Extra care is required wherever pipe must be coated because of its cylindrical shape. The larger the cylinder, the better the application conditions. Since the application of a coating to the pipe is usually made longitudinal with the pipe, many holidays may be formed in the coating due to insufficient overlapping during the coating process. Spray application to pipe is made with a fan from a gun; thus, some of the spray on each side of the fan is applied to the pipe at a tangent to the pipe surface rather than directly impacting the surface as it does in the center of the fan. While these tangent sections may appear to be coated, the coating in these areas is actually both thin and porous. This is the cause of longitudinal holidays on pipe sections. Actually, it is necessary to coat pipe from at least four positions, and it is preferable to spray from at least six in order to make certain that the coating is fully overlapped. The number of passes naturally depends on the size of the pipe.

In addition to the cylindrical structure, pipe flanges, threaded joints, pipe hangers, and similar changes in surface configuration are common to piping. All of these areas are focal points for corrosion because they are difficult to coat. Crevices are formed in threaded couplings, which allow penetration of moisture and subsequent corrosion. While such areas occur frequently on pipe racks and similar installations, they generally do not exist where pipe is used for primary construction sections such as shown in Figure 7.31. Despite the possibility of insufficient overlapping or additional surface configurations, a cylinder is still preferable to almost any other shape from a coating and a corrosion standpoint (Figure 7.32).



FIGURE 7.33: Typical pitting in low areas of horizontal steel in a tanker. The dark areas around the pits are discoloration caused by water standing in the low spots. Pits were ¼ to ⅜ in depth. Note the blistering in the coating around the edge of the low spot (upper left). Source: C.G. Munger, "Deep Pitting Corrosion in Sour Crude Tankers," MP 15, 3 (1976): p. 22.

Water Pockets and Recesses

Water pockets, recesses, low spots, horizontal flat areas, or catch basins where channels or other structural shapes are used in a horizontal position are all areas that should be eliminated during the initial design of the unit or structure. If they are not noted at the design stage, they can often be altered without any change in structural strength during actual construction. Rudolf[1] cites one example, as follows.

> One further point should be noted on the part of the designer, this is the matter of drainage of moisture from every part of the structure. Angular coupling of shapes usually provides some sort of haven for moisture that cannot drain away but has to evaporate in place. Angle, channel or I-beam should never be placed to leave a sort of vessel to retain moisture. Either the position of the shape should be changed or drain holes cut to provide rapid movement of moisture downward away from the piece. With good drainage of all members of a structure, one of the strongest measures of corrosion mitigation has been taken.[1]

One area where water tends to accumulate and evaporate on a continuing basis is on the upper surface of a floating roof tank. These are large, flat areas and it is extremely difficult to fabricate such a roof without the plate buckling in numerous areas. When rain or condensation occurs, the low areas in the roof accumulate water. If there are corrosive fumes in the area, these also are concentrated in the water as the water evaporates. A strong corrosive solution often develops with the consequent danger of severe corrosion taking place in these spots. Such depressions should be eliminated during initial design, if possible. During construction, low areas should always be watched, as extra care is required during the coating process in order to make sure that a full coating thickness is applied. Even if the entire floating roof is well coated, low spots are still the areas where the coating will initially break down, first by blistering, followed by pitting.

This is also true of the horizontal areas on the interior of tankers and storage tanks. These areas occur on the large horizontal stiffeners and other structural members. While weep holes may be designed into the stiffeners, many times low spots occur because of warped steel during formation for tank fabrication (Figure 7.33). Such areas should be eliminated either by drilling holes in the stiffeners to drain the water away, or the area should be filled with an epoxy troweling cement.

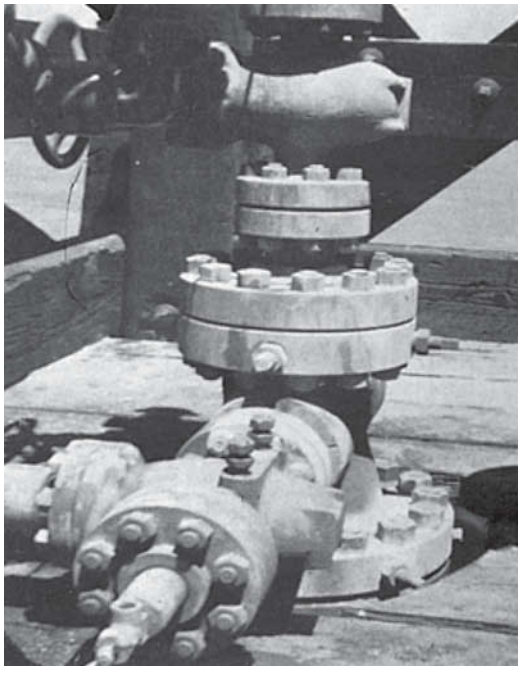


FIGURE 7.34: Valve manifold (Christmas tree) on an offshore production platform. Note the bolt heads, nuts, threads, and crevices between flanges that serve as focal points for corrosion and coating breakdown.

Flanges

Flanges of all types are difficult areas to protect with coatings. Figure 7.34, which shows a Christmas tree on an offshore well, is a good example of the complexity that can arise in piping systems due to the use of flanges. In this case, the protection was particularly good since the entire wellhead was coated with IOZ. It does, however, show the various focal points for corrosion, including the myriad of bolt heads, threads, valve handles, and the crevice between flanges. Only a very thorough coating application can keep such a unit corrosion-free.

These corrosion focal points are almost impossible to eliminate by design. Flange spaces should therefore be coated wherever possible, and galvanized nuts and bolts should be used as a base for whatever organic coating may be applied later. Where piping is already installed and flanges exist, it is often practical to use a glass-reinforced vinyl or polyethylene tape with a butyl rubber adhesive to seal the opening between the two flanges. This can then be overcoated with vinyl coatings or other similar materials. Taping, in fact, has successfully eliminated corrosion between the flanges in many areas and prevented rust staining that inevitably flows from such areas. In particularly aggressive corrosion areas, it is not unusual to see flange openings covered with stainless steel (SS) bands that have grease fittings through which the flange opening can be filled to reduce the ability of corrosive media from reaching into these crevices.

Flange connections are not an isolated problem, but rather one that exists in almost all industries. Figure 7.35 is a typical cooling tower piping manifold, which shows the many necessary flange connections.

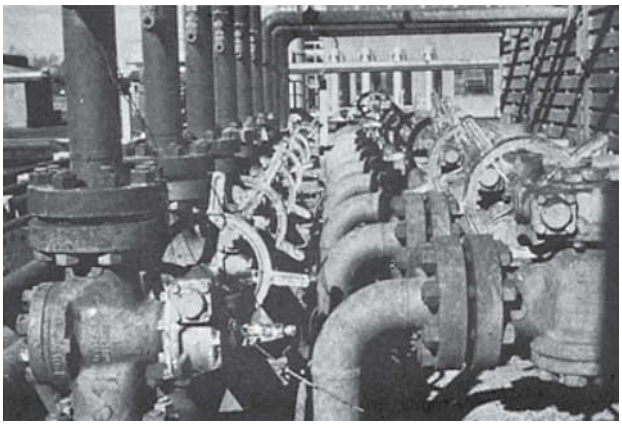


FIGURE 7.35: Cooling tower intake piping manifold coated with inorganic zinc. The piping was subject to elevated temperatures and continual water spray.



FIGURE 7.36: Typical stairway on the exterior of a tank with its many sharp edges, corners, and hidden recesses.

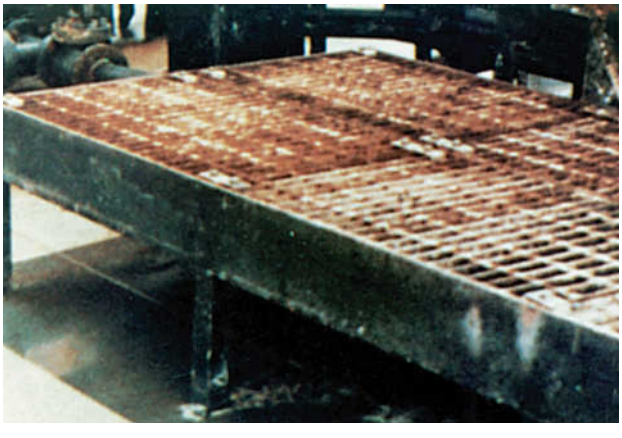


FIGURE 7.37: An aboard-ship open-work grating installation such as this should be heavily galvanized and protected by an organic coating to withstand marine exposure.

Stairways

Designs for stairways, ladders, and similar access structures are, for the most part, still done conventionally with the possible corrosion factors generally overlooked. Although areas like stair treads and handrail risers are critical safety areas, they are often seriously corroded due to their original design and subsequent coating difficulties. Figure 7.36, which is a typical stairway on the exterior of a tank, demonstrates the numerous focal points for corrosion and areas where it is most difficult to obtain a proper coating. In this case, the rail is an angle, the riser and braces for a handrail are angles, and the side rails on the stair proper are channels with the stair risers fitted in the channel itself, creating many isolated areas difficult both to clean and to coat. Not only are these isolated areas the first to corrode, but also corrosion is less obvious than on the exterior of the structure.

In the example shown in Figure 7.36, if the stair tread had been seal welded to the flat area of the channel with the arms of the channel extending out rather than in, a much more corrosion-resistant structure would have resulted with better access to properly clean and coat the steel. Also, if the handrail risers, braces, and handrail itself had been made from pipe, both cleaning and coating would have been more effective. Open grating should not be used for stair treads, unless it is absolutely necessary, because of the complexity of the grating structure and the difficulty of providing proper corrosion protection to such areas. Heavy galvanizing is suggested wherever such stair treads are used in order to provide an effective anticorrosive base for organic coating.

Open Grating

Open grating is a common structural material used for elevated walkway design on ships, refineries, offshore structures, chemical plants, and many similar structures. At best, it is an extremely difficult shape to protect, but more often than not, it is an area where corrosion rapidly decreases the safety of such construction. Figure 7.37 is an example of a galvanized grating used as a platform in the loading area of a large tanker. The galvanizing has largely disappeared from the grating, which displays general corrosion. In contrast, the deck in the foreground is coated with one coat of IOZ and has been fully protected for the same time span as the galvanized grating.

Where it is necessary to use open grating from a weight or safety standpoint, it is recommended that the grating be galvanized and coated as well as possible with organic topcoats to provide a maximum life span. When corrosion starts, such tread should be re-galvanized or coated with IOZ before corrosion has progressed to the point of dangerously reducing the steel cross section. It is possible to effectively coat grating with IOZ, even though it is difficult, and the grating must be blasted and coated from four different angles on both sides (Figure 7.38).

Another option in dealing with the corrosion of open work grating is the use of plastic grating made from glass-reinforced corrosion-resistant resin. Such grating has been used rather extensively in serious areas of chemical corrosion. Its design is not completely without problems, since the plastic can weather, and over a period of time become quite brittle, thereby reducing the safety of the structure. Wherever its use is practical, however, it is preferable to use a deformed plate (diamond tread) as stair treads and walk- ways, since it can be effectively protected and maintained by the use of coatings.

Pipe Supports

Pipe supports are a constant problem in corrosive areas. The pipe hanger or fastener is always closed with a bolt, which serves as a focal point for corrosion. Since this design is not easily eliminated, pipe supports and hangers should be galvanized to provide a solid base for an organic anticorrosive coating. The innumerable edges, corners, and inaccessible places presented by pipe supports design must all be treated with care in order to provide a proper continuous coating.

Figure 7.39 shows a typical pipe support or pipe hanger. Condensation is obvious on the overhead, and corrosion has started on the pipe clamps. While the pipe in this example is small, similar installations are used for many types of pipe, all with the same problems involved. Where pipe clamps such as these are used, it is recommended that a plastic or rubber gasket be used around the pipe to insulate the pipe from the clamp and to protect the pipe from corrosion.

Where pipe is installed on pipe racks, and particularly where the pipe moves, it is recommended that pipe slides be installed on the pipe and on the rack in order to prevent abrasion at these points. These can be made of heavy plastic sheet laid on the pipe rack itself. Pipe slides have been designed and made from anticorrosive plastic or graphite, which fit both on the pipe and on the pipe rack. When these are used, the pipe movement is taken up by the plastic slides and the pipe does not fret, thus preventing an aggravated corrosion problem. Coatings can be applied under the pipe slides so that both the pipe and the structure are protected. Since pipe supports can create serious corrosion problems, every precaution must be taken in the design, steel preparation, and coating stages in order to keep them corrosion free.

Blind Openings, Remote Areas, and Small Areas

In nearly all steel fabrications, there seems to be at least a few areas that are remote or form blind openings, which cannot be either cleaned or properly coated. These openings accumulate blasting materials, dust, dirt, moisture, and similar contaminants so that it is impossible, or at least very difficult, to provide an effective coating in such areas. Steel grit, sand, or similar abrasive media, when lodged in such places, form focal points for corrosion over which a coating cannot be effectively applied. These areas should therefore be noted and eliminated in every steel fabrication, preferably at the design stage, but at least during construction.

Welding of Pre-coated Structures

Even with the best designs, there are inevitably areas of changes and additions to the structure where welding is required. If the structure has been pre-coated, there may be serious damage to the coating at those points. Even more of problem is tank areas that have been coated on the interior followed by repairs or changes on the exterior of the tank. The heat from the welding on the exterior damages the coating on the interior and the coating must be thoroughly repaired before the interior lining is effective (Figure 7.40). While this problem is not one involved in basic design, it certainly is associated with design changes during construction. The problem demonstrates that changes in a design after a structure has been essentially completed may cause considerable coating damage and therefore must be taken into consideration before the unit can be placed in service.

Tanker Interiors

Tanker interiors are included in this chapter because of the complex design they require. Not only are these areas subject to many stresses, but they also are subject to some of the most severe corrosion problems possible. The transportation of refined products or sour crudes makes these areas subject to such extreme corrosion that any design that can be used to eliminate the complex nature of these tanks should be used (Figures 7.41 and 7.42) in such areas.

Galvanic Cells

The use of two or more different metals in corrosive areas should be carefully considered and, wherever possible, eliminated in the initial design stage. A variety of metals are often used due to the particular requirements of a process or design. One area that has caused difficult corrosion problems is the use of aluminum deckhouses on ships. These ships, ranging from tuna clippers to destroyers, are often designed improperly so that the aluminum has rapidly deteriorated.

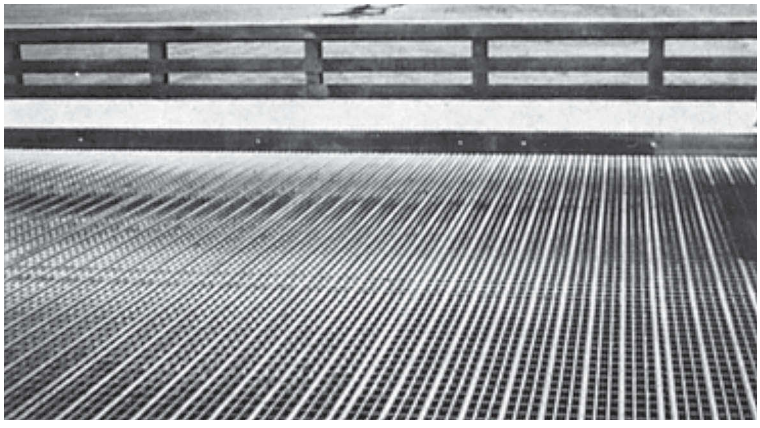


FIGURE 7.38: Drawbridge using open work grating as a roadway, with a walkway of deformed steel plate. The entire structure was re-coated with inorganic zinc that has provided excellent protection after 10 years of continuous use.



FIGURE 7.39: Initiation of corrosion where condensation has occurred on the various coating danger points presented by this common type of pipe hanger.



FIGURE 7.40: Welding burn caused by welding on the exterior of a tank or opposite side of a bulkhead. The weld area is covered with iron oxide scale. The entire heat-affected zone surrounding the actual weld area must be re-prepared before the coating can be reapplied

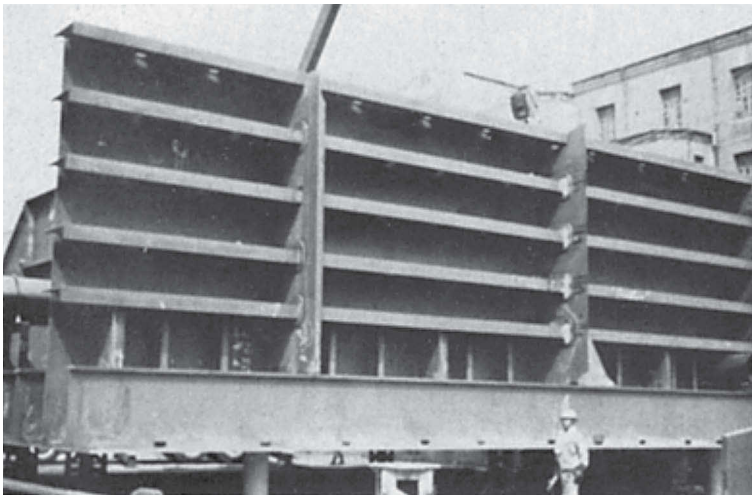


FIGURE 7.41: An internal bulkhead block section of complex design with many coating danger points.

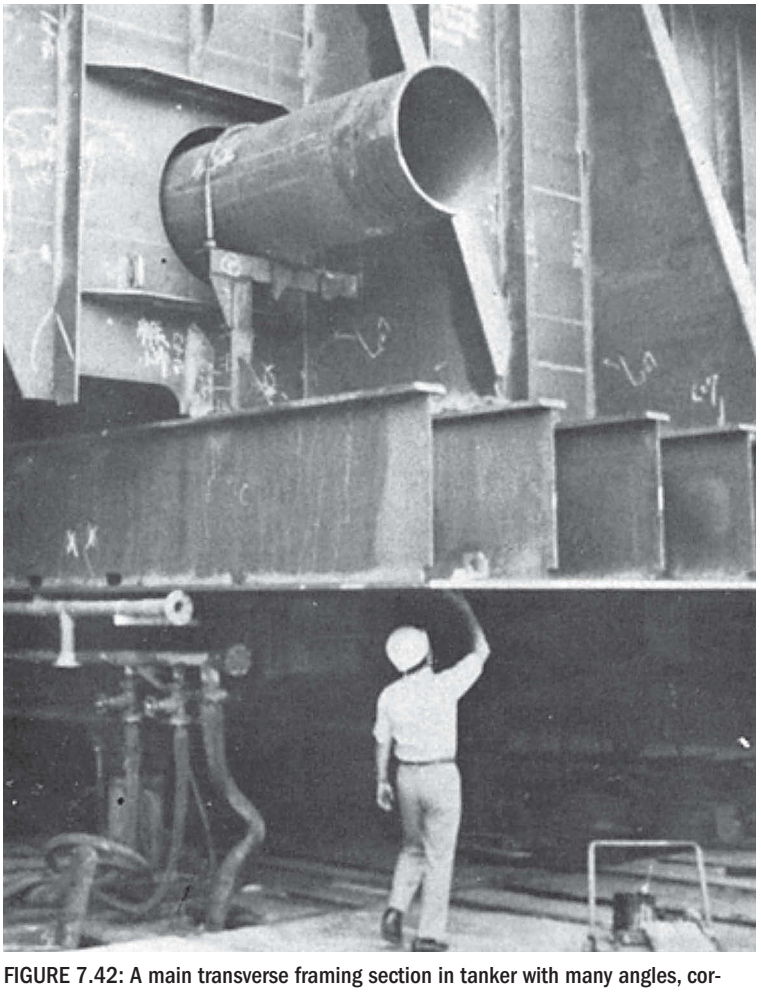


FIGURE 7.42: A main transverse framing section in tanker with many angles, corners and blind spots.

This is due to the marine atmosphere and the fact that the aluminum is anodic to steel.

Massive amounts of both aluminum and steel are used in these installations. Coating is therefore not the entire answer for such extreme conditions. The coating can protect both the steel and the aluminum and insulate the surface of the two from each other. There are, however, inevitable crevices, cracks, and similar openings between the steel and the aluminum, which collect water and quickly create difficulties. Where aluminum deckhouses or aluminum structures are joined with steel, the aluminum should be thoroughly insulated from the steel through use of inert plastic or rubber gaskets that are sufficiently thick and sufficiently extensive to make a complete break between the two metals.

Bronze valves, which act as a small cathode in relation to the deck (large anode), also create corrosion problems at the junction between the two different metals. Wherever bimetallic couples are formed, the basic design should provide for insulating the two metals from each other, and for the proper coating of both metals in order to increase the insulation.

Pre-coated Equipment

On any new project there is usually some, if not a quantity of equipment or structural parts that have been fabricated away from the job site and pre-coated. In the case of structural steel, pre-coated, fabricated units are often coated with a shop primer that was applied at the fabricating plant and failure has already initiated before erection takes place. This is because such primers are usually low-cost products, made primarily for dressing up the steel as it goes out of the fabricating plant. These products make an extremely poor primer for the more sophisticated coatings. They have little corrosion resistance and result in poor adhesion of the topcoat to the steel. Also, in many cases, they are applied over mill scale, which in itself is an invitation to failure for the better grade coatings.

The corrosion engineer should be on the watch for such shop-primed units, particularly if the unit is to be used in a corrosive area. If such units are received on the job site, they should be completely blasted free of the shop primer prior to the application of any of the more corrosion-resistant materials. The best procedure, however, is to specify in the original design that such units be completely blasted and that a compatible and satisfactory preconstruction primer be applied so that it can be used as a base for the corrosion-resistant topcoats. Preferably, the preconstruction primer should be an IOZ coating, which would provide a proper base for the organic topcoats.

Pre-coated equipment is also common. In this case, the coating on the equipment may be adequate for the corrosive atmosphere involved. Usually, however, it is a standard coating used by the equipment company and applied in one or two coats. In most cases, it is an enamel-type coating cured with heat or infrared to a hard, glossy, thermoset state, which may be entirely adequate for limited equipment usage. It probably is not, however, satisfactory for severely corrosive atmospheres. Glossy thermoset enamels, for example, might consist of a low or medium oil-based alkyd. These generally make a poor base coat for the adhesion of the more corrosion-resistant topcoats.

In order to protect the equipment properly, it is therefore necessary to determine the compatibility of this equipment enamel with the corrosion-resistant topcoats. If it is compatible, then it is necessary to at least break the gloss of the coating in order for the topcoat to adhere. The best procedure, however, is to remove the original coat and then apply a complete system of the anticorrosive product required. Again, the most acceptable procedure is to specify in the original design and specifications that all of the equipment to be used in the corrosive area must be either primed with a proper primer or coated with the full anti-corrosive coating system at the equipment manufacturer's shop.

Such problems involving shop coating are frequently overlooked in the design stage of a project and can thus cause serious problems

once the structure or the equipment is put into use. The corrosion engineer should be aware of this problem and should be on the lookout for equipment that may be coated with less than the required coating for the atmosphere in which it is to operate.

Mill Scale

There is yet another serious problem encountered wherever structural steel shapes are used: mill scale. Although this is not a problem in design, it certainly should be covered in the design specifications for any job in an area where corrosion is a factor. Mill scale, or iron oxide scale, invariably appears on the exterior of steel plate, steel shapes, or pipe that has been hot rolled. It has been proven many times, and under many different circumstances, that mill scale is cathodic to the steel itself, and because of this, will cause the steel to pit badly and rapidly.

During World War II, it was found that if ships were not descaled prior to being placed in service, such severe pitting took place in a six-month period that, in many cases, there was actual penetration of the bottom plates. While overcoating with coatings helps to lengthen the life of the plate under such conditions, it is only a temporary stopgap, since moisture will pass through the coating and into black iron oxide, causing it to swell slightly and pop off or loosen from the steel surface. When this happens, coating failure proceeds rapidly and the steel at these spots goes into solution at an exaggerated rate.

Steel need not be under continuous damp or immersion conditions for this reaction to take place. There are instances on almost every steel structure that has been coated prior to removal of mill scale, where the coating has been broken because a piece of the scale has lifted from the steel surface. Acidic fumes or chlorides greatly exaggerate such a condition, and as soon as the breaks are formed, rapid corrosion takes place. In designing a structure to resist corrosion, the specifications should call for the complete removal of mill scale prior to the application of any coating.

Insulation

Another danger spot, which requires attention and which is often overlooked in the design stage, is the coating of insulation. In areas of severe corrosion in a plant, the insulation itself may go to pieces if there is any way for the fumes to reach it. Also, the steel underneath the insulation may corrode rapidly in an area where it is impossible to notice. It is essential, therefore, to properly coat the underlying pipe or structure and to seal the insulation against water and fume penetration. If fabric-covered insulation is used, it is usually difficult for a thin coating to seal all of the openings in the fabric. If these are not sealed, the fabric disintegrates rapidly in many corrosive atmospheres and the insulation itself absorbs moisture and disintegrates. The pipe or structure being insulated can then corrode underneath.

One remedy is to apply a heavy mastic-like coating over the surface of the insulation in order to make certain that all of the holes are filled. This can then be followed with a thinner, chemical-resistant coating, if required. Wherever pipe hangers enter into the insulation, such areas should be thoroughly sealed by heavy mastic that is compatible with the topcoat to be applied. Metal insulation cover also can be used to protect the insulation if all joints are properly sealed against moisture and fumes.

A more effective practice is to coat the steel under the insulation with epoxy or epoxy phenolic barrier coating systems designed to resist the essentially immersion conditions that often occur under insulation. A new (2011) two-component, high-build, high-temperature resistant "cold spray" applied coating based on titanium modified inorganic copolymer technology pigmented with aluminum flake is capable of providing corrosion protection under thermal insulation operating in thermal cycling conditions between −321°F (−196 °C) and 752 °F (400 °C) without the need of heat curing. 100% solids epoxy syntactic foam introduced about the same time by the same global scale manufacturer is capable of providing corrosion protection between –40 °C (−40 °F) and 120 °C (248 °F).

Summary

The following is a summary list of design details, which should be taken into consideration by the corrosion engineer on any structure subject to corrosive atmospheres.

1. Structural steel shapes: Particular attention should be paid to the coating of all angles, channels, and H- or I-beams on both edges and in corners.
2. Sharp edges: Sharp edges and corners should receive additional attention. They should be ground smooth or to at least 1mm radius (preferably 2 mm) before surface preparation and coating.
3. Rivets and bolts: Particular attention should be paid to riveted and bolted areas. These are focal points for corrosion. Use galvanized or other corrosion-resistant bolts wherever possible. Unnecessary corrosion problems often result from using un-galvanized, electrogalvanized, or cadmium-plated bolts and nuts. Hot dip galvanized bolts and nuts are preferable. Where the bolt size is small, SS bolts or fasteners can provide a much more corrosion-resistant system.
4. Welds: Welds should be checked for rough areas, undercut areas, and areas that retain weld slag. Rough welds should be ground to a smooth contour, and surface imperfections such as weld spatter, metal slivers, and sharp protrusions should be eliminated by chipping or grinding prior to surface preparation. NACE SP0178 (2007), "Standard for Design, Fabrication, and Surface Finish Practices for Tanks and Vessels to be Lined for Immersion Service" is an excellent tool to use for specifying the level of uniformity of welds desired for a particular service.
5. Seal welds: Use seal welds wherever there are joint crevices, skip-welded areas, or where brackets, plates, or other attachments are left on the structure.
6. Skip welds: Skip-welded areas should be seal welded in order to seal all crevice areas and to prevent corrosive liquids or fumes from penetration into the joint.
7. Void areas: Seal weld plates over openings of difficult-to-reach, inaccessible void areas, pipe columns, or closed box girders. An additional precaution is to pressure check the seal-welded void areas by installing an air connection in the plate. If the void area can maintain air pressure, it prevents the breathing of moist air and corrosive fumes into the void and thus prevents internal corrosion.
8. Steel trusses: If steel trusses are formed with back-to-back angles or similar construction, particular attention should be paid to the area between angles or structural shapes. This is a dangerous area for corrosion to start and must therefore be sealed before coating the structure.

9. Adjacent structural members: Avoid placing two structural members close together so that the adjoining surfaces cannot be properly prepared or coated.
10. Lap welds: Where lapped steel plates are used and welded on only one side, serious corrosion can occur. Such lapped plates should be seal welded on both sides if they are to be coated.
11. Pipe construction: Where pipe design or construction is used, make certain that all openings are seal welded to prevent internal corrosion. When coating the exterior, each spray pass should be overlapped 50%.
12. Flanges: Rust and staining from the corrosion of flange faces and the use of un-galvanized stud bolts can be reduced by using hot dip galvanized flanges and bolts, or by pre-coating the flange face up to the raised base before the flange is installed. If coating must be done after the flange is in place, seal the opening between the flanges through use of reinforced adhesive plastic tape that is compatible with the proposed topcoat.
13. Pipe contact surfaces: When long runs of pipe are on a pipe rack, the pipe may move back and forth on the rack causing wear-related corrosion. Plastic or steel wear plates should be specified.
14. Water pockets: Eliminate recessed areas, low spots, or water pockets by draining through a one-inch drilled hole or by filling such recesses with a trowelable epoxy or other grout.
15. Scaffold or other permanent brackets: Scaffold or permanent brackets are usually skip welded. They should be permanently seal welded to prevent corrosion and provide a continuous surface for proper coating.
16. Pre-coated equipment: Pre-coated equipment or structural steel receiving the shop primer should be given particular attention to make certain that the existing coating provides a proper base for anticorrosive topcoats. If it does not, it should be removed.
17. Electrical boxes and connections: Electrical connection boxes and conduits consistently give corrosion problems. Cast aluminum or die cast boxes must be given particular attention during coating in order to provide sufficient corrosion resistance. These corrode readily from the interior as well as the exterior if not properly sealed. Electrical conduit must have particular attention during the coating process in order for a continuous coating of adequate thickness to be applied.
18. Bimetallic couples: Avoid bimetallic couples wherever possible. If it is impossible, make sure that the two metal surfaces are thoroughly insulated from each other in order to prevent galvanic corrosion.
19. Structural modifications: Structural modifications are a continual problem during construction, particularly where changes are made on a portion of the structure already coated. Such modifications made by cutting and welding destroy the coating on both sides of the plate or structure.
20. Open gratings: Deformed plates should be used in place of open gratings whenever possible. Coatings can properly protect the plate, while the openwork grating is a constant coating problem. Any openwork grating used should be galvanized prior to top coating.
21. Insulation: Insulation can both disintegrate and cause corrosion to the underlying pipe. Both pipe and the insulation should be properly coated.

All of the above types of construction and construction problems are common throughout today's industry. Coatings are usually the last item to be considered by a design engineer and they are the last item to be accomplished on a construction project. It is little wonder then that less attention is paid to coatings than to any other part of the structure. Coatings are, nevertheless, critical to the life of any structure where corrosion is a problem. The design and construction of a structure should be such that as many of the difficult areas as possible are eliminated during the design stage or, when necessary, during construction. Also, every care should be taken on existing buildings and equipment to make sure that the difficult or problem areas are properly protected.

The possibility of corrosion should be taken into consideration in the planning of any structure, and it must be considered as much of a design problem as any other engineering factor. A structure that is designed with corrosion in mind, and where all of the possible problems are eliminated (e.g., sharp edges, corners, crevices, rough welds, etc.), will operate much longer, more effectively, and more economically than one that is conventionally constructed and then coated and recoated at short intervals because of areas that cannot be properly protected.

References

1. H.T. Rudolf, "Design Against Atmospheric Corrosion" *Corrosion*, 2, 8 (1955): pp. 35–38.
2. NACE SP0178-2007, "Design, Fabrication, and Surface Finish Practices for Tanks and Vessels to be Lined in Immersion Service" (Houston, TX: NACE International, 2007).

8 The Substrate—Importance to Coating Life

Usually, we think of the coating as the most significant factor in the protection of a surface, and in one sense this is quite true. On the other hand, consider the substrate (surface) and its effect on the permanence, durability, and effectiveness of the coating. The substrate, or surface over which the coating is applied, is the groundwork or foundation of the coating, thus its characteristics have a direct bearing on the life of the coating.

The construction of a building on sand, clay, or rock demonstrates a similar relationship. The same house could be built on each base; however, the one built on clay would have a shorter life and therefore be less satisfactory than the one built on rock. Also, the foundation necessary for a house built on sand would differ from that needed to be built on clay.

In the same way, coating systems vary according to the substrate. For example, consider a coating exposed to sodium hypochlorite. Sodium hypochlorite is a reactive chemical, which gradually breaks down into nascent oxygen and sodium chloride (NaCl). While vinyl coatings are resistant to this reagent, if the coating is applied over steel, the nascent oxygen will penetrate any coating defect and thus initiate rapid metal corrosion. However, the same coating applied over a smooth concrete surface will last for a much longer period of time. This is because the concrete surface does not react with either the nascent oxygen or the NaCl, so that full coating effectiveness can be realized.

Another example is that of a coating applied over both steel and aluminum in an alkaline atmosphere. The coating can be thoroughly resistant to the alkali and yet fail over the aluminum because of that metal's reactivity with the alkali. Any break or imperfection in the coating will allow the aluminum to corrode, leading to early coating failure. The same coating applied over steel, however, would have a long, effective life because of the low reactivity of the steel and alkali.

Thus, the surface to be protected is a key factor in the life and effectiveness of a coating. This is an important point to be considered when selecting structural materials for any corrosive atmosphere.

There are many types of substrates over which coatings are applied: for example, steel, concrete, wood, aluminum, copper, lead, zinc, stainless steel (SS), cast iron, concrete block, plastic, plasterboard, masonite, reinforced plastics, and even rock. Each of these has a different effect on the coating applied over it, and different coatings may be required to provide effective protection. Some of these substrates and the characteristics that are important in terms of the life of a coating are described in the following sections.

Types of Substrates

Steel

Steel is the most common surface over which high-performance coatings are applied. Steel makes up the mild hot-rolled plate, sheet, and structural shapes that are commonly used for construction throughout the world. There are many other forms of steel available; however, none is as widely used as the carbon hot-rolled variety. Fortunately, that variety provides one of the best surfaces for coating application. Steel, with the exception of areas that might have been previously corroded, presents a relatively uniform, even, smooth surface without any changes in the basic metal surface that might cause variable coating adhesion. This is particularly true of new steel, either in the form of cold-rolled plates or hot-rolled steel that has been pickled or blasted free of all original mill scale. This is important, since two of the other most widely encountered surfaces that require coating are concrete and wood, neither of which have a uniform surface.

The steel surface is also dense and nonporous, so that a coating that has good adhesion characteristics and is properly applied should have relatively uniform adhesion over the entire surface. Steel surfaces are reactive with acids, chlorides, sulfides, and numerous other chemicals. Where these materials have access to the surface, rapid corrosion results. On the other hand, with the proper adhesion of coatings over the steel surface and with a smooth, dense, uniform surface, coatings can prevent these reactive materials from coming in contact with the steel and therefore provide full protection. Most coating materials are compatible with steel surfaces, which with proper surface preparation such as abrasive blasting or acid pickling, provide a good surface over which to apply high-performance coatings.

Figure 8.1 illustrates the normal surface of new steel after sandblasting. It is relatively uniform in texture, with few variations in surface structure to cause uneven coating reaction or adhesion.

Low-Alloy Steels

Low-alloy steels have the advantages of good strength and mechanical properties that make them useful for particularly critical areas of a structure. Thus, many questions have been asked about the effectiveness of coatings over these products. This issue is addressed in a paper by Copson and Larrabe,[1] as follows.



FIGURE 8.1: White sandblasted steel panel providing an excellent coating substrate with a smooth, uniform texture and even color.

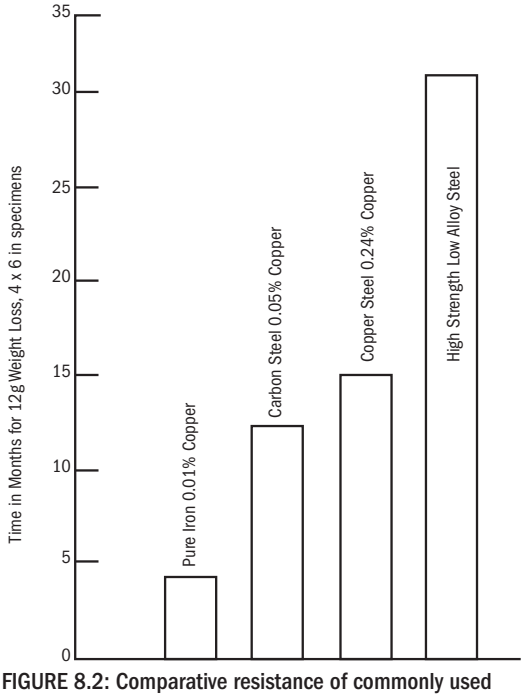


FIGURE 8.2: Comparative resistance of commonly used steels exposed bare in a marine atmosphere. Source: H.R. Copson, C.P. Larrabee, "Extra Durability of Paint on Low Alloy Steels," ASTM Bulletin, December 1959.

It is quite well known that most of the low-alloy constructional steels also have improved resistance to atmospheric corrosion. The extent of the improvement depends upon the composition, with the copper, nickel, chromium, and phosphorous contents being particularly advantageous. Some of these grades have roughly four to six times the atmospheric corrosion resistance of carbon steels. This pertains to bare uncoated steels that are free to rust.

It is not so well known that this improved corrosion resistance makes paint coatings more durable. Rust will form, of course, at any breaks or discontinuities in the paint coating. Rust also forms to some extent underneath many paint coatings. The accumulating rust tends to break down the paint film. Owing to their better corrosion resistance, much less rust forms on the low-alloy steels than on carbon steels. The smaller amount of rust from the low-alloy steels causes much less damage to paint coatings than does the more voluminous rust from carbon steels. Any rupturing of the paint film permits larger amounts of moisture to contact the steel surfaces, and this accelerates the deterioration.

By prolonging the life of paint, the use of low-alloy steels makes it possible to go much longer before repainting is necessary. The corrosion damage at any rusting areas and the spread of rust from a scratch or other holiday is lessened greatly. The labor in preparation for repainting is reduced. The net result is that the use of low-alloy steels can effect a considerable savings in the cost of labor and materials for maintenance painting.[1]

This work, along with similar work reported by Hudson[2] and LaQue,[3] is further indication of the importance of low-alloy steel to effective coating use.

The comparative resistance of several commonly used steels in a marine atmosphere is shown in Figure 8.2. These tests were conducted at the International Nickel Testing Station at Kure Beach, North Carolina on bare steel panels. The composition of the steels is shown in Table 8.1. Even relatively small changes in steel composition can change the life and effectiveness of any coating applied over it.

Stainless Steel

The term "stainless steel" is a generic term that represents the many different types of stainless available. Stainless is a good substrate over which to apply an organic coating because of its inert characteristics, both to the atmosphere and to chemicals. It does provide a smooth and dense surface that can, in itself, create difficulties in terms of coating adhesion. Where coated SS is exposed to high humidity or immersion conditions, it may provide a sensitive surface over which to apply organic materials because the dense smooth surface does not allow maximum adhesion. Coating adhesion is improved over stainless where the surface is lightly etched, blasted, or treated to a dust blast prior to the application of the coating.

TABLE 8.1: Composition of Steels Shown in Figure 8.2

	Composition, %							
Material	**Carbon**	**Manganese**	**Silicon**	**Sulfur**	**Phosphorus**	**Nickel**	**Copper**	**Chromium**
Open-hearth iron	0.02	0.02	0.002	0.03	0.005	<0.05	0.014	Nil
Carbon steel	0.04	0.39	0.007	0.02	0.007	0.01	0.05	0.07
Copper steel	0.06	0.32	<0.01	0.02	0.010	<0.05	0.24	Nil
Low-alloy steel	0.08	0.37	0.29	0.03	0.089	0.47	0.39	0.75

Source: H.R. Copson, C.P. Larrabee, "Extra Durability of Paint on Low-Alloy Steels," ASTM Bulletin (December 1959).

While a stainless surface is inert to many common chemicals, chlorides can often reduce the protective oxide film on the stainless surface, causing it to pit at breaks in the coating. Some coatings may tend to break down and release hydrochloric acid (HCl) when heated or exposed to strong sunlight. These have most often been clear coatings, and, when used over stainless, have caused underfilm corrosion and cracking.

Concrete

Concrete could be considered the antithesis of steel in terms of the characteristics that may affect coating life. While concrete is a porous material, this property in itself may vary widely from one portion of the surface to another. Cast concrete surfaces tend to contain numerous water and air pockets, some of which are small and others that are quite large. Some may extend into the concrete surface as much as one inch.

Figure 8.3 is a view of a typical poured concrete surface showing the air pockets and pinholes that are always present. This is an average concrete surface shown after the forms were removed. The difference in cast surfaces depends on the way the concrete was poured into the forms, the surface of the form itself, the water/cement ratio, and the mix of the concrete. A concrete that has the optimum water content and is well vibrated or puddled will provide the best cast surface, but even this will be somewhat porous and will contain some water and air pockets. Concrete that is improperly cast with little regard for proper placement may have sizable rock pockets and other areas that cannot be coated. This makes for a nonuniform surface that varies from one pour to another, and may change in character within a matter of a few inches. It often varies from a smooth, hard, trowelled surface that is almost glasslike, to one that is rough and porous, and requires considerable surface preparation before the application of any coating.

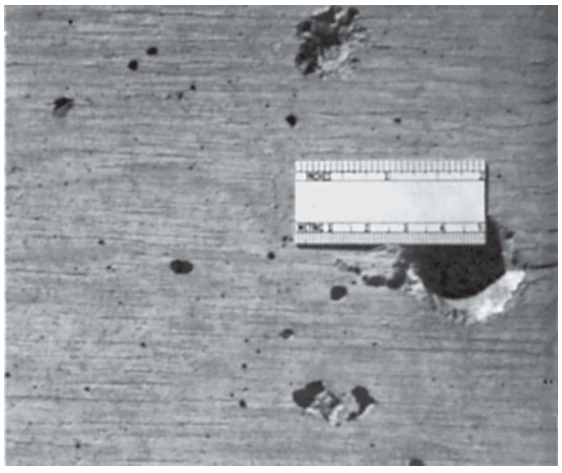


FIGURE 8.3: Typical poured concrete surface soon after form removal showing the form tie hole, air pockets, pinholes, and the texture of the wood form.

Concrete surfaces may also contain a surface residue called laitance. This material is derived from some of the nonreactive materials in the cement or in the aggregate that are worked to the surface during placement. The interior surface of centrifugally spun concrete pipe, for example, contains a heavy layer of concrete laitance. Trowelled surfaces that appear to have a glaze often have a thin layer of the laitance, which gives the glazed appearance. The laitance, either heavy or thin, is a weak, powdery (crystalline) material that has little adhesive strength. It will ordinarily act as a parting agent between the concrete surface and the coating.

In order for coatings to satisfactorily adhere to the concrete, laitance must be removed by acid etching or by a light abrasive blast. However, the best concrete surface for coating application is a hard trowelled surface, since it produces the most uniform surface for concrete. It is also quite dense so that a smooth, continuous coating film can be easily applied. Figure 8.4 illustrates the uniform, dense, slightly granular surface provided by trowelled concrete. Care should be taken when working with steel trowels to avoid overworking the concrete into a glazed surface, unless the surface is not to be coated.

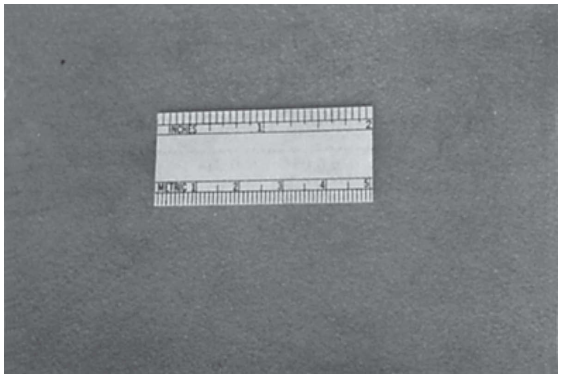


FIGURE 8.4: A troweled concrete surface.

One of the major problems in coating all substrates is the development of a continuous film. Poured concrete is filled with pinholes (porosities) so that it is almost impossible to obtain a continuous coating. As a matter of fact, in any area where concrete corrodes readily, such as in a septic sewer, the surface porosity is such that very few sprayed on coatings will provide a completely continuous film and prevent corrosion. Under these conditions, concrete must be specially treated by trowelling a coat of cement plaster over the surface, or by using some of the resinous surfacers to fill the pores and provide a base over which the coating may be applied.

Concrete surfaces are chemically reactive with any material of an acidic character. This includes pure water. Many examples have been seen of concrete surfaces in mountain areas where pure snow water has flowed over the surface and left it completely etched, with the aggregate heavily exposed after only a few years in service.

Some of the most advantageous coatings for concrete surfaces are those that use the porosity of the concrete to the advantage of the coating. Historically these have usually been epoxy-type products, which penetrate the pores of the concrete and react in place. More recently the development of aromatic elastomeric polyurethanes and polyureas have proven to be quite satisfactory, depending on the type of media to which they were exposed. This provides for maximum adhesion of the coating. Care must be taken to avoid bubbling of the coating, either from solvent entrapment or from the out-gassing of concrete during rising ambient temperatures.

The penetration of coatings into the concrete pores is important, and even vinyl coatings, which are applied as a dilute solution, will penetrate into a concrete surface and obtain good adhesion. Coatings that remain mostly on the surface, such as water-based emulsion-type coatings, are not recommended for concrete where severe corrosion is a problem. Generally, coatings for the corrosion protection of concrete require greater thickness than coatings applied over less porous and more uniform surfaces. Thicker coatings are able to provide a more continuous coating than a thin material. One hundred percent solids epoxies, polyurethanes, and polyureas have a very good service history over concrete.

Aluminum

Aluminum provides a generally smooth, dense surface covered by a thin film of aluminum oxide. Coating adhesion over an aluminum surface is often improved by the use of chemical surface treatments. However, this may not always be possible in the field. If a coating is desired on the exterior of an aluminum tank, process vessel, or deckhouse on ship, the best surface treatment is to lightly dust blast the exterior of the aluminum. This increases the surface area and vastly improves the adhesion of most high-performance coatings.

Aluminum reacts with a large number of chemicals, particularly those that are alkaline. Thus, coated aluminum surfaces in an alkaline atmosphere tend to corrode wherever there are thin areas, holidays, or breaks in the coating. Where sulfides are the corrosive agents, aluminum may do quite well since it does not react as readily with sulfides, as do many of the other metals such as iron, copper,

silver, lead, and other metals.

Generally, aluminum makes a good surface over which to apply high-performance coatings. This is especially true of lightly blasted surfaces. For instance, aluminum crew and work boats have been prepared in this manner, followed by either vinyl or epoxy and polyurethane coating systems with excellent results in all of the world's offshore oil production areas.

Zinc

Zinc as a substrate, either in the form of hot-dipped galvanizing, electrogalvanizing, or metallic zinc, provides a smooth, uniform surface that is quite reactive. The surface of zinc reacts with carbon dioxide (CO_2) over a period of time to form a dull, gray surface. Zinc also reacts readily with most acids, with galvanizing only lasting a short period of time when exposed to an acidic atmosphere.

Zinc also has some beneficial reactions, notably its being anodic to steel and thus providing cathodic protection (CP) to steel surfaces. The effectiveness of coatings that are compatible with zinc, and thus applied over it, is increased in a substantial way because of this CP reaction. Holidays or damaged areas in the coating are protected from undercutting by the tightly adherent zinc on the steel surface, as was mentioned previously. Compatible organic coatings applied over zinc surfaces such as galvanizing or inorganic zinc (IOZ) coatings will have a much longer life than the same coatings applied over bare steel in most corrosive atmospheres. Even in acidic atmospheres, it has been shown that a zinc-base coat underneath an organic coating will prevent undercutting and will reduce blistering and corrosion at any break in the coating because of the strong adhesion of the zinc to the steel.

Zinc, then, as a substrate for organic coatings, generally adds to the life and effectiveness of coatings that are compatible with it, in spite of the chemical reactivity of metallic zinc. Not all coatings, however, are entirely satisfactory over a zinc surface. There are many (such as oil-based and alkyd coatings) that will react with the zinc, forming zinc soaps, which do not allow long-time continued adhesion of the coating over the zinc surface. The coatings that benefit most from a zinc surface are the high-performance, nonreactive coatings used throughout the chemical, marine, petroleum, and other similar industries.

As has been previously described, zinc may react rapidly underneath a rather thin and porous topcoat. This is particularly true in a chemical or chloride atmosphere when water and chlorides are able to penetrate through the organic topcoats to the zinc. Alkali is developed and zincates may be formed. Voluminous white powdery deposits are built up under a porous organic film, which destroy the effectiveness of the topcoat as well as the zinc surface.

Copper

Copper has a dense surface covered with a copper oxide (CuO) film. Because of the smooth oxide film, some coatings may fail to obtain proper adhesion to this surface. In many ways, copper is similar to aluminum as a substrate, with its dense, tightly adherent oxide film. Copper does not react readily in many chemical exposures and has a long history of permanence when used as flashing or roofing in an urban atmosphere. However, a copper surface is reactive in a sulfide atmosphere, where the copper surface turns black in a short period of time.

Where sulfides are a problem and copper is involved, a good protective coating is required. Breaks in the coating will allow the sulfides to react with the copper substrate, causing failure of the copper at the break. Breaks in the insulation on copper wire have been noted to cause the copper to be reacted away (dissolved) in a matter of a few weeks in a sulfide atmosphere.

Most acids react readily with copper. This is true both of the inorganic acids (sulfuric, hydrochloric, nitric, phosphoric) and the organic acids (acetic, butyric, stearic, etc.). Ammonia reacts readily with copper, as demonstrated by a copper water pipe, which was penetrated after being exposed to soil where a large amount of ammonia-type fertilizer was present.

These factors indicate that any coating applied over copper should be well applied, since holidays or breaks are focal points for substrate failure. Copper generally presents a good surface over which vinyls, epoxies, asphalt, chlorinated rubber, and similar inert coatings can be applied.

In order for most coatings to obtain good adhesion to a copper surface, it is suggested that the surface be lightly blasted prior to application. Dust blasting or baking soda blasting merely breaks up the copper surface and reduces the amount of copper oxides that are present. This is recommended over even a fine sandblast since the impact of the abrasive grains can cause the copper metal to warp and expand, while a light dust or soda blast (which has little or no heavy impact on the surface) will scour without the tendency to warp. The industrial-grade baking soda may be used in either a dry or wet-abrasive equipment set-up.

Cast Iron

Cast iron provides a rather rough, porous substrate, as previously mentioned. The surface is porous to various gases, and unless these are removed, they can cause adhesion problems. Most cast iron surfaces are blasted at the foundry in order to remove the sand or core material from the surface, which adds to their surface roughness. However, cast iron is iron, and it has many of the same characteristics as steel when in a corrosive atmosphere.

Cast iron differs from steel in that it is more granular in nature and contains free graphite or carbon. Its surface is less homogeneous and dense than that of steel. Under soil or immersion conditions, the iron may be dissolved from around the carbon particles, causing a condition called graphite corrosion. Such a condition can exist where there are breaks or holidays in the topcoat. Where the cast iron surface is properly prepared, it provides a good substrate over which to apply protective coatings.

Lead

While it is not often that a coating is applied over a lead surface, they do tend to perform well since the lead provides an inert base for the coating. Lead is resistant to many acids and alkalis so that a variety of coatings can be used over it successfully. Lead provides a soft, smooth, and extremely dense surface and one that feels almost greasy. Because of this, some roughening of the surface is necessary. Good adhesion of organic coatings can be obtained over lead by lightly blasting the surface or lightly roughening the surface by power sanding or hand sanding.

Wood

Wood generally provides a smooth surface, depending on the way it is sawed and surfaced. It is not, however, a uniform surface. The smooth wood surface varies between the summer and winter wood, so that it can vary in density to a marked degree all across the surface (Figure 8.5).



FIGURE 8.5: Summer and winter grain on a wood surface.

The dark grain is winter wood and the light grain is summer wood. Each has a different density and physical structure. This is particularly true of plywood surfaces, which have their own inherent characteristics caused by peeling the wood ply from the circumference of the log. This exaggerates the summer and winter grain.

Wood is moisture sensitive, and will swell during times of high humidity and shrink when conditions are dry. Also, it will tend to expand and contract at a different rate between the summer and the winter grain. This fact makes it difficult for many high-performance coatings to cover a wood surface, since they are not sufficiently flexible and extensible to withstand the continuing change in dimension. The change in both the wood and grain dimension can take place on a daily cycle, in addition to larger climatic changes that can take place over an extended period.

This difference in the winter and summer grains is particularly characteristic of woods such as Oregon pine, cedar, ash, and many other open-grained woods. Maple, birch, and similar dense woods are considerably less of a problem from a grain standpoint. While all woods contain both types of surfaces, the hardwoods can tolerate a less flexible coating than that required for the softer woods. Interestingly enough, wood is quite resistant to many chemicals, particularly those that are acidic. Thus, coatings applied over wood exposed to an acidic atmosphere generally stand up well because of the resistance of the wood itself. Even some of the alkyd-type coatings will perform acceptably in an acidic atmosphere.

So far, we have looked primarily at new, unused substrates over which to apply coatings. However, not only do different substrates create varying coating requirements; contamination, corrosion, and corrosion residues multiply the surface conditions that can affect coating life. Under real-life conditions, most surfaces are either used or have been corroded or contaminated with some type of material, and this entirely changes the surface/coating relationship.

In industry, it can almost be stated as a rule of thumb that a surface over which a coating is to be applied has been contaminated in one way or another. As an example, any steel that has been stored near marine conditions or transported by barge or ship for even a short distance over ocean will have some chloride contamination. Pitting can and does occur prior to the use of such steel. Although the pits may be quite small, they are also focal points for coating breakdown, particularly if any chloride contamination remains in the pit itself.

Contamination, then, must be taken into consideration as a substrate condition whenever coatings are to be applied. The coating of contaminated or previously corroded surfaces can be considered a worldwide industrial and marine problem. Unless such a surface is given serious consideration, both in proper surface preparation and proper coating selection, limited life may be expected. The various types of contaminants, because of their varied reaction with coatings, will be considered individually.

Types of Contamination

Rust

One of the most universally encountered contaminants is common iron oxide or rust. Rust is considered a contaminant of a steel surface and must be recognized as such, since areas of steel that previously have been rusted and then thoroughly cleaned by blasting will tend to rust again in the same areas where the rust formed the first time. As has been previously discussed, the corrosion of iron is electrochemical, and in order for iron to corrode, it first ionizes after which it reacts with other ions in the area and with oxygen from the air, eventually changing to Fe_2O_3, or common red rust, as we know it. These general reactions are as follows.

$$\text{Fe water} \rightarrow Fe^{++} \tag{8.1}$$

$$Fe^{++} + 2OH^{-} \rightarrow Fe(OH)_2 \tag{8.2}$$

$$2Fe(OH)_2 + O2 \rightarrow Fe_2O_3 + 2H_2O \tag{8.3}$$

Red Rust

The type of reaction involved in the formation of rust (i.e., the formation of iron ions and their immediate reaction with any moisture to form ferrous hydroxide) is an intimate reaction on the steel surface. Anodic and cathodic areas are created. The grain structure of the steel is involved, as well as the grain boundaries. It is because of this complex microscopic reaction that it is difficult to clean the surface of the iron reaction products. The surface can be abrasive blasted to white metal, but if allowed to stand in a humid atmosphere, it is soon obvious that the previously corroded areas begin to corrode before other areas of the steel. Such a condition is shown in Figure 8.6, where previously corroded steel was blasted and yet, within a matter of a few minutes, the pattern shown in the photograph had developed on the surface.

Chloride Contamination

Many different phases of chloride contamination have been previously discussed. Chloride contamination is most prevalent in marine environments where almost all surfaces are exposed. It is also found in the salt refining industry, chloralkali industry, coal mining, and any industry where soluble chlorides are used.

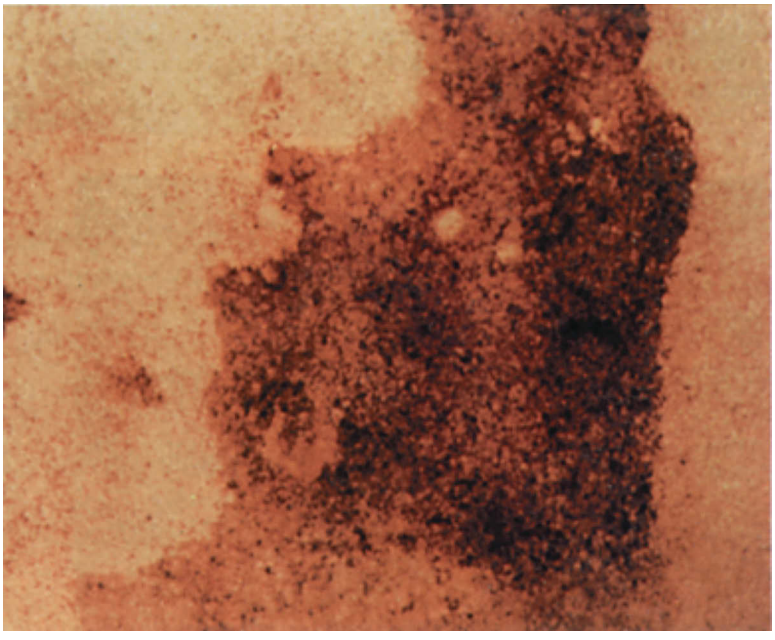


FIGURE 8.6: Previously corroded steel was white sandblasted and allowed to remain uncoated in relatively high humidity for a short time.

The problem with steel and chlorides is the formation of ferrous chloride wherever the two materials come into contact. For example, a chloride ion is absorbed into rust, and held on the steel surface. The iron ion, the chloride ion, and water form an iron chloride salt solution, which is not only conductive and can aid in the electrochemical corrosion reaction, but is in itself a strong corrodant of the steel surface. The ferrous chloride oxidizes upon exposure to air to form ferric chloride ($FeCl_3 \cdot H_2O$). Ferric chloride is a hydroscopic salt, which tends to draw moisture from humidity in the air, creating a ferric chloride solution on the steel surface. In this case, even though the steel is thoroughly abrasive blasted, even a few molecules of either ferric or ferrous chloride remaining on the surface or in the area of a pit tend to accumulate moisture from the air, causing a concentrated iron chloride solution.

This was once seen where a chloride-contaminated steel surface was abrasive blasted thoroughly. The areas of the pits were watched with a microscope and the water could be seen to condense from the air on the steel surface in the pit areas. Almost immediately, the condensate turned to a light green, indicating a ferrous chloride solution. The absorption of the moisture continued and in a relatively few minutes, the droplet of water that was forming was changed from a green to a light yellow, indicating a change to the ferric ion. The color change then continued with the solution becoming darker in color. Eventually, some of the iron in solution reacted with oxygen, forming a brown deposit. The last reaction involved the surface of the steel under and around the water condensation, which become dark brown or black.

Even a surface that has been dry abrasive blasted two or three times can still show this type of a reaction in areas of previous corrosion. Organic coatings applied over such a surface would tend to fail by the iron salt drawing water through the coating by osmosis and creating an area of poor adhesion or blistering. This type of surface contamination has caused untold coating failures around the world and is one of the reasons why corroded areas in the marine industry are so different to recoat. Wet abrasive blasting or water jetting alone is a more efficient method of removing chlorides.

One solution to this problem is to pretreat the metal surface after the initial blast with a material that will form an insoluble iron compound, such as phosphoric acid. The iron phosphate is formed preferably to iron chloride so that when the surface is again blasted, if any iron contamination remains, it is in the form of an insoluble iron phosphate.

Chloride contamination of concrete can also be a problem, although of a much different nature than the chloride contamination of steel. Concrete itself is not chemically reactive with neutral salts such as NaCl. This does not mean, however, that there are not problems involved. NaCl will penetrate into porous concrete, creating a hydroscopic condition. Coatings applied over such a chloride-contaminated surface may well have poor adhesion to the concrete because of the hydroscopic nature of the NaCl.

One area where concrete is disintegrated or seriously affected by salt is in salt marshes and bays where there is a constant wetting and drying of the surface. This action can build up a heavy crystalline deposit of NaCl on and in the concrete. These crystals form within the pores of the concrete, and as they grow, they swell and spall the concrete at and above the mudline. Concrete that has been exposed to chloride solutions provides a difficult surface over which to apply protective coatings.

Chlorides affect wood in a similar manner. The chlorides penetrate into the wood structure, but do little or no harm to the wood itself other than to provide a hydroscopic surface over which any coating would have poor adhesion. Also, as in the case of concrete, where wood is subject to a salt marsh condition or where there is constant wetting and drying of the surface, the salt will crystallize within the wood and tend to make it spall at and above the mudline.

Wood exposed to salt solutions presents a difficult surface over which to apply coatings. Lumber is often made from logs that have been floated in seawater. The moisture in the wood dries out slowly because of the hydroscopic salt, and when the wood is dry, salt crystals can still remain. Coatings applied over such a wood surface are often subject to blistering and poor adhesion.

Surfaces contaminated with chlorides present one of the most widespread coating problems found. All chloride salts are more or less soluble, many extremely so. Silver chloride (AgCl) is the only common exception. This almost universal solubility makes for conductive solutions that are seriously corrosive to many metals, as well as creating ideal conditions for osmosis, should a coating be applied over them.

Acid Contamination

Acid corrosion can be a catastrophic type of failure. It occurs wherever acids are manufactured or used, which is, for the most part, in the process industries. Acid salts should also be included in the acidic category since some of these materials are quite active and therefore extremely corrosive. All iron salts of the various strong acids are considered acid salts. Acid salts are the reaction product of a strong acid and a weak alkali. For instance, ferric chloride is the salt of a strong acid, HCl, combined with a weak alkali such as iron hydroxide. These salts then hydrolyze to provide the acid, with the consequent corrosion of both steel and concrete surfaces.

We have discussed the chloride contamination of steel and noted that HCl is one of the most trouble- some of the acid contaminants. The problem is that once the HCl is in contact with steel or iron, it leaves a chloride salt on the surface, either ferrous or ferric chloride. This has all of the characteristics of the chloride exposure previously described, in addition to being a relatively strong acid. Instances

of such contamination illustrate the dramatic failure that can occur where coatings are applied.

In one particular case, a new HCl plant was erected. However, because of the rush of construction, and in order to put the process into production, the plant was started prior to the initial coating of the structural steel. Even under the best operating conditions, some HCl escapes from the process and the reaction of steel and HCl is immediate, so that the steel surface was contaminated immediately after the plant was put into production. As might be expected, the HCl reacted with the steel surface, forming ferric chloride.

Even though every effort was made to prepare the steel surface properly, it was still done during production and the coating applied during operations. Contamination was almost continuous. Within a matter of a few weeks, the coating was almost a complete failure. The chloride contamination on the surface was, of course, microscopic. However, because the deposit was on the surface, the coating tended to blister quickly in many areas. In the areas where the structural steel was most difficult to coat, holidays resulted in uncoated steel where the HCl continued to react rapidly. In a matter of six months, the webs of the steel were actually penetrated so that major structural repairs were required.

Any plant that uses HCls can have the same problem unless the steel is thoroughly and properly coated prior to any contamination of the structure. HCl pickling plants, titanium dioxide pigment plants, and some iron oxide pigment plants have contamination problems similar to the HCl plant described. Every care must be taken in the coating of these plants to prevent the HCl contamination of the steel. Once the contamination occurs, there is no easy method of removal.

Volatile Acids

HCl, in addition to being extremely reactive, is also volatile. Hydrogen chloride is a gas, and the liquid HCl is composed of water and the gas, which combine to form a solution. HCl not only acts as a liquid acid, but also as a gaseous acid, and thus can penetrate any crack or crevice in the structure. The volatile hydrogen chloride is also extremely hydroscopic so that, even in gaseous form, it rapidly picks up moisture from the air and can react on any metal surface where it makes contact. Surfaces, therefore, do not need to be close to splash or spray of the liquid acid to be quickly contaminated. Being a gas, it can be carried by air currents to any part of a plant and react with the steel in remote or inaccessible areas where surface preparation, at best, is difficult.

Other metals can also become contaminated. Zinc, copper, and aluminum all form soluble salts with HCl. Once contaminated, such surfaces are as difficult to prepare and coat as is steel.

Nitric acid is another volatile acid with extremely strong penetrating powers. Both acids can cause contamination of the surface underneath certain types of coatings. Even some strongly acid-resistant coatings, when thinly applied, can be penetrated by these materials, so that in order to provide protection against them, the coating must not only have extremely strong adhesion and be acid inert, but they also must be applied in full thickness over the entire area. Thin spots, breaks, and holidays are all areas that are rapidly attacked and can become contaminated to the point where repair of the areas is very difficult. Iron salts of volatile acids can actually form beneath some coatings. In some cases, entire coatings have been penetrated, with the underlying substrate becoming contaminated to the point where complete removal of the coating was required prior to repair.

Nonvolatile Acids

Common examples of nonvolatile acids are sulfuric acid (H_2SO_4) and phosphoric acid. Products such as ammonium sulfate, ammonium phosphate, and ammonium nitrate are found in general use throughout the fertilizer industry. These are all acid salts, which hydrolyze to form the acid when under moist conditions. All of the iron salts formed from these acids are soluble, with the exception of iron phosphate, so that steel or metal surfaces are easily contaminated and easily corroded.

Concrete also can be severely contaminated with acid. Since concrete is a strongly alkaline material, the acids themselves are quickly neutralized by the cement, causing a disintegration of the concrete structure. Both HCl and nitric acid form soluble cement reaction products that generally can be washed from the surface by thorough scrubbing with clean water. Unless the concrete itself has been badly disintegrated, coatings can be satisfactorily applied over such surfaces once it is dry.

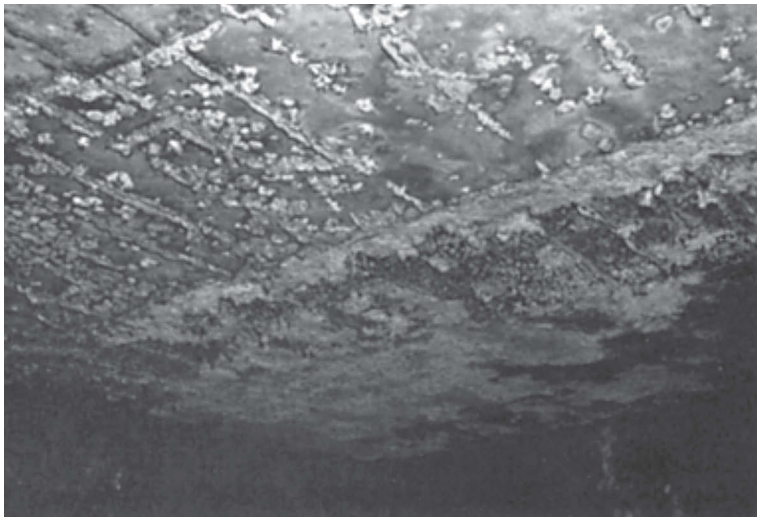


FIGURE 8.7: A coated concrete sewer structure seriously penetrated by sulfuric acid. Note the large sulfate tubercles formed underneath the coating due to the reactivity of the substrate.

H_2SO_4 is quite a different problem since it does not form a soluble reaction product with cement, but instead forms a voluminous insoluble calcium sulfate. One of the areas most affected by H_2SO_4 is that of concrete sewers and sewer structures. Here, the H_2SO_4 is developed from hydrogen sulfide (H_2S) by bacteria. Droplets of condensate in the upper portion of sewers have been shown to have concentrations of H_2SO_4 upwards of 10%. This provides a constant source of acid to react with the cement. Disintegration of unprotected sewer structures has been found to be as much as 2 in (51 mm) per year. The formation of the voluminous calcium sulfate, which has a volume roughly five times that of the cement particle, causes physical disruption of the concrete, as well as the reaction of the H_2SO_4 on the cement particles.

H_2SO_4 also tends to penetrate any imperfection in a coating. Since the concrete substrate is rapidly attacked, a pinhole in the coating can create a large tubercle due to the expansion of the calcium sulfate underneath the coating.

Figure 8.7 is an example of coatings applied to the interior of a concrete sewer chamber. The coating was penetrated through so many pinholes that it was almost completely lifted from the surface by the formation of calcium sulfate underneath. Such surfaces are difficult

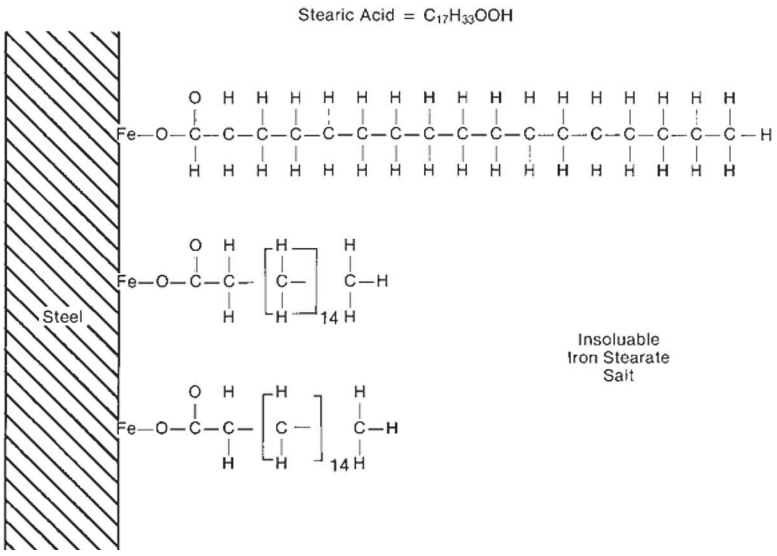


FIGURE 8.8: Insoluble iron stearic acid salt (soap) as it might appear on a steel surface contaminated with a fatty acid.

to repair as, in most cases, not only must the contaminated concrete be removed from the surface, but also the concrete must be resurfaced prior to the application of any coating.

Phosphoric acid can aid in some areas of acid contamination on metal surfaces. As previously discussed, iron phosphate is insoluble so that it remains as a solid on the surface. Thus, it can more easily be removed from the surface by abrasive blasting than can the soluble salts. Minor residues of the iron phosphates, because of their insolubility, usually will not provide adhesion problems for a strongly adherent compatible primer.

Fatty Acids

Fatty acids are common throughout many industries, including the paper, food, and soap and detergent industries, as well as in the processing of grain. Surfaces contaminated with fatty acids are much more difficult to prepare and repair than are surfaces that are reacted with mineral acids. Many fatty acids react readily with metals to form insoluble soaps, with the fatty part of the molecule being the most difficult part of the contamination. These metal fatty acid salts are insoluble in water, difficult to remove from the grain boundaries of the steel surface, and, if they are overcoated, adhesion loss and blistering are quite common.

Organic acids and fatty acids range from formic acid, which is the lowest homolog of the series, to materials such as stearic acid, palmitic acid, and many similar long carbon-chained acid products.

Fatty acids on a substrate (e.g., steel, concrete, cast iron, copper, or others) react with the surface and create a metallic fatty acid salt such as iron stearate, copper stearate, calcium palmitate, and so on. These metal fatty acid salts are also called soaps. Sodium stearate is the most common. The metal part of the metal fatty acid molecule is at one end of a long carbon chain. If this could be visualized, the metal would still be associated with the base metal. However, the long-chain fatty part of the molecule would be free, except at the metal attachment end. This makes for a chemically bonded molecule, which creates a monomolecular hydrocarbon film on the surface.

A schematic drawing of such a situation is shown in Figure 8.8. Any coating that is not thoroughly compatible with such a metallo-organic film will have little or no adhesion. The calcium and aluminum atoms in cement act in the same way, tying the fatty molecule to the surface. Contaminated concrete can be an even worse substrate than steel since the fatty acid can penetrate into the porous concrete and react in-depth.

The food industry is one that has a major problem with fatty acid contamination. In this case, the preparation of contaminated surfaces is more difficult since abrasive blasting may not be possible or practical because of possible contamination of the foods involved. Fatty acid contamination has proven to be an extremely serious problem in the food industry. Only a thorough and meticulous cleaning of the surface can result in a satisfactory coating.

There is no practical means of removing a fatty acid where it has penetrated concrete. Hot steam detergent washing removes some of the contamination from the surface, but does not remove that which has penetrated. Coatings applied over such a surface, even though the surface looks clean, invariably tend to fail from loss of adhesion. The only acceptable method of removing the contamination is abrasion of the concrete beyond the penetration of the fatty acids. In most cases, the concrete must then be resurfaced prior to being properly recoated. Some of the newer high solids (up to 100%) resinous concrete surfacing compounds do an excellent job in this area. They not only provide excellent adhesion to the abraded concrete surface, but also provide a smooth surface, and are resistant in themselves to fatty acid contamination. The addition of fumed silica to the concrete surfacing compounds increases the acid resistance measurably, to the point that a 30% addition has been shown to totally stop acid degradation of the concrete.

Wood also presents a problem where fatty acid-type materials are found. The fatty acid does not necessarily react with the wood, but it does penetrate the wood and is extremely difficult to remove by any means. Thorough washing with alkaline detergents and hot water are a less than satisfactory practical answer. Following washing, drying, and resmoothing the wooden surface where conditions permit, it is suggested that a primer with fatty acid compatibility be used (a medium oil alkyd).

Alkali Contamination

A common example of an alkali contaminant is caustic soda. The alkali grouping should also include alkali salts. By definition, an alkali salt is one that is a reaction product of a weak acid and a strong alkali. Sodium carbonate is an example. This is a reaction product of sodium hydroxide (NaOH) and carbonic acid. Alkali salts tend to be strongly alkaline and hydrolyze to a hydroxide when in contact with moisture. Many industries such as the paper, rayon, and food industries, as well as refineries and many chemical companies use alkalis in their processing.

Surfaces that have been exposed to caustic or other alkalis are generally poor insofar as coating adhesion is concerned. Coatings that are based on an oil (e.g., linseed oil, alkyds, or even some epoxy esters), may be expected to react with any caustic that might remain on the surface. Phenolic coatings would also tend to be adversely affected by any alkali that might be on the surface over which they were applied, resulting in lack of adhesion or possible disintegration.

Even vinyl resins, which are one of the most alkali-resistant of the synthetic resins, are definitely affected by alkali contamination of the surface over which they are applied.

Where alkali dust or solution has been allowed to contaminate a steel surface; even though it is cleaned by normal procedures such as abrasive blasting, there is usually sufficient alkali remaining on the surface to neutralize the acidic groups that are attached to the

vinyl resin molecule. These groups normally provide the adhesion for the coating. When these acidic groups are neutralized, the coating merely lays on the surface without the benefit of chemical or polar adhesion. The vinyl resins involved are the tripolymer vinyl chloride-vinyl acetate-maleic acid polymers.

The treatment of alkali-contaminated surfaces is fairly straightforward. The caustic contamination should be removed by washing the surface with water, followed by a dilute phosphoric acid wash prior to abrasive blasting. Phosphoric acid neutralizes the caustic that is on the surface, reacts with the steel to form an insoluble phosphate, and provides a slightly acidic rather than alkaline surface over which to apply the coating. This is a satisfactory base for almost any high-performance coating available today.

Concrete contaminated with alkali poses yet another problem. Many of the alkaline salts can react with the concrete, spalling the surface and creating a poor surface over which to apply any coating. The alkalis penetrate the concrete and tend to remain within the pore, even though the surface is thoroughly washed. Any severely contaminated concrete surface must be abraded down to solid concrete prior to the application of any coating. Alkali contamination that remains on the surface and does not necessarily react with the concrete can be removed by water washing, steam cleaning, and washing with dilute HCl to neutralize the alkali. Once this has been done, the surface must be thoroughly washed and scrubbed free of the acid salt reaction product, and the surface thoroughly dried prior to the application of the coating.

Wood also presents a problem in terms of alkali contamination. Wood is actually attacked by alkalis, breaking down the cellulose and providing a fibrous surface. In this case, all of the reacted and contaminated areas must be removed prior to the application of any coatings.

Sulfide Contamination

Sulfide represents a difficult type of steel contamination. H_2S is an insidious material, although sulfide contamination can come from other sources as well. It is a fairly widespread type of contamination, particularly in the marine industry and in the area of oil production and refining, as well as in chemical processing, such as the rayon industry. The marine industry can develop sulfide contamination through the breakdown of marine organisms on the surface of marine structures. When a marine organism, such as a barnacle, oyster, or other marine animal, dies, sulfides are formed immediately on, around, and underneath them. The sulfide then reacts with whatever iron or steel is available.

The production, transportation, storage, and processing of sour crude oil also creates a sulfide problem. Sulfides can react directly with iron without the need for water; they can form a rather heavy iron sulfide scale which, when it has access to air, oxidizes quite rapidly to iron oxide. Iron sulfide is cathodic to steel, and therefore increases the corrosion problem where sulfide contamination exists. Iron sulfide oxidizes on exposure to air, but in so doing, also liberates sulfur or sulfide dioxide as reaction products.

In closed areas, this makes for a continuing contamination problem. Iron sulfide is sufficiently reactive with air so that it will ignite spontaneously if found in heavy concentration. A number of corrosion engineers have discovered this while taking samples of iron sulfide corrosion, which they have wrapped in paper or cloth and stored in a pocket or briefcase. Sulfide is an extremely reactive material, and when ignited with a match, it burns with a blue sulfur flame.

When iron sulfide is present as contamination, it is also difficult to remove from the surface. Single abrasive blasting will not remove the H_2S from the grain boundaries of the steel. The retention of sulfide is obvious in the oil industry where new plates have replaced old, corroded plates in a tank. When abrasive blasted, the new plates will remain bright and free of corrosion for a considerable period of time, while the old plates, blasted at the same time and to the same condition of surface preparation, will turn black in a short period. When such tanks have been coated, it has also been observed that, on the new plates, coatings will remain intact and unaffected by the high-sulfur crude and saltwater conditions, while the coating on plates that have been previously exposed to sulfide will break down quite rapidly.



FIGURE 8.9: The two round blue anode areas represent contamination with hydrogen sulfide in a gelatin indicator bath. Blue indicates iron going into solution, while red indicates a cathodic reaction.

Sulfide contamination remains on steel, even though the steel is brought to a white metal by abrasive blasting. In order to remove the sulfide and to provide a proper surface for coating, the surface should first be blasted to white metal, then washed with water and allowed to rust, or washed with dilute phosphoric acid to form an iron phosphate salt on the surface. The surface then requires re-blasting before a coating can be applied.

An indication of the surface contamination effect of H_2S is shown in Figure 8.9. Here, two areas of a clean steel panel were wetted

with a dilute H_2S solution. The surface was allowed to dry and the plate was then placed in the gelatine indicator solution previously described. Recall that the anode area turns blue and the cathode red. As can be seen, the H_2S-contaminated surface turned into a strong node. When pure water was placed on the metal and placed in the same gelatin test, only a light anodic reaction took place.

H_2S is also developed by sulfate-reducing bacteria. These are found in many soils, particularly in boggy areas where there is plenty of decomposing organic matter. They are also found in some petroleum products and particularly in sewage. Here, they react not only on the organic matter in the sewer, but also on the sulfate that is in the water. This bacteria is found in a slime underneath the water level, and releases H_2S into the water. The H_2S evaporates from the water into the air where it can react with steel directly, or, as we have previously seen, the aerobic bacteria on the surface of sewer structures above the water ingest the H_2S and form H_2SO_4. This acid reacts rapidly with both concrete and steel.

Any copper surface that is in such an atmosphere must be thoroughly protected, as it also reacts readily with both the sulfide and the H_2SO_4. Sulfide contamination is therefore much more widespread than the majority realize. The sulfide-contaminated surface must be cleaned and completely freed of sulfide prior to the application of any coating if long-lasting protection is to be obtained.

Organic Contamination

Organic contamination is a prevalent problem throughout all industry, particularly where high-performance coatings are required. All industry uses oils, grease, and other similar lubricants. In addition, many industries use wax in some of their processes, and sugars as well as fats are used throughout the food industry. This type of contamination can be difficult since organic material (e.g., oils, greases, and waxes) tends to penetrate into the grain boundaries of metals; they wet the metal surface quite well and are therefore difficult to remove.

In oil production, for example, paraffin waxes, which are soluble in many of the oils, preferentially wet out a metal surface and accumulate in any area where the bare metal is exposed. Unlined steel tubing and pipe are often completely clogged with paraffin due to this preferential wetting and because of the decrease in solubility of the paraffin as the temperature of the crude oil is reduced.

Such surfaces, both on pipe and in tanks, are extremely difficult to prepare properly. The surfaces must be thoroughly steamed in order to melt the paraffin and allow it to be washed away from the surface. Even this does not completely eliminate the problem, because of the active wetting characteristics of the paraffin on the metal surface. Once the surface is thoroughly washed, it must be blasted and again washed with water in order to bring out any areas where paraffin may remain on the surface. These are readily recognized since they do not oxidize as rapidly as the surface, which is free of this type of contamination. Coatings that are applied over even a minute film of wax will not dry, but will remain tacky for several days. Even if they do eventually dry, they will have little or no adhesion to the metal. Cast iron surfaces are even more difficult than steel because of the porosity of the cast iron and the strong penetrating qualities of the wax.

In the early days of the wine industry, both steel and concrete tanks were coated with waxy compounds to prevent contact of the wine with either the metal or the concrete. As high-performance coatings became available, they were tested on both types of surfaces. They were singularly unsuccessful because of the wax contamination of the surface. Many of the early tank cars also were lined with wax, which was particularly unsatisfactory as a coating.

The expansion of the wine industry from local to worldwide distribution was a result of lining tanks with vinyls, epoxies, and similar high-performance coatings. However, it was only after it was discovered that it was the wax on the steel surfaces that was causing coating problems that they went to the trouble of properly preparing the surfaces by thoroughly removing the wax. This was only accomplished by the same procedure outlined for the petroleum tanks (i.e., a thorough steaming of the surface to melt and float the wax away). A thorough blasting of the surface, followed by an oxidation of the surface by a water wash in order to determine where any wax remained, and then a thorough reblast of the surface prior to the application of the coating were required. Unfortunately, there was not a less costly surface preparation method that would provide an uncontaminated surface over which to apply a coating.

Many other organic materials also present difficult coating problems. For instance, protein-contaminated metal or concrete surfaces are difficult to prepare for coating since organic coatings will not properly adhere where protein compounds remain on the substrate. Sugars are also difficult, particularly on concrete, since sugars penetrate and react with the concrete so that coatings applied over such surfaces do not have any adhesion.

Concrete surfaces contaminated with protein or sugar must be abraded to the point where the contaminants have ceased to penetrate. Such areas then require resurfacing. Organic resurfacing materials have proven quite satisfactory. Once applied over an uncontaminated surface, they provide good protection against further penetration into the concrete.

Where ordinary oils and greases are encountered, steel surfaces are reasonably easily prepared. This primarily involves steam cleaning the surface to remove the oil, followed by a thorough abrasive blast or acid pickle to prepare the surface for acceptance of the coating.

Concrete, on the other hand, poses a more difficult problem. Preparing and washing the surface with detergent and steam will not remove the oil and grease from the concrete to a sufficient depth to obtain a satisfactory adhesion. Organic coatings normally contain solvents, and the solvents penetrate to the oil and grease that have accumulated within the concrete. They then dissolve the oil and grease and tend to bring it to the surface beneath the coating that has been applied. This not only makes for a porous coating where the oil and grease are not compatible, but it also produces poor adhesion of almost any applied coating. Again, if the contamination is serious, the concrete surface needs to be deeply abraded prior to the application of surfacers or coatings.

Much of the previously discussed contamination concerning steel also applies to cast iron. In the case of cast iron, however, because of its different crystalline structure and the fact that contamination of almost any type—chloride, acid, alkali, sulfide, or organic—is attracted to the surface, it is a much more difficult material to decontaminate than the denser steel surface.

Blasting of the cast iron is normal procedure, but this will not remove all of the contaminants. Heating the cast iron is a second procedure, which often aids in the removal of contaminants from the surface. Heating must be carried to a relatively high temperature (i.e., several hundred degrees) where such treatment is possible. The surface then requires a reblast prior to the application of coatings. It is also preferable to apply the coating to cast iron when the surface is still warm to the touch, which allows the coating to penetrate into the surface and to wet the cast iron surface to a better degree than were it applied over a cold surface.

Aluminum, copper, brass, lead, and galvanized steel are all subject to the same organic contamination problems as is steel. Fortu-

nately, they are all dense surfaces so that contamination does not tend to penetrate, unless the contaminant chemically reacts with the surface such as alkali with aluminum, sulfides with copper, or acidic contamination on zinc. Organic contamination of these surfaces, because of their density and smooth surface, is usually less severe than with steel and, particularly, cast iron. Nevertheless, similar surface preparation methods are required in order to eliminate all contamination prior to coating.

Summary

Contaminated substrates present a critical coating problem, which must be recognized in order to obtain effective protection of those surfaces by coatings. Contaminated surfaces range from those that are merely rusty, to those exposed to chlorides, H_2S, and organic contaminants. All must be considered important factors in the proper application of any coating.

Substrates have a major effect on coating performance and life. If the substrate prevents the coating from developing its full properties of adhesion and resistance, then the substrate cannot be satisfactorily protected. The substrate and the coating must be completely compatible before a coating can provide protection from any type of corrosive atmosphere.

A resistant substrate can improve coating life substantially as indicated by Larrabee,[1] Hudson,[2] and LaQue.[3] Reactive substrates also can improve coating life (e.g., coatings applied over zinc in a marine atmosphere). Hard, strong substrates can provide a strong base and long coating life, while a soft substrate may mean a much shorter existence for the same coating because of reduced resistance to impact, abrasion, and physical abuse. Contaminated substrates even further complicate the problem by downgrading the properties of the original substrate, which otherwise might have been a satisfactory base for the coating. A thorough understanding of the substrate and its condition must be developed before a proper coating can be selected and applied.

References

1. H.R. Copson, C.P. Larrabee, "Extra Durability of Paint on Low Alloy Steels" ASTM Bulletin (December 1959).
2. J.C. Hudson, "Protection of Steel by Painting Against Atmospheric Corrosion," Schweiger Archiv fur Augewnadte Wissenschaft und Tecknik, Vol. 2 (1958).
3. F.L. LaQue, J.A. Boylan, "Effect of Composition of Steel on the Performance of Organic Coatings in Atmospheric Exposure" *Corrosion* 9, 1953.

10 Application of Coatings

A coating is a unique product. It is manufactured, placed in a container, and sold as a packaged unit, which is what the consumer buys. Yet in this state, as merely a liquid in a can, the coating is valueless. It is only after application that the coating becomes valuable and useful. The manufacturer can be as scientific and as careful as possible in producing the liquid coating, yet the final variable in the product's usefulness lies in the hands of a third party; that is, the applicator. That is why proper and careful application is often stressed as the key to the success of any coating. A less effective yet well-applied coating can provide better and longer-lasting protection than the best coating material poorly applied.

The application of a coating is actually only one of the keys to proper coating protection. Coating protection is like a tent supported by three poles: (1) the material; (2) the surface preparation; and (3) the application. If any one of the poles is weak and breaks, the whole tent collapses and the protection it provided is gone.

This concept is illustrated in Figure 10.1. If the material is ineffective, the coating protection is nil. If the surface preparation is improper, the protection provided by the coating is short-lived. Finally, if the application is poor or careless, coating protection will not be achieved, regardless of the strength of the material and surface preparation. Application, then, must be considered one of the important factors in arriving at effective coating protection.

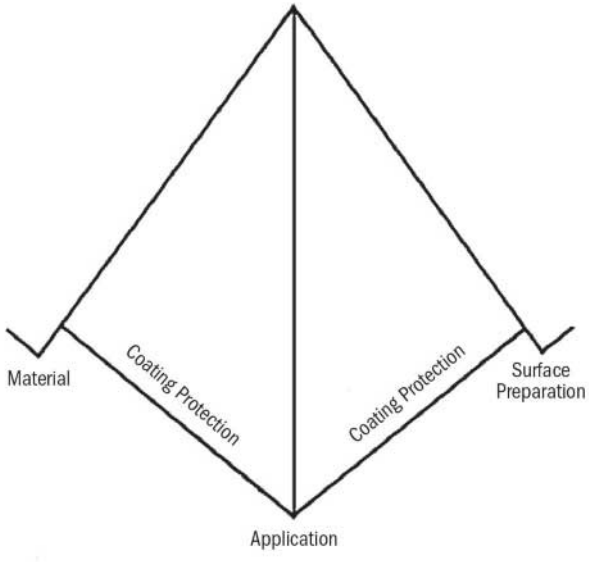


FIGURE 10.1: The three keys to coating protection.

The purpose of coating application is first to develop a protective layer of material over the substrate. Second, this layer must provide a continuous film over the surface. Third, the continuous film must be of a relatively constant and even thickness. Fourth, the film must adhere tightly to the substrate. The overall purpose, then, is to develop a continuous, highly adherent film of an even thickness over the substrate. The achievement of this purpose must take into consideration many additional factors, which will be discussed individually.

The Type of Coating

The application characteristics of various types of coating are one of these factors. Each coating type has its own application characteristics; in fact, many of the individual coatings have unique characteristics. However, because of the large number of coatings available for corrosion-resistant applications, it is only possible to describe the unique characteristics of the coating types. While there may be individual differences within the coating type, such as the differences in two coatings supplied by two different manufacturers from the same base material, they nevertheless would have some general properties that are common to both. These are the properties that will be described in the following sections (Table 10.1).

Oil-Based Coatings

Oil-based coatings include materials that are based entirely on oil, such as linseed oil-based products, alkyds, alkyd enamels, oil-based varnishes, and similar materials. One of the principal characteristics of this type of coating is that it is generally applied in thin films. If a thick, overall coating is desired, the oil-based material must be applied in several coats. In fact, these materials produce the best results when they are applied as thin films in several coats. This is because they react with oxygen from the air, which is external to the coating. The oxygen must penetrate through the coating and react throughout the coating in order to provide a strong, resistant film. Thickly applied coats of these materials tend to react on the surface, which may cause a number of coating problems, for example wrinkling, checking, or cracking.

A second important characteristic is that these materials generally have good workability. Since they are based on oil, they have good lubricating characteristics, which makes application by brush much easier than most other protective coatings. Another outstanding

TABLE 10.1: Application Characteristics of Various Coating Types

Application Characteristics	Oil-Base	Lacquers	Coreactive Coatings	Water-Base (Emulsion)	High Solids	Inorganic
Application by:						
Brush	Excellent	Poor	Fair	Good	Poor	Poor
Roller	Excellent	Poor	Good	Excellent	Fair-Poor	Poor
Spray	Good	Good	Good	Excellent	Good	Good
Film Thickness	Low	Low	Med.-High	Low	High	Medium
Flow	Excellent	Fair	Good	Poor	Good	Fair-Good
Drying Time	Slow	Fast	Med.-Slow	Fast	Fast-Med.	Fast
Wetting of Surface	Excellent	Poor	Fair-Good	Poor	Poor-Fair	Fair-Good
Film Build/Coat	Low	Medium	High	Low	High	Medium
Consistency	Oily		Sticky	Thixotropic	High	Thixotropic
					Viscosity	
Pigment/Vehicle Ratio	Medium	Low-High	Med.-High	Low	Low-Med.	High
Curing Method	Air	Solvent	Internal	Evaporation	Internal or	Air
		Evaporation			Melt	
General Application Characteristics	Excellent	Good	Good	Easy	Fair	Good

characteristic is their good wettability of most surfaces. Due to the oil content, they wet both metal and wood surfaces easily and effectively. This is also true of their application as repair materials; they easily solvate previous coatings of the same type. Because of their good wetting characteristics, oil-based coatings also flow well. In many cases, it is necessary to design some thixotropic properties into the coating to prevent the rapid formation of runs and sags on a vertical surface.

Good workability is the overriding characteristic of oil-based coatings.

Lacquer-Based Coatings

Lacquer-based coatings are based on synthetic resins, which are dissolved in solvents and do not change in properties upon application. One of their best application characteristics is that they generally dry rapidly. This is dependent on the solvent structure of the coating. However, even if the solvents are relatively slow, the drying characteristics are reasonably fast, since it only requires the evaporation of the solvents for the film to be formed.

Materials included in the lacquer category are nitro-cellulose, vinyl, and chlorinated rubber. These materials usually have relatively low solids content compared with co-reactive materials, and therefore result in thin films once the coating is applied and has dried. Lacquer-based materials are principally composed of relatively large molecular weight resins. Thus, the coatings have relatively poor wetting characteristics, since the large molecules tend to remain on the surface and therefore do not wet it to the same degree as the oil-based products. The large molecular weight resins also make for difficult workability.

Thus, lacquer-based coatings are usually applied by spray. Even in this case, however, the characteristic of difficult workability can be a disadvantage, particularly when combined with relatively fast solvents. Since these coatings easily dry before they reach the surface, overspray and similar application-related difficulties sometimes result.

The most important characteristic of lacquer-based coatings is the ability to form a fast-drying coating over the substrate.

Co-Reactive Coatings

Co-reactive coatings include epoxies and urethanes. One of their principal application characteristics is that since they can leave a relatively high solids content in the film, they can be applied at a greater thickness per coat than is possible with the much higher molecular weight lacquer-type products.

Co-reactive coatings begin at a relatively low molecular weight, and upon application, react with a catalyst or other reactive resin that increases the molecular weight and forms the film. The film formation is generally an internal reaction of the coating; therefore, coating thickness is less critical than for coatings that are primarily oxygen reactive. These coatings have good build characteristics, and thick films can be applied that still retain the resistant characteristics of the basic materials.

One of the disadvantages of these coatings is that they are relatively sticky. This means that even though they are of an intermittent molecular weight, they are not easy to brush or sometimes to apply by roller because of the sticky characteristic of the resins.

One factor that must be taken into consideration during the application of co-reactive coatings is their curing. Because of their internal cure and because chemical reactivity is related to temperature, many of these materials must be applied and cured at temperatures above 50 °F (10 °C). Some of the newer epoxy and urethane materials may be reacted at lower temperatures. Nevertheless, the curing and surface temperature must be taken into consideration as a possible application problem.

Water-Based or Emulsion-Type Coatings

Water-based or emulsion-type coatings are based on vinyls, acrylics, epoxies, or other materials dispersed in water in the form of an emulsion. Undoubtedly, the primary application characteristic of these materials is that of easy workability. Because of the dispersion of the resin as small individual particles in water, these materials are more thixotropic than viscous. The resin particles are therefore

relatively easy to move, making for easy brushing and spraying. Because of their thixotropic nature, these coatings are buttery and have a relatively limited flow. Also, due to the nature of the emulsion, even though the water easily wets the surface, there is relatively little penetration of the resin into the underlying surface.

One important factor in the application of this type of coating is its water content. In order for these materials to be effective, the water must evaporate out of the emulsion in a relatively even, regulated fashion. The best film formation occurs at moderate humidity and temperature. If the humidity is high and the temperature is relatively low, evaporation of the water is extremely slow, which can cause the formation of poor films and poor adhesion. If the temperature is too high and the humidity low, the water evaporates from the coating too rapidly, often causing the formation of mud cracks or checks. Temperature and humidity are therefore extremely important in the application of these materials.

Easy workability is undoubtedly the outstanding characteristic of the water-based materials.

Very High or 100% Solids Coatings

Very high or 100% solids materials vary from hot-melt coatings such as asphalts and coal tars, to epoxies and polyurethanes. One of the principal application characteristics of this type of coating is poor wetting. This is primarily due to their high solids content. Newer un-pigmented epoxy and urethane sealers are an exception as they are formulated specifically to provide wetting and sealing of less than perfectly cleaned surfaces. While some of them may be liquid (e.g., liquid epoxy), they must be catalyzed in order to form a solid coating. The reaction is often rather rapid, requiring mixing of the catalyst and the resin at the time of application and not before. Many application problems arise when materials are catalyzed at the spray gun and then applied to a surface. Because of the rapid reaction, wetting of the surface is extremely poor and results in a complete lack of adhesion in many cases.

Hot melts, on the other hand, such as the asphalts and coal tars, also have wetting difficulties, since they often are applied as a hot melt to relatively cold surfaces, so that the phase of the coating changes from a liquid to a solid in a very short period of time. Much lower solid and molecular weight primers are usually required along with these materials in order to obtain effective adhesion.

While the hot-melt coatings may be applied by flowing on the surface, or by daubing in the case of hot asphalt or coal tar, most of the high solids coatings are applied by spray. This is the most effective way of distributing the high solids coatings over the surface in a relatively thin, yet continuous film. Some coatings also require in-line heaters to reduce the viscosity sufficiently for easy application.

High solids materials generally have more critical application characteristics than many of the other coating types.

Inorganic Coatings

Inorganic coatings primarily refer to the zinc coatings (although there are a limited number of inorganic topcoats) of either a water or solvent base. The principal application characteristic that must be considered in the use of these materials is their high pigment:vehicle ratio. This characteristic makes it somewhat more difficult for them to flow through hoses and gun orifices, and in certain instances permits the high zinc loading to build up and create uneven flow conditions. Due to the type of vehicle and the high pigment content, these materials do not have the lubricating characteristics of organic coatings, and are therefore much more difficult to apply by brush or roller.

The principal method of application for inorganic zinc (IOZ) coatings is by spray. The IOZ coatings have a base of either water or solvent, which affects application characteristics. The cure is one of the key elements. Water-based materials are not satisfactory under cold, highly humid conditions. Solvent-based materials are difficult to apply under hot, dry conditions because of the moisture cure requirement for the ethyl silicate-base in organic products. If the humidity is too low, these materials will not cure. Hot, dry conditions also tend to increase the incidence of mud cracking and overspray.

Preparation for Coating Application

Coatings, as they are packaged at the manufacturing plant, are thoroughly dispersed, with the pigments fully suspended and of a uniform consistency in terms of both texture and color. Unfortunately, very few coatings are applied within a short time after manufacture. They may be placed in inventory at the manufacturing plant or sent to a distribution point where they will be held for a period of time. Also, the coating may be purchased several months before its actual use and again stored under any number of different conditions. Thus, coatings generally must be remixed and re-dispersed prior to actual applications.

A pigment, which is usually heavier than the vehicle, tends to settle and may even cake in the bottom of the container. Coatings vary to a wide degree in this particular characteristic. Some may stay suspended for many years; others settle out hard in the bottom of the container. While this makes for difficult re-dispersion on the job, it does not necessarily mean that the coating is poorly manufactured or that it will be ineffective. On the other hand, coatings that have gelled in the container or in which the pigment livered (i.e., became thick and rubbery) are not satisfactory for use and cannot be practically re-dispersed.

The purpose of remixing and re-dispersion is to make the coating completely homogeneous, so that upon application, the pigment and vehicle can produce the film that was intended by the manufacturer. In certain cases, particularly in oil-type vehicles, there may be skins on the surface of the liquid. These skins are actually oils and pigments that have begun an oxidation reaction with available oxygen in the air space of the container and should be removed before re-dispersion, since they will not re-dissolve into the vehicle.

Mixing

The mixing process is never particularly easy, even if the coating has not settled hard. It is a process that is often neglected by applicators, particularly in coatings that have settled rather solidly. There have been examples of coatings that were applied with at least half of the pigment remaining in the bottom of the container undispersed and later thrown away with the container. This procedure does not allow for the maximum performance of coating properties and normally leads to rapid coating failure. There have also been numerous instances of the IOZ pigment being only partially dispersed into the liquid portion of two-component IOZs because the applicator felt it was too thick to apply easily. While this improves the application properties, it decreases the protection properties in direct proportion to the amount of zinc pigment that is left out of the mix.

Mechanical Mixing

It is always best to use a mechanical mixer of some type, since mechanical mixing always produces a more uniform coating and does so much more rapidly than manual mixing. Manual mixing should only be done under unavoidable circumstances and only in containers with the maximum of a 5-gal (19-L) capacity.

There are many types of mechanical mixers available. These range from propeller attachments for hand drills and mechanical vibrating shakers, to large portable mixing units that can be used to mix as much as 55 gal (208 L) of coating at one time. Except for the vibrating shakers, most of these attachments are the propeller type that can be driven either by electric motor or by air-powered motors. Even where the coating has settled rather hard, the propeller-type agitator can break it up and re-disperse it to a point that is closely equivalent to its original manufacture. Newer types of mixers include screw types and one that resembles a quart can with sides and top cut out into inverse positioned vanes. These Jiffy mixers, usually made of rugged stainless steel, are much more efficient that propeller types and can even be used to mix highly viscous and highly pigmented materials such as grouts, non-skids, and so on. Nevertheless, care should be taken in the mixing operation, particularly to ensure that the material on the bottom and lower sides of the container has been well separated from the container and re-dispersed. Some materials settle into soft sediment, which clings to both the sides of the container and the bottom, making it necessary to scrape these off before they can be properly dispersed. This is usually a manual operation.

The mixing should be done in such a manner that splashing is avoided. Splashing not only makes for a messy mixing area, but is also a fire hazard to both the person mixing the coating and the surrounding area. The speed of a mechanical mixer should be as low as possible in order to obtain the re-dispersion of the pigment in the vehicle. The coating should have a slight vortex at the surface. A large vortex tends to mix air into the coating, which can cause pinholes and air bubbles during application. This is particularly true of latex-type coatings. Air in a thixotropic material, such as a latex, is extremely difficult to eliminate.

The mixed coating should appear uniform throughout the container, and should not show any separation pigment or color streaks on the surface.

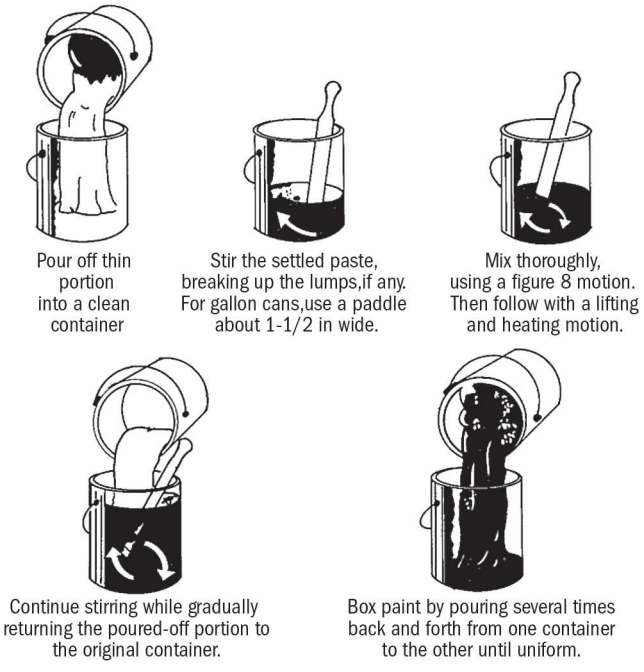


FIGURE 10.2: The manual mixing procedure. Source: Department of Defense, *Paints and Protective Coatings,* Chapter 4, Army TM5-618.

Manual Mixing

If manual mixing is necessary, the liquid portion of the coating should be separated into a clean container. The lower, thicker part of the coating can then be more readily mixed into a heavy paste, including the material clinging to the sides of the container. Once the heavier material is mixed into a smooth paste, the remainder of the liquid from the second container can be remixed into the original container with the heavy material, making sure that the two are thoroughly mixed into a uniform coating. While not always necessary with mechanical mixers, this pouring off of liquid does make even mechanical mixing easier and results in more uniform dispersion. One way to ensure thorough manual mixing is to pour the material back and forth between the two containers. This is called boxing. The materials should be poured back and forth several times to ensure complete uniformity (Figure 10.2).

Two-Component Coatings

In the case of two-component coatings, there are two materials that must be checked to determine whether or not they are properly dispersed prior to being mixed together. Two-component coatings are extremely common. They include numerous kinds of epoxy coatings, coal tar epoxy coatings, polyurethane coatings, and IOZ coatings. With two-component coatings, it is essential that the two components be separately and thoroughly mixed. Two-component materials are designed to react chemically, so that if they are not thoroughly mixed, the chemical reaction may not take place properly. Mechanical blending of the two components is recommended to obtain a thoroughly mixed product. The two-component materials often are different colors so that a satisfactory mix can be readily determined. The fully mixed coating should have a uniform color and consistency.

Mixing Dry Powder and Liquid

The primary purpose in mixing dry powder and liquid components is the use of IOZ coatings. IOZ coatings are made from a liquid component and dry powdered zinc. The first step is to determine whether or not the liquid component is thoroughly mixed and dispersed to a completely homogeneous liquid. This usually is not difficult since most liquid components are lightly pigmented Second, stir the total contents of the powder slowly into the total content of the liquid until it is a well dispersed, semi-thixotropic material. In the case of the IOZ coatings, the manufacturers supply the liquid and the powder in two different containers in the exact amount that should be mixed. It is essential that the total powder and total liquid be used in order to obtain the desired final coating. Mixing small portions of zinc and liquid is not recommended, since correct proportions are seldom measured under field conditions.

Materials other than IOZ often are mixed in the reverse order; that is, a small amount of liquid is added to the powder until a paste is formed, thoroughly dispersing the dry powder with the liquid. The remainder of the liquid is then added to the paste. Some mastics, caulking materials, and floor compounds are mixed in this manner.

Thinning

Most manufacturing procedures today produce coatings with the correct proportion of liquid and pigment so that no thinning is necessary. Therefore, do not thin unless it is recommended by the manufacturer or where local conditions (e.g., cold or hot temperatures) require thinning for proper spray. In this case, the amount of thinning should be only that recommended by the manufacturer and using only the manufacturer's thinner for that particular product. Applicators too often think that any thinner will work with any coating. This is not the case, and a number of severe failures resulting from improper thinning have proven it.

The thinner should be of the same composition as the solvents in the coating, which is normally only known by the manufacturer. In one instance, kerosene was added to a vinyl coating. While some kerosene can be added to a vinyl coating without precipitating the resins, once the coating was applied and because the kerosene was the slowest solvent in the system and incompatible with the resins, it was squeezed out of the coating onto the surface being coated. The vinyl coating came off in sheets almost as large as the structure being coated. Other solvent combinations in other coatings may precipitate the resins or may coagulate the pigment so that an uneven coating is applied to the surface.

Do not use just any thinner with any coating, and do not thin excessively. Thinning reduces the total solids content of the film, and therefore reduces the thickness of the film applied to the surface. If the coating is thinned 50%, then only 50% of the pigment and vehicle will be applied to the surface in one pass, and it will be half as thick as the coating should be, making additional passes necessary to achieve the specified dry film thickness (DFT). Thinning should be discouraged, except where recommended by the manufacturer's representative or in accordance with the manufacturer's instructions.

Straining

Most coatings are thoroughly strained prior to being placed in their container. When the container is opened, if the contents have not settled to a hard deposit in the bottom, straining in the field may not be necessary. On the other hand, if the pigment has settled hard, if used buckets are used in the field for boxing or mixing, if the coating has a skin on the surface, or if the product is a material such as IOZ, straining is recommended. Straining prior to spraying often eliminates considerable downtime due to gun clogging by small particles that restrict the orifice in the gun.

Straining can be done with a fine window screen or through a nylon stocking. A nylon stocking does not contain any lint and is a very fine mesh that most coating materials can readily pass through. However, the nylon can stretch or become bonded and burst. Mosquito netting or similar materials also are used, although they often contain some lint, which can cause problems.

Keeping the material clean in the field is essential, not only to prevent gun stoppages, but also to prevent imperfections in the coating due to particles of dirt that were allowed into the coating material.

Temperature

The temperature of the coating material is a factor that must be considered during any application. Coating materials often are stored in a cold warehouse. As the temperature drops, the coating tends to become thicker, more viscous, and even, in some cases, turn to a gel. If the coating has been stored for a long period of time in cold temperatures, the coating should be brought back to normal temperatures (i.e., somewhere between 65 and 85 °F [18 and 30 °C]) at least 24 hours before use. If this is not done and the temperature is not stabilized, then the cold liquid will be sufficiently thick to make it difficult to apply, and it may require excessive thinning in order to be applicable at all. As previously stated, any thinning reduces the solids content of the film, thus reducing its thickness.

High temperatures also can cause difficulties. In some cases, such as with epoxies, it may cause the epoxy materials to react too rapidly and even gel once they are mixed. With some amine-type epoxies, if the liquid is at elevated temperatures and the catalyst is added, they may react violently and boil up out of the container. Other coatings may be reduced in viscosity to the point where they are so liquid that a thin film is applied to the surface or excessive running and curtaining takes place. Thus, the temperature of the coating material should be taken into consideration at the beginning of any application.

Application Methods

There are a number of application methods by which coatings can be applied. The three principal methods are by brush, roller, or spray. Other methods consist of paint pad applicators, paint mitts, electrostatic spray, electro-coating, dipping, and fluidized bed coating. The latter methods, from electrostatic spray on, are primarily for in-plant application and generally are used for product finishes rather than for the field application of coatings.

TABLE 10.2: Application Methods

Relative Coverage Per Day		
Method	Sq. Ft.	Sq. Meter
Brush	650	93
Roller	1,200-2,600	186-372
Air Spray	2,000-6,000	372-744
Airless Spray	3,000-8,000	744-1115

Source: S.B. Levinson, S. Spindel, *Paint Application*, Chapter 5 (Pittsburgh, PA: Steel Structures Painting Council, 1982), p. 160.

Of the three principal methods, brushing is the slowest and spraying is by far the fastest. The relative coverage per day is indicated in Table 10.2.

The actual choice of application methods depends on a number of factors. The first is the type of coating. Most oil-based coatings can be easily applied by brush; however, for large, flat surfaces, roller or spray application is much faster. For small and relatively intricate areas, brushing probably would be the recommended method. The repair of small areas or touch-up coating often is done by brush because the areas are small and brushing allows better control of the application. Fast-drying coatings (e.g., lacquers) are difficult to uniformly apply by brush or roller. Thus, spraying is the preferred method for these materials. Slower drying materials usually can be applied by any of the three methods.

The type of surface is also a factor to be taken into consideration. As stated previously, brushing is probably the best method for small areas and odd shapes. Also, if the surface is pitted, brushing of the first coat is recommended. Rolling is practical for large, flat areas (e.g., tanks, side walls, or flat tank roofs). However, spraying would be an even faster method in such cases. Spraying usually is

preferred on large areas and is not limited to flat surfaces. It can be used on curved surfaces, such as pipe, or irregular surfaces, such as structural steel shapes.

Environmental problems also should be considered. Brushing and rolling can be done in almost any area, since the liquid coating is transferred from the brush or roller directly to the surface. Spraying, however, represents problems with toxic solvents, as well as a possible fire hazard due to fume buildup. Many municipal agencies have banned the spraying of high-gloss polyurethanes on elevated water tanks because of the potential exposure of the people in the neighborhood of the elevated water tanks to Isocyanate curing agents. Spraying in small, enclosed areas usually is not suggested if either brushing or rolling can be done. Also, areas close to parked cars or areas where welding is being done should be avoided when spraying. When spraying in the open, overspray may be a problem since slow-drying liquid coatings can be carried for a long distance under windy conditions. Spraying where there are parked cars or where coating contamination may occur on adjacent structures should be limited to fast-drying coatings, since any overspray would dry before hitting the other surfaces.

Cleanup is also a factor to consider. Cleaning a brush is the least difficult procedure, cleaning a roller is second, and cleanup of spray equipment is the most time-consuming and the most complicated procedure. Where a small area is involved, brushing or rolling would be preferable because of easier cleaning procedures.

TABLE 10.3: Paint Brushes

Width, in	Name	Apply	On
6-8	Calcimine Flatting	Water-thinned paint	—
3½-5 (4 in usual)	Wall	Flat, semi-gloss primers, industrial paint	Walls, siding structural steel
2-3	Enamel, varnish	Enamel, varnish metallic paint	Woodwork, small areas, trim, rolled areas
1-1 ½	Sash, Trim	Enamel, varnish metallic paint	Narrow woodwork, radiators
1-2	Angular sash	Enamel, varnish metallic paint	Windows, sash
No. 2 to No. 12	Oval	Enamel varnish metallic paint	Irregular surface piping, railings

Source: S.B. Levinson, *Facilities and Plant Engineering Handbook—Painting* (New York, NY: McGraw-Hill Book Co.).

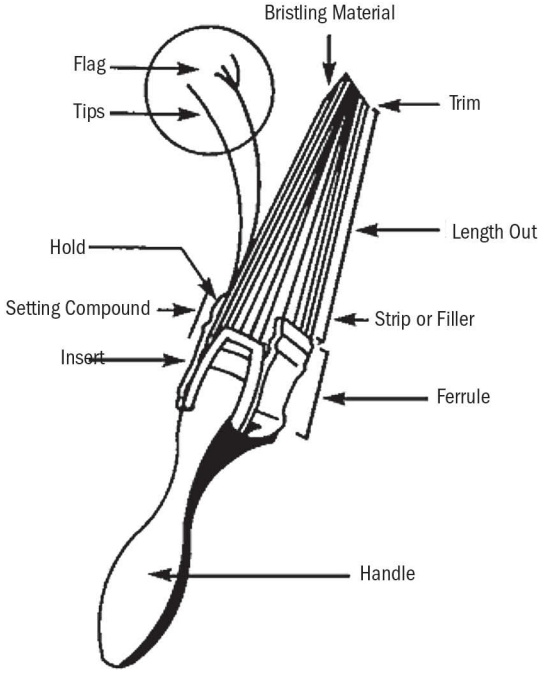


FIGURE 10.3: Typical standard paint brush. Source: Department of Defense, *Paints and Protective Coatings,* Chapter 4, Army TM5-618.

Brush Application

Brush application is not an outmoded method of applying coatings. This may seem to be the case because many of the high-performance corrosion-resistant type of coatings are preferably applied by spray. Nevertheless, there are areas and conditions where brushing is a valuable method of application for even these types of materials. In many instances, it is recommended to brush difficult areas, for example, edges, around rivets, in corners, around bolt heads, along welds, and similar areas, prior to the application of a general spray coat. Also, brushing is useful in obtaining improved wetting of primers, particularly on surfaces that are difficult to coat, such as those just mentioned. Brushing the first coat of surface-tolerant primers improves their ability to adhere to marginally cleaned substrates. It is particularly advantageous during the application of surface-tolerant epoxies over damp surfaces. The mechanical movement of the brush forces the surface moisture to be taken up into the interstices of the epoxy and the moisture is kicked out of the film by the curing reaction of the epoxy. Brushing is worthwhile for blending in edges and corners prior to spraying the general area. Brush application definitely should not be overlooked in the application of high-performance coatings.

There are a number of types of brushes. The most common type, which is used for structural steel and similar areas, is the conventional wall-type brush, which may vary in width from 3 to 6 in (76 to 152 mm) and with varying lengths of bristles up to 7 in (179 mm). Oval brushes often are used for structural steel and marine applications. These can be used for the application of coating around irregular surfaces, such as rivets, bolt heads, and similar areas, as well as piping, railings, and other such surfaces. A list of the various types of brushes and their general uses is given in Table 10.3.

The most commonly used brush is the conventional type with a 4-in (102 mm) width. Larger sizes can be used (e.g., up to 6 in). However, these usually are only satisfactory for the most easily worked coatings, such as latex-type wall and masonry coatings. Other materials have sufficient pull so that the 4-in brush is the optimum for easy handling. Figure 10.3 is a cutaway view of a typical standard type of brush. All good brushes would have this or a similar type of construction.

The flat brush is a new type of brush that generally is made up of short nylon bristles of 1 to 1.5 in (25 to 38 mm) long, attached to a flat base of about 4 × 7 in. This provides much wider coverage on the surface, and this type of brush can hold a considerably larger quantity of coating than the conventional brush. It also generally applies the coating to flat surfaces more rapidly; however, it cannot be used effectively on complex surfaces. It is effective in forcing coating into cracks in wood, into pitted surfaces, and into similar un-areas on flat surfaces. The 5 to 7 in brushes require the use of a roller tray in order to fill the brush, since its size does not allow it to be practically placed in a container.

There are generally two types of bristles used in paint brushes. Synthetic fibers are satisfactory for most brushes. However, where they are used in lacquers, which contain powerful solvents such as ketones, the synthetic fibers may be affected by the solvents. Nylon is an excellent synthetic fiber. It is not affected by most solvents, although strong lacquers may affect the nylon bristle. Hog bristle used to be the primary material used for paint brushes. It is still the best quality bristle and gives better leveling for most coatings. Hog bristle brushes are expensive, since most of the hog bristle comes from China. They are water sensitive and should not be used for water-thinned coatings, but can be satisfactorily used for lacquers. Nylon can be used for almost all coatings, with the limited exception of very strong solvents. It is less expensive than the hog bristle and is good with water-thinned coatings. Nylon also has excellent abrasion resistance where coatings are applied to rough, uneven steel, concrete, and masonry surfaces.

The proper application of a coating by brush depends on the proper handling of the brush. The brush should be held with the fingers, much like holding a pencil. It should not be held in the fist as with a club. Proper handling techniques, as shown in Figure 10.4, give a lighter brush touch, provide better control, leave fewer brush marks, and cause less fatigue than other brush handling methods.

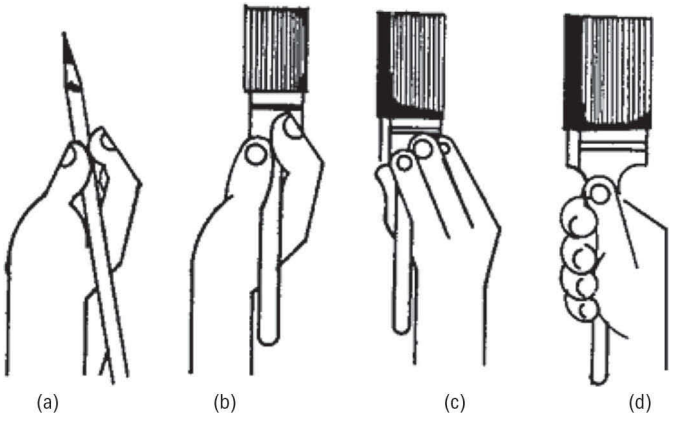


FIGURE 10.4: Brush handling techniques: (a) and (b) grasping brush with pencil grip. (c) Grip used for painting walls and floors. (d) Simple grip with all fingers around brush handle, suitable for use when painting ceilings. Source: Department of Defense, *Paints and Protective Coatings,* Chapter 4, Army TM5-618.

Brushes should not be dipped deep into the paint. Dipping into the paint approximately 1 in is adequate for most applications. This keeps the liquid out of the heel of the brush and prevents dripping and running of the coating onto the handle. The proper technique of loading a brush is shown in Figure 10.5.

The coating should be spread over the surface holding the brush at an angle of approximately 45 degrees to the work. The coating should be spread evenly and quickly by a number of light strokes, using the wrist and arm to spread the brush-loaded coating on the surface. Once the coating is evenly spread, it should be smoothed by light parallel strokes of the brush over the surface to eliminate any irregularities in the coating. Do not push down on the brush during application; this only makes for hard work and does not improve the brushing procedure. Pushing the brush too hard, especially on the finish coats, can create brush marks, which can be focal points for eventual coating failure.

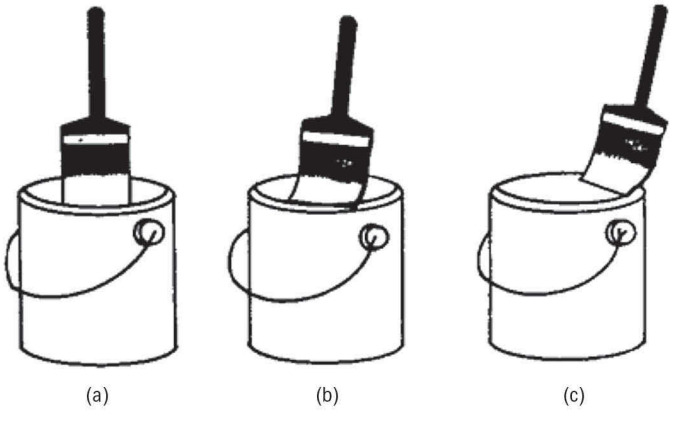


FIGURE 10.5: Loading a paint brush. (a) The brush should not be dipped into the paint more than half the length of the bristles. (b) Excess paint should be removed from brush by gently tapping against the side of the can as shown at left. (c) Not by wiping brush across top of can.

When the next brush load of coating is applied, the final smoothing strokes should be from the latest applied coating into the previous brush load in order to spread the overlap between the two areas of coating and to provide a smooth, uniform coating over the whole surface. Always brush the final strokes from the last application into the previous one, sweeping the coating into the wet edge of the previous application to prevent lap marks. It is often best to use cross strokes for both spreading and smoothing the coating; however, the final strokes should all be parallel and in one direction.

In applying fast-drying coatings by brush, the brush should be dipped and filled. The coating should be applied to the surface as rapidly as possible and then left undisturbed. Going back over such coated surfaces only results in piling up the coating and roughening the surface. Use a few rapid strokes to apply the coating to a small area and then leave it alone. Apply the next brush load adjacent to it in the same manner, always brushing the lapped area from the new into the wet edge of the previous brush load. Where there are edges to be coated, brush out over the edge, pulling the coating out over the edge. This helps build the coating on this critical area (Figure 10.6).

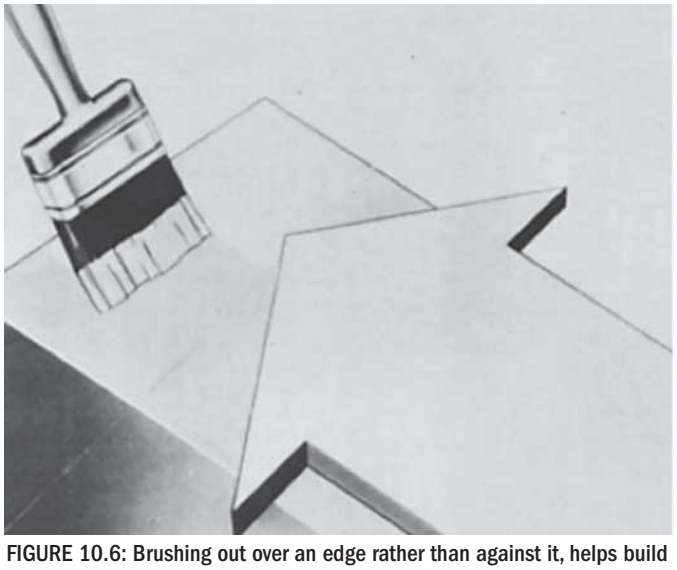


FIGURE 10.6: Brushing out over an edge rather than against it, helps build the coating in the critical area.

Do not brush against an edge, as this pulls the coating away, causing a thin area on the edge. This is particularly true when brushing chlorinated rubber, vinyl, and some lacquer-type coatings, since they are permanently soluble in their own solvents. The rubbing of the brush on the sharp corner will dissolve any previous coat that might be there.

It must be stressed again not to overload the brush. A brush with a heel full of coating (i.e., coating up to the handle) will cause dripping, runs, and continual application problems. A brush that is loaded to the heel is much more difficult to clean than a brush that

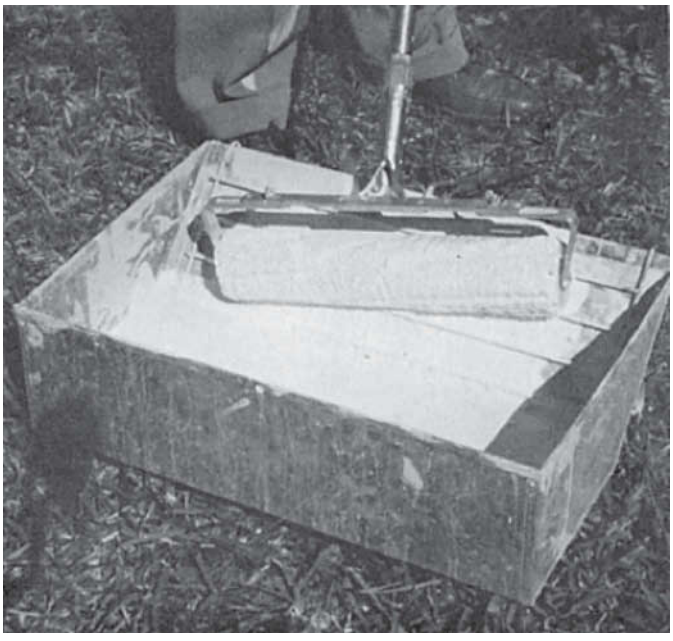


FIGURE 10.7: Industrial paint roller and tray. Photo courtesy of Arsco Paint Rollers, Inc., reprinted from "Good Painting Practice," *Steel Structures Painting Manual,* vol. 1 (Pittsburgh, PA: Steel Structures Painting Council), with permission.



FIGURE 10.8: Roller and grid screen in a 5-gal bucket.

is kept properly loaded. When the coating dries in the heel area, the brush loses its flexibility, the bristles tend to stand out, and the brush usually is destroyed.

Roller Application

Rollers are excellent for large, flat areas (e.g., tank tops, decks, ship hulls, side walls of tanks, walls, ceilings, etc.), and wherever application does not require the skill needed for brush or spray application. Roller application is more rapid than brush, but not quite as rapid as spray. The roller generally holds considerably more coating than a brush, so that a much larger area can be covered with one roller load of coating.

Rollers are much more satisfactory on smooth surfaces as compared with rougher, difficult-to-wet surfaces such as hand-cleaned, rusted, or pitted steel, or even blasted steel that is badly pitted. Brushing or a good, wet spray coat would be preferred on such surfaces.

The paint roller consists of a simple roller with a cover that slides over the roller mechanism and to which a handle is attached (Figure 10.7). The roller covers are 1.5 to 2 in in diameter, and may vary from a narrow roller to one as much as 18 in (457 mm) long. The average length is approximately 9 in (229 mm), and the cover consists of lamb's wool, mohair, or a synthetic fabric attached to an impregnated paper, plastic, or wire mesh holder. The length of the fiber on the cover or the pile ranges from ¼ to 1¼ in (6.4 to 32 mm) depending on the use of the roller. For most smooth surfaces, the shorter fiber is preferred. The very long fiber is only used for very rough surfaces or for coating wire fencing. A very long fiber will hold a great deal of coating. However, for smooth surfaces, it will not apply as smooth a coat as the shorter fiber.

The roller must be used with a tray, which holds the coating. The tray has a sloping ramp on which the roller is cleared of excess coating before applying it to the surface. There is also a roller grid, which is used in 5-gal cans of coating and attaches to the side of the can (Figure 10.8). The roller is worked over this surface to remove the excess coating.

Rollers also come with extension handles up to 16 ft (5 m) in length. Extension handles and poles enable the relatively easy coating of high rank surfaces, walls, and ceilings without the use of ladders. The extension handle with the roller is much easier than using a ladder or scaffold to reach high, smooth areas. It is a decided advantage on high, broad, flat surfaces such as a ship hull. The types of rollers available are shown in Table 10.4.

Some special roller equipment also is available. For example, a pipe roller is made up of narrow roller segments on a flexible spindle, which can be made to conform to curved surfaces such as piping (Figure 10.9). The size of the pipe determines the number of segments. However, only one-fourth to one-third of the round surface should be coated with a roller at any one time. This is a good method for applying coatings to round or curved surfaces. There are also rollers for use on fencing. In this case, the roller has a very long nap that surrounds the wire in such a manner that it can coat both sides at the same time. While a wire fence can be brushed, the only practical way of applying the coating to an open mesh fence is by such a fence roller (Figure 10.10).

Pressure rollers also are available. The coating is pressurized in a normal coating container through a hose to the handle of the roller. The amount of coating is controlled by a fingertip valve on the handle, allowing a continuous rolling procedure over very large surfaces.

Use of the roller requires less skill than either brushing or spraying. Nevertheless, rolling should not be considered a poor application method. It can be effectively used with many high-performance coatings, particularly those that have some leeway in drying time so that the roller can always be worked into a wet edge.

The proper procedure for using the roller is to immerse it in the coating tray or bucket. The roller should then be rolled back and forth on the tray ramp or on the grid on the interior of the bucket to remove the excess coating from the roller so that excessive drip

TABLE 10.4: Paint Rollers

		Type of Surface		
		Smooth	Medium	Rough, wire fence
Roller Cover:	Dynel (D)	¼ – ⅜ in	⅜ – ¾ in	1 – 1¼ in
	Lamb's Wool (L)	¼ -⅜ in	⅜ – ¾ in	1 – 1 ¼ in
	Mohair (M)	3/16 – ¼ in.		
Paint				
Solvent Thinned:				
	Enamel	D or M	D or L	D or L
	Flat	D	D or L	D or L
	Oil Paint	D	D or L	D or L
	Floor Paint	D or M	D	
	Varnish	D or M	D	
Water Thinned		D	D	D
Lacquer		M	L	L
Two-Package		M	L	L

Source: S.B. Levinson, *Facilities and Plant Engineering Handbook—Painting* (New York, NY: McGraw-Hill Book Co.).

and spatter will not result. Apply the roller to the surface to be coated, and spread the coating liquid in the roller over the surface by forming a "W" or an "M" in the area that the amount of coating in the roller will cover. The amount of area to be covered depends on the coating used. However, generally a 9 in × 2.5-in roller with a 3/8-in nap will cover about 10 ft2. After the initial spread of the coating, fill in the area by rolling the roller back and forth over the entire area to be covered. The finished rolling of the coating should all be in one direction so that the appearance will be uniform.

When one block of coating is completed, start another block adjacent to that one and repeat the procedure. Roll the new area into the previous one so that there is a continuous film over the surface. The roller should be rolled evenly, smoothly, and relatively slowly, so that the nap on the roller will not spatter the coating. Spatter is particularly a problem on ceilings and on vertical structures. The finish of the rolled coating will not be as smooth as by brush or by spray because the nap on the roller will make a slightly stippled effect on the surface. The thicker the nap on the roller, the greater the stippling effect on the surface.

A coating with good flow characteristics will flow smoothly. Faster drying coatings will show a greater amount of stipple than thixotropic coatings. When rolling materials like chlorinated rubber or vinyl, which are permanently soluble in their own solvents, the roller performs much like a brush. The application of the second coat may very well pick up the first coat. In other words, if a white vinyl is to be applied over a red primer, the finish may very well be a pink or a rose-colored topcoat rather than white. Either brushing or rolling tends to do this, which is another reason why spray application of lacquer-type materials is preferable.

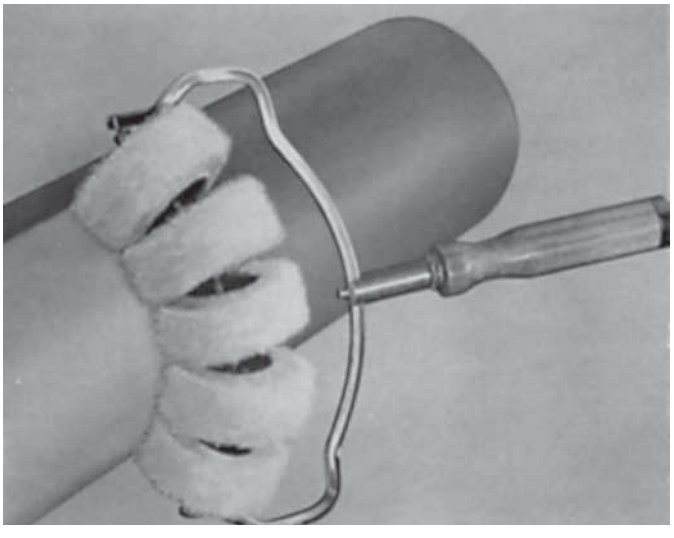


FIGURE 10.9: Pipe paint roller. Photo courtesy of EZ Painter Corp., reprinted from "Good Painting Practice," *Steel Structures Painting Manual*, vol. 1 (Pittsburgh, PA: Steel Structures Painting Council), with permission.

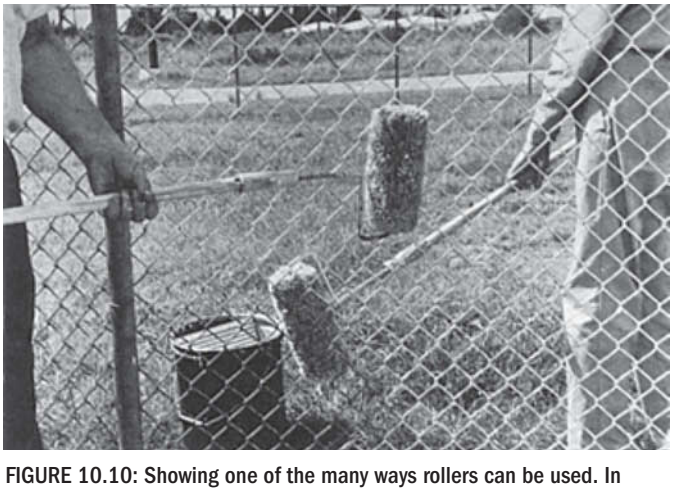


FIGURE 10.10: Showing one of the many ways rollers can be used. In coating chain link fence, material is applied by one roller, in which a second roller is used on the other side to distribute material evenly. Photo courtesy of Arsco Paint Rollers, Inc., Hialeah, FL.

Spray Application

The largest volume of all maintenance and high-performance coatings is applied by spray. This method of application is not only faster than any of the alternative methods, but the resulting coating films are more uniform in thickness, more evenly applied, and contain fewer imperfections than with other methods.

The spray method of coating utilizes a stream of highly atomized coating particles, which are directed to the surface in a uniform pattern. The particles then flow together to form a continuous and even film. Obtaining the finely atomized spray is the key to spray application, along with directing the spray toward the target so that a continuous film is formed. This is normally done by two types of

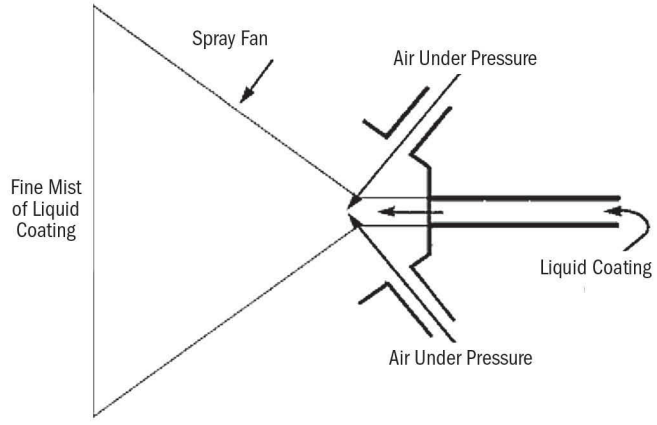


FIGURE 10.11: The external air spray principle.



FIGURE 10.12: Spraying a heavy epoxy mastic with a typical air spray pole gun with external atomization.

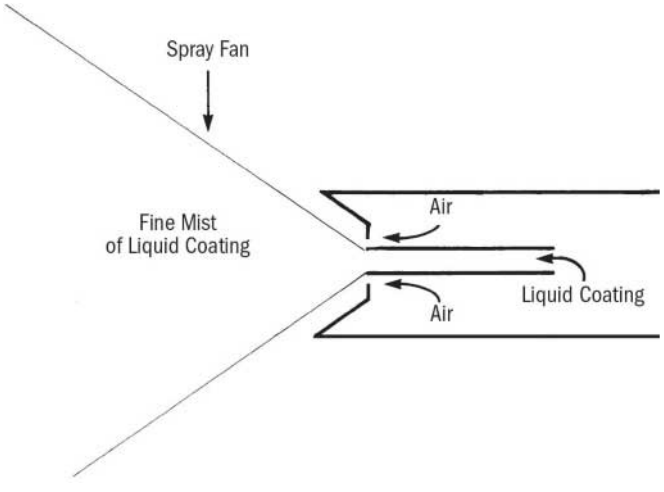


FIGURE 10.13: The internal air spray principle.

equipment: (1) the conventional air spray gun, and (2) the airless spray equipment, which uses hydraulic pressure to form the fine mist. Newer equipment combines the capabilities of both methods in an air-assisted airless spray unit.

Air Spray

Air spray is a process where compressed air and the coating liquid are brought together in a way that forms a fine spray. The spray gun is the key element in the spray system and is the mechanism that brings the air and the liquid coating together. This is accomplished in such a way that the liquid is broken up into a fine spray, which is also directed toward the surface to be coated by the air stream.

There are two types of spray guns. The first and most common is the external mix gun. In this case, the liquid and the air first contact each other outside of the spray gun. The jets of air impinge on the stream of liquid coating coming out of the gun, dispersing it and forming the fine spray. The air is directed toward the liquid stream through a specially designed air cap, which may have from only two to as many as eight or 10 air openings to help break up the liquid stream.

There are two adjustments on most spray guns. One regulates the amount of fluid that passes through the gun when the trigger is operated, and the second controls the amount of air passing through the gun, also actuated by the trigger mechanism. In most production-type spray guns, the trigger operates both the liquid and the air; however, there are some spray guns where the air flows in a continuous stream and only the liquid is controlled. The design of the air cap, with the number of holes involved, determines the fan or the stream of dispersed coating particles that is directed toward the surface.

In conventional air-spray equipment systems, compressed air is used to perform two functions. The first, as previously discussed, is to atomize the coating at the tip of the gun. The second is to apply pressure to the liquid coating and force it through the liquid orifice in the gun. The pressure of the air going through the gun, as well as the pressure on the liquid, has a great influence on the type of air spray and the type of fan developed. If there is too little air pressure at the gun, the liquid stream will not be broken up satisfactorily and the spray will merely be spattered when it reaches the surface. This does not provide a satisfactory coating film. If the air pressure on the liquid is too high in comparison to the air pressure at the gun, the same thing can occur.

If the air pressure at the gun is too high in comparison with the liquid pressure, the coating will be over dispersed, with a great deal of turbulence that will not apply the liquid coating to the surface, but will disperse it into the surrounding atmosphere. Also, if the liquid pressure is too low in comparison with the air pressure, turbulence will also occur, forming an unsatisfactory film on the surface. The latter type of gun adjustment often creates what is called overspray, and, with fast-drying coatings, will form a rough, uneven film on the surface. The principle of external air spray is shown in Figure 10.11.

The external type of spray system is one of the simplest and most versatile of all of the spraying units. It consists essentially of an air source applying air at a constant pressure of 100 lb in a volume of approximately 25 cfm. The compressed air in the pressure tank for the liquid coating forces the liquid from the tank to the gun. It also supplies the air hose carrying air to the gun, which brings the air and the liquid coating together.

The system has been widely used over the past 100 years. During this time, the gun, nozzles, regulating devices, and so forth have been developed and refined to the point of making them practical for almost every conceivable type of coating material and use. The conventional air spray provides a wide variety of spray patterns, degree of atomization, and wetness of the coat applied to the surface. It is therefore the most practical solution to problems where the above factors are required on the job. This type of spray equipment, using the proper liquid orifice and tip, can spray everything from heavy mastics to water-thin coatings by adjusting the variables of air and liquid pressure. Because of the many variables, follow the coating manufacturer's recommendations as to the proper spray gun, air cap, fluid tip, and air and liquid pressure for the application of any specific material. Using the manufacturer's recommendations, the adjustment of the gun for both air and liquid pressure then allows the specific coating to be applied under optimum conditions.

Figure 10.12 shows the application of a heavy epoxy type mastic coating to the leg of an offshore platform. Note the even, smooth finish obtained even with the heavy coating.

The second method of applying coatings by air spray is by use of the internal air spray gun. In this case, rather than the air impinging on the stream of liquid coating outside the spray gun proper, the air within the spray gun surrounds the liquid coating nozzle and the two are mixed right at the tip of the liquid tube (Figure 10.13). The actual fan, shape, and size is determined by the shape of the air cap. Advocates of this air spray principle claim that a much finer dispersion of the liquid coating can be obtained by this method. While this is true for many coatings, one of the disadvantages of this type of air spray is that, with relatively fast-drying coatings, the coating may build up in the head itself and cause gun stoppages.

Hot Spray

Hot spray is primarily used with conventional spray, although it also can be used with either conventional or airless spray. With hot spray, the same type of application equipment is used, including the cap and tip of the gun. However, the difference lies in the heating unit, usually located in the feed line between the pressure pot and gun. This can offer several advantages with certain types of coatings and under certain operational conditions.

Most organic coatings will become more fluid at higher temperatures. In other words, as the temperature goes up, the viscosity of the solution goes down, making a viscous coating into one that will spray and be dispersed by the air-spray mechanism. However, it is also possible, using the hot-spray system, to apply higher solids content organic coatings. This, of course, produces a heavier coating and reduces the amount of solvent that is required to evaporate from the coating. With the heater in the line, the warm liquid coating has better atomization at lower air pressure, and under many circumstances can reduce the amount of overspray produced. Better flow-out of the coating may be obtained, and, under some conditions, pinholing of some coatings is effectively reduced. The temperature of the liquid coating is normally raised to between 130 and 160 °F (55 and 70 °C), although it may be lower or higher depending on the liquid coating being sprayed.

In general, the advantages of hot spray are as follows.

1. Faster application due to lower viscosity.
2. Lower pressure required.
3. A satisfactory spray at below ambient temperatures.
4. Less overspray.
5. Less solvent fumes, and no added solvent to reduce viscosity.
6. Increased thickness per coat.
7. Somewhat faster drying overall.
8. A possible smoother finish because of faster flow-out of the warm coating.
9. Less atomization air pressure required.
10. Greater cross-linking of two component coatings, resulting in denser films.

Conventional Spray Equipment

The application of coatings is similar to many other operations (e.g., abrasive blasting). Many people use the wrong spray equipment and then cannot understand the reason for their poor results. Good spray equipment is like a good tool of any kind; it is essential for the proper application of coatings. Spray equipment consists primarily of an air compressor, pressure spray pot and fluid hose, spray gun, ample air supply, respirator, air mask, and air transformer. A diagram of a typical conventional air spray gun is given in Figure 10.14.

There are two methods for bringing fluid to the gun: suction or pressure feed.

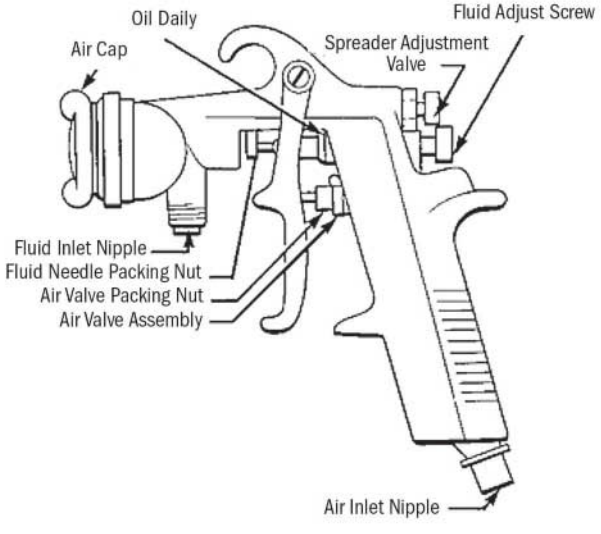


FIGURE 10.14: A typical air spray gun. Source: *Corrosion Control Principles and Methods,* Sect. 7, Ameron Inc., Monterrey Park, CA.

Suction-Feed Gun

For suction-feed, the gun is usually fitted with a 1-qt cup that holds the fluid to be sprayed. When the trigger is pulled, suction is developed at the tip of the gun, drawing fluid out of the cup and up to the nozzle where it is sprayed. This type of equipment has severe limitations; for example, the gun works best when only pointing horizontally, it will not spray viscous material, spraying is relatively slow, and the cup must be refilled frequently.

Pressure-Feed Gun

With the pressure feed, the fluid to be sprayed is forced to the gun under pressure. The pressure type has several advantages; for example, material of higher viscosity can be sprayed, a heavier coat can be applied, and spraying is much faster. Although a 1- qt pressure cup is sometimes used for small applications, the majority of pressure-fed spray operations are conducted with a separate pressure pot. This system ensures better pressure control and permits faster spraying.

Pressure Pot

The pressure pot is a closed chamber of a usually 2- to 10-gal capacity, which contains the fluid to be sprayed. A large air hose, preferably 3/4 inner diameter (ID) or better, connects the pressure pot to the air source. A fluid hose and an air hose connect the pot to the spray gun. Air is directed into the pot through a regulator, which maintains the proper pressure upon the fluid. The fluid is forced under pressure out through the fluid hose to the gun. The adjustment of the pressure regulator on the pot determines the amount of fluid available to the spray gun. Air is also bypassed from the main source into the air hose leading to the gun. Figure 10.15 shows the main components of a paint spray pot.

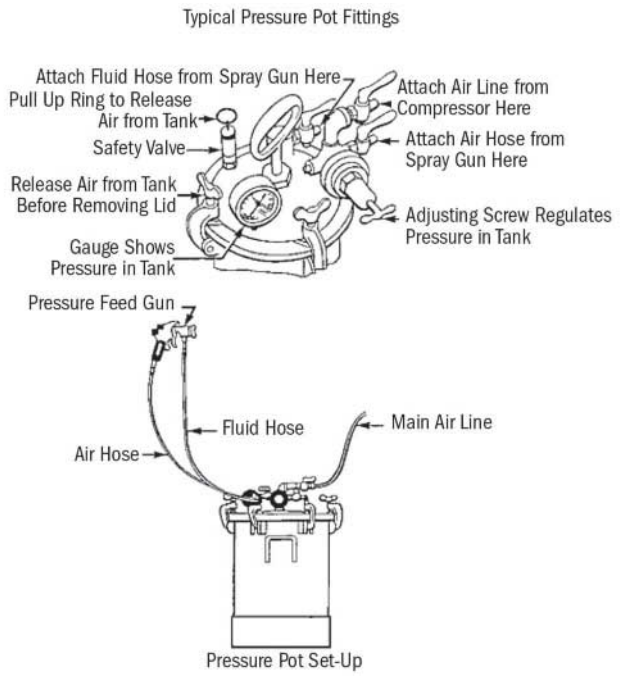


FIGURE 10.15: The main components of a paint spray pot. (a) Pressure pot fittings. (b) Pressure pot setup. Source: Corrosion Control Principles and Methods, Sect. 7, Ameron Inc., Monterey Park, CA.

It is extremely important from an efficiency standpoint that threads on all hoses, spray guns, regulators, and pressure pots be standardized so that any gun or hose will fit any other gun, hose, or pot on the jobs. This used to be a greater problem than it is at the present time, although threads of different dimensions may still be found on equipment produced by various manufacturers. This point cannot be overemphasized, since a great deal of time can be lost obtaining and installing proper adapters. All fluid hoses should be of the special paint-grade type made for materials containing strong solvents. The powerful solvents used in vinyls will dissolve the lining of some types of hose. This not only leads to coating contamination, but the lining in the hose swells and prevents the proper material flow through the hose. The hose should be made with a working pressure of 150 psi.

It should be emphasized that all material hoses, pots, and guns should be perfectly clean. If one has been used for oil-based coatings or alkyds, it should not be used for lacquers. Lacquer solvent is sufficiently strong that it can dissolve any trapped or remaining oil-based coating. Most epoxy solvents are also strong and may do the same thing. Internally reacted, coal tar epoxy, epoxy, and urethane coatings also can leave residues in the hoses if they are not properly and promptly cleaned after use. Subsequent use may cause these to separate from the hose and clog the gun or, worse, contaminate the coating. Clean material hoses are essential. In fact, it is recommended that new hoses be used on any large new application. This can save enough downtime to more than pay for the new hose.

Water and Oil Separator

A water and oil separator is an essential piece of equipment and may be part of the air transformer. This is installed in the main air line prior to the pressure pot so as to remove all oil, grease, water, and similar contamination that may be carried through the air line from the compressor. There are many coating problems that can result from such contaminating materials getting into the liquid coating (e.g., loss of adhesion, blistering, delamination, cratering, bug eyes, etc.).

Air Supply

There should be a compressor capable of supplying a minimum of 25 cfm of free air at 100 psi to each spray gun. Most industrial spray guns work well with this quantity of air. If an air mask is used for spraying on the interior of tanks and similar vessels, an additional 5 to 10 cfm should be added for each operator.

Spray applications which take place in enclosed space or which involve tank linings may require additional equipment. In confined areas, the worker should wear an air mask such as Devilbiss P-MPH 527 and MPH 529. Forced air, supplied to the mask through 1/4-in hose and discharged in front of the eyes, provides clear visibility and freedom from fumes.

Miscellaneous Equipment

In confined areas it is essential that fans or blowers be provided to remove solvent fumes. If fumes are allowed to accumulate, they cause acute discomfort to the workers and create a serious fire hazard. For safe application, the concentration of fumes must be kept below 0.05% by volume of air.

To best accomplish this, the blower should suck air from inside and exhaust it outside. Blowing into the tank normally results in stirring up rather than removing the vapors. Since the solvents used in most maintenance coatings are heavier than air, it may be necessary to attach a conduit or tube to the blower to draw the vapors up from the bottom of the tank.

When used for continuous immersion, many tank lining materials should be force-dried. Small coated units should be dried in an oven with circulating air at 140 to 200 °F (60 to 93 °C).

For large tanks, a heater is required to circulate warm air through the tank. One of the most practical systems uses a gas- or butane-fired heater with a blower to force air through the heater and into the tank. Explosion-proof and spark-proof equipment should always be provided for coating operations in enclosed areas. This includes motors, junction boxes, lights, and any other equipment that could generate a spark or flame.

Setting Up Spray Equipment

Cleaning

Spray equipment first must be cleaned with a suitable solvent. If the equipment is not thoroughly cleaned, old, dried paint from the interior of equipment and hoses may be removed by the new solutions, causing gun stoppage and unsatisfactory results. If possible, new fluid hoses should be used.

Adjusting Fluid Pressure

Most manufacturers' application instructions give approximate pressures for spraying a particular coating. However, the exact pressure depends on temperature, size of hose, length of hose, and other factors. The equipment should be adjusted as follows.

1. Pour the mixed coating into the pressure pot and clamp on the lid.
2. Turn on the air supply to the pot.

3. Turn on the fluid hose to the gun.
4. Turn off the air hose to the gun.
5. Remove the air cap from the spray gun.
6. Open the fluid-adjusting screw on the spray gun several turns and pull the trigger all the way back.
7. Holding the gun waist high, pointing out in a horizontal position, screw the pressure regulator on the pot until the fluid is forced out in a stream that travels 4 to 6 ft before hitting the ground. This is the proper fluid pressure.
8. Replace air cap.

Adjusting Air Pressure

The air pressure at the gun is the air pressure of the air source, it is not controlled by the fluid pressure regulator on the pot. The pressure at the source, that is, line pressure, usually should be 90 to 100 psi. (Using 50 ft of 5/16 in. air hose to the gun, this will result in about 75 to 80 psi at the gun.) After fluid pressure is adjusted as described above, test for proper air pressure as follows.

1. Turn on the air to the gun (fluid also turned on).
2. Pull trigger back.
3. Adjust fan to about 6 to 10 in by turning fan adjustment screw on gun.
4. Spray a test pattern, holding gun about 10 in from the surface, and make a rapid pass to produce a thin coat. If droplets of liquid hitting the surface appear to be less than 1/16 in across, air pressure is adequate. If coating is spattered with drips appearing 1/8 in or larger, coating is not being atomized and air pressure must be increased.

Adjustment at Gun

Adjust the fan to produce a spray pattern 6 to 10 in wide. Adjust the fluid control at the gun so that a smooth, wet film is produced on the surface when the gun is moved at the desired speed. Figure 10.16 shows some typical fan adjustments possible with standard air spray guns.

Spraying Procedure

The most important point to keep in mind when spraying high-performance coatings of almost any type, particularly the relatively fast-drying synthetic resin-based materials, is that they must be applied in an even, heavy, wet film. The film should not be so heavy that it will run on a vertical surface. However, if the coating is allowed to dry before it hits the surface or thin spots occur in the film, the protective value of the coating is greatly reduced. The proper spraying technique is essential to the success of the job, and the following points should be observed when using air-spray equipment.

1. Hold the gun no more than 10 in from the surface.
2. Use a normal fan, as shown in Figure 10.17. It is possible to check this by holding the gun the proper distance from the surface and pulling the trigger quickly. This will leave a spot on the vertical surface, which indicates the type of fan you will obtain with the gun setting. Figure 10.17 shows the normal fan. With a normal spray pattern, the spray area will be an even, smooth oblong with no heavy center or dry spray at the ends.
3. Figure 10.18 shows the type of fan you would obtain by the above procedure. This makes a heavy liquid cream in the center of the fan with too little liquid at the ends. Air may be blown into this heavy liquid area creating bubbles, which become pinholes upon drying. This type of gun adjustment generally will cause pinholes in the wide area of the fan.
4. Figure 10.19 shows the type of fan obtained when the gun adjustment is such that the liquid pressure is too low and the air pressure is too high. The high air pressure tends to split the fan, causing a thin center and dry spray at the ends. The liquid-starved spray will cause overspray with fast-drying coatings and a spatter coat with relatively slow-drying materials.

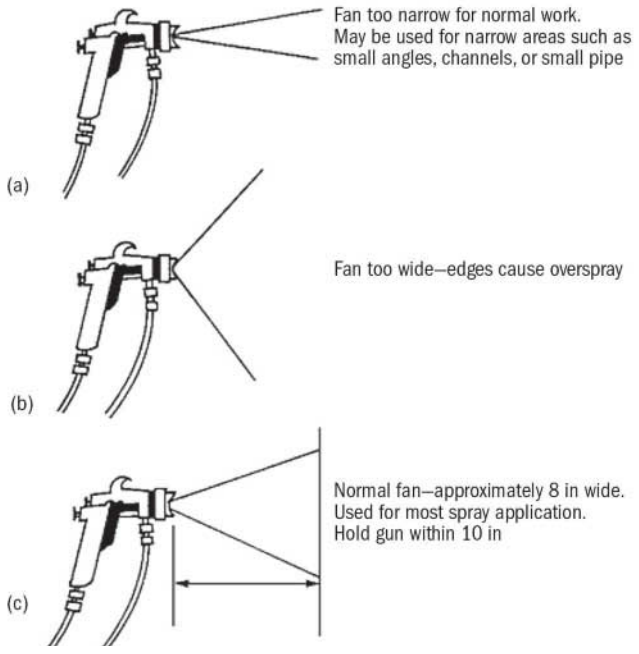


FIGURE 10.16: Typical fan adjustments for air spray guns. (a) Fan too narrow for normal work, may be used for narrow areas such as small angles, channels, or small pipe. (b) Fan too wide as the edges cause overspray. (c) Normal fan is approximately 8 in. wide with the gun held within 10 in. of surface and is used for most spray applications. Source: *Corrosion Control Principles and Methods,* Sect. 7, Ameron Inc., Monterey Park, CA.

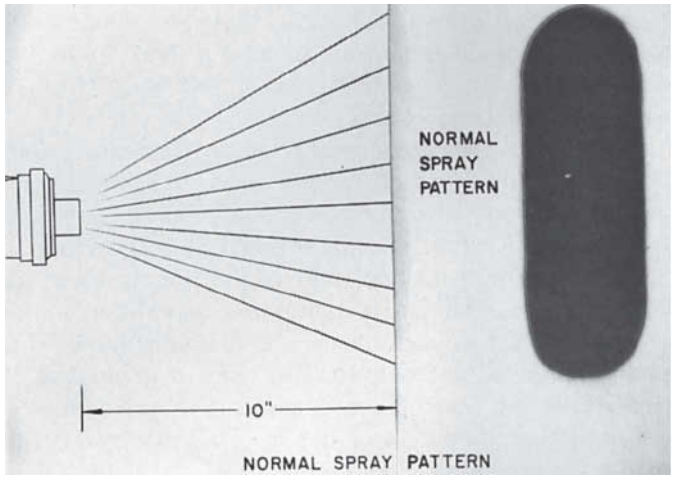


FIGURE 10.17: A normal fan and spray pattern.

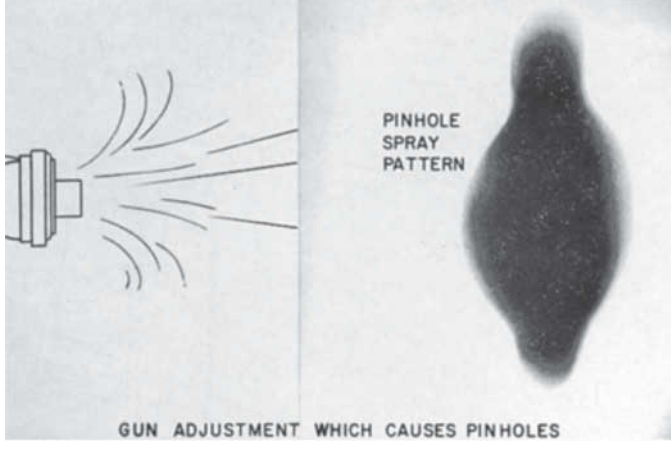


FIGURE 10.18: A gun adjustment where the liquid pressure is too high and the air pressure is too low causes pinholes.

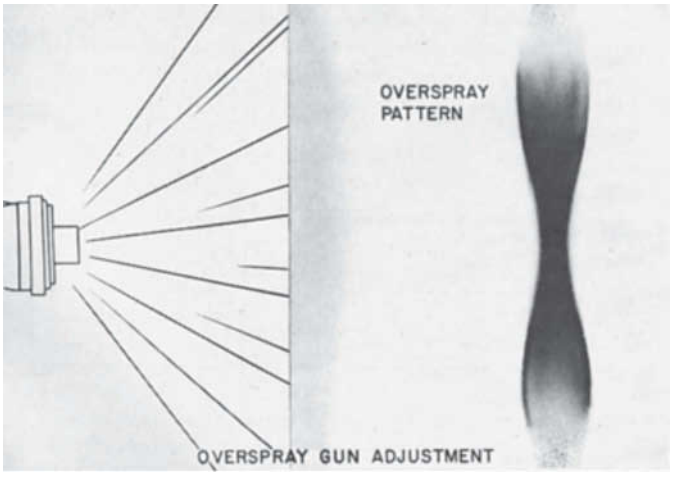


FIGURE 10.19: An overspray gun adjustment, where the liquid pressure is too low and the air pressure is too high.

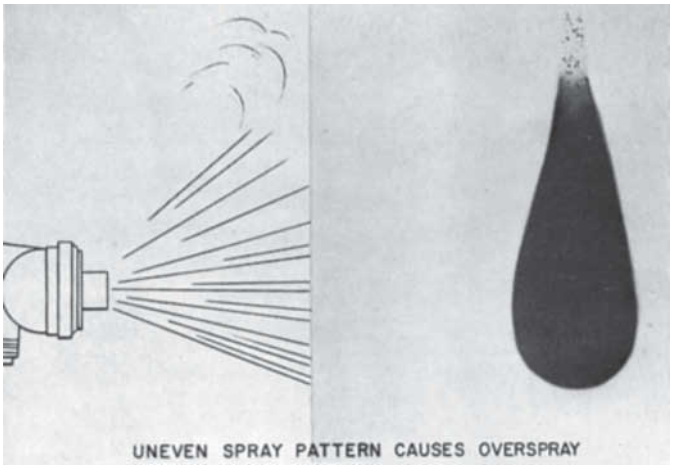


FIGURE 10.20: An uneven spray pattern caused by gun difficulties results in overspray.

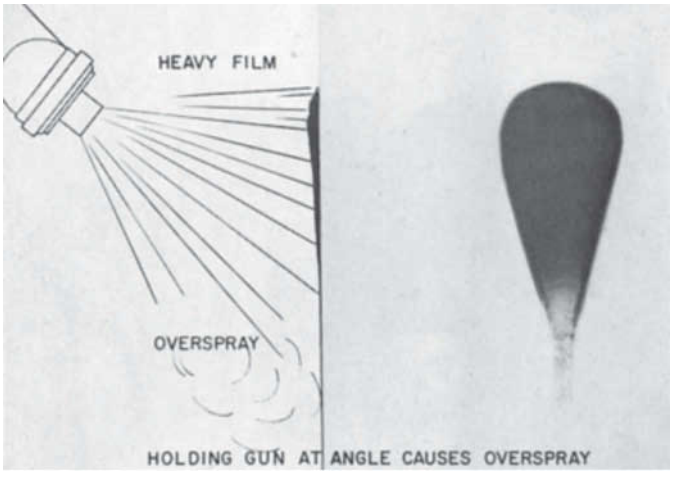


FIGURE 10.21: Holding the gun at an angle causes overspray.

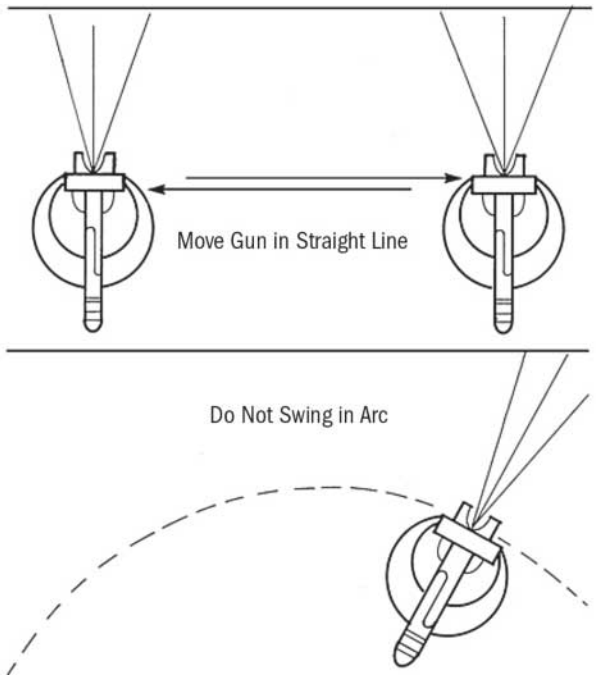


FIGURE 10.22: Proper and improper gun movement. Source: *Corrosion Control Principles and Methods,* Sect. 8, Ameron Inc., Monterey Park, CA.

5. Figure 10.20 demonstrates the type of fan that may be obtained if the gun has a problem. The cause might be by a nick in the needle seat, a partially clogged tip, or the tip of the needle could be bent slightly. In this case, the fan is teardrop-shaped, with too little liquid at the top, which may cause overspray, and too much liquid at the bottom of the fan, which may cause running or curtaining. If such a fan is obtained, the gun should be thoroughly inspected to determine the difficulty.
6. The gun should be pointed perpendicular to the surface. The tip of the gun should not be pointed either up or down from the perpendicular angle, as the spray will again be uneven (Figure 10.21). In that case, the shape of the fan would be heavy at one end and very light at the other end, resulting in either spatter or overspray at one end and running at the other.
7. Keep the gun parallel to the surface at all times. Do not swing the gun in an arc or shoot it off at an angle at the end of a pass. The gun should be kept an even distance from the surface, so that the fan is maintained at an optimum width. Work should be done with straight, uniform strokes, moving backward and forward across the surface so that the spray pattern will overlap the previous pass by 50%. Overlapping each pass is essential in preventing holidays and missed areas.

The preferred method of spraying is to cover an area approximately 3 to 4 ft wide with one pass, triggering the gun at the start and the end of each pass. Do not hold the trigger open at the end of the pass and then make a return pass. This builds up heavy coating at the end of the pass, which causes uneven coating thickness and runs and other coating problems in a heavy area. Let up on the trigger of the gun at the end of the pass; however, continue to go past that point with your stroke. In returning, trigger the gun at the same point that the previous spray pattern was stopped. Continue this type of operation until a practical area has been blocked out.

Correct and incorrect movement of the gun is shown in Figure 10.22. Figure 10.23 shows the proper procedure to use in the starting and stopping of the stroke and in overlapping each pass. Figure 10.24 shows the procedure to use in blocking out sections and in joining sections where a large area is being sprayed.

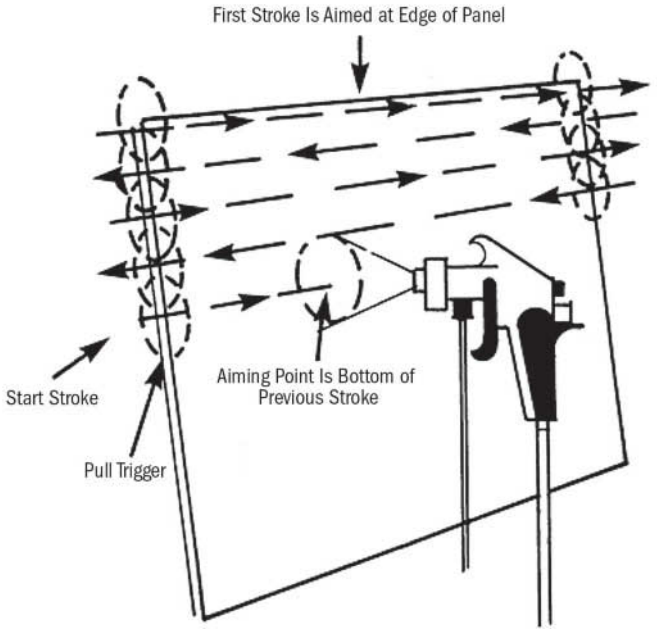


FIGURE 10.23: When spraying a panel use alternate right and left strokes, triggering the gun at the beginning and end of each stroke. The spray pattern should overlap one-half of the previous stroke for smooth coverage without strokes. Source: *Industrial Maintenance Painting* (Houston, TX: NACE, 1973), p. 99.

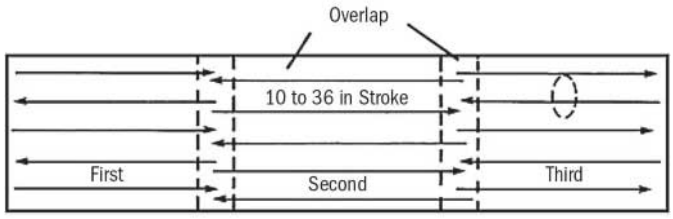


FIGURE 10.24: Long work is sprayed to sections of convenient length, each section overlapping the previous section by 4 in. Source: *Industrial Maintenance Painting* (Houston, TX: NACE, 1973), p. 88.

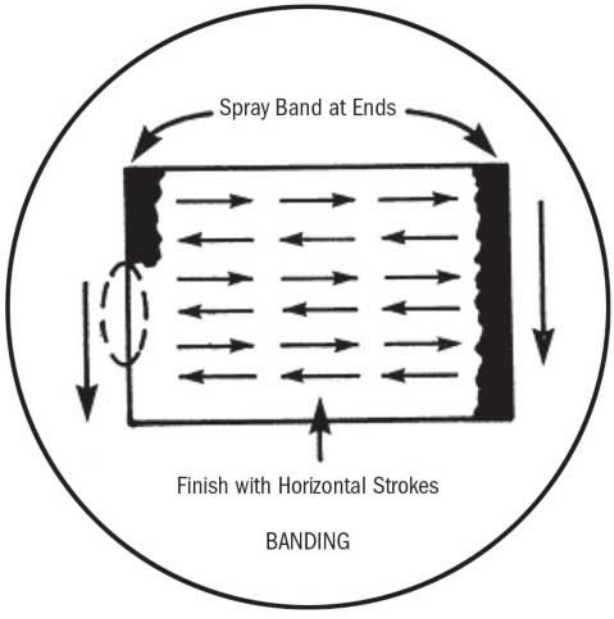


FIGURE 10.25: Vertical bands sprayed at the ends of a panel prevent overspray from horizontal strokes. Source: *Industrial Maintenance Painting* (Houston, TX: NACE, 1973), p. 88.

Banding is a method often used by some spray operators to block out the sections on which they are working. Some believe that it reduces overspray at the end of each stroke. This method is demonstrated in Figure 10.25. The single vertical stroke at the end of each panel assures complete coverage and eliminates the waste of coating that results from trying to spray right up to a vertical edge. During the usual horizontal stroke at the top and bottom of the panel, the gun is aimed at the edge and is automatically a banding stroke. This procedure is more often used in spraying smaller surfaces than it is where there are a number of sections to coat on a very large surface.

9. Apply an extra coat to all corners, welds, rivets, bolts, or other sharp edges. This is similar to banding in that the edges are given a pass prior to the body of the surface. This is important in order to assure full coverage of the above areas. This is demonstrated on an edge in Figure 10.26. As shown in the "wrong" procedure in the figure, the spray pattern is tangent to the edge of the corner and there is no direct spray impingement on the corner using such a procedure. The proper procedure is to point the spray gun straight at the corner and make a stroke covering not only the corner, but a small area on each side of the corner. When the body of the surface is then sprayed, each pass is carried onto the previous corner area. An inside corner can be sprayed in a similar way, spraying directly into the corner and moving the spray gun lining early with the corner. However, this produces a somewhat heavier coat on the sides of the corner, and a thin coating in the corner itself. This can lead to early corrosion problems in the corners and solvent entrapment in the heavy areas near the inside corner (Figure 10.27).

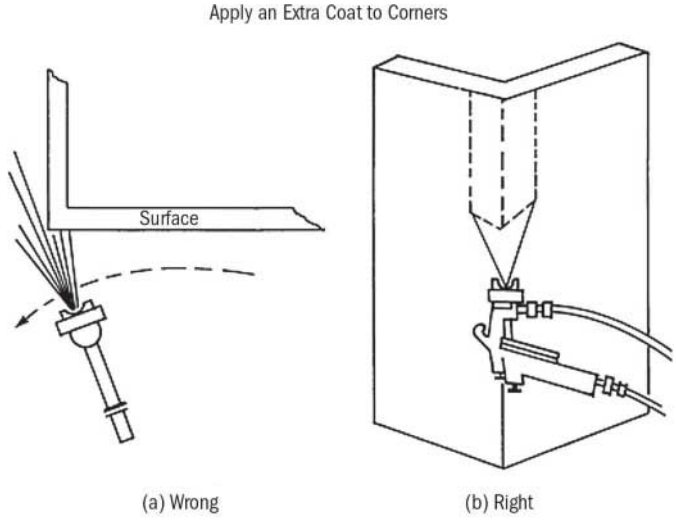


FIGURE 10.26: Applying an extra coat to corners. (a) Wrong procedure. (b) Right procedure. Source: *Corrosion Control Principles and Methods*, Sect. 7, Ameron Intl. Monterey Park, CA.

A second method is to apply a band of coating linearly with the corner, not spraying directly into the corner. In this case, a band is sprayed on each side of the corner, overlapping into the corner in order to fully cover it (Figure 10.28). Overlapping strokes from each side of the corner normally provide satisfactory coverage to the corner.

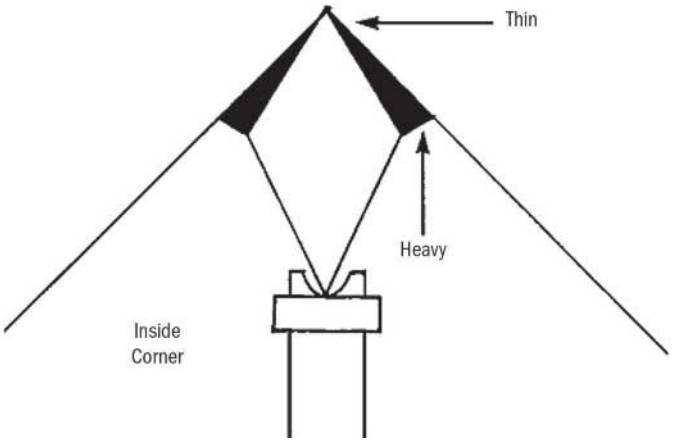
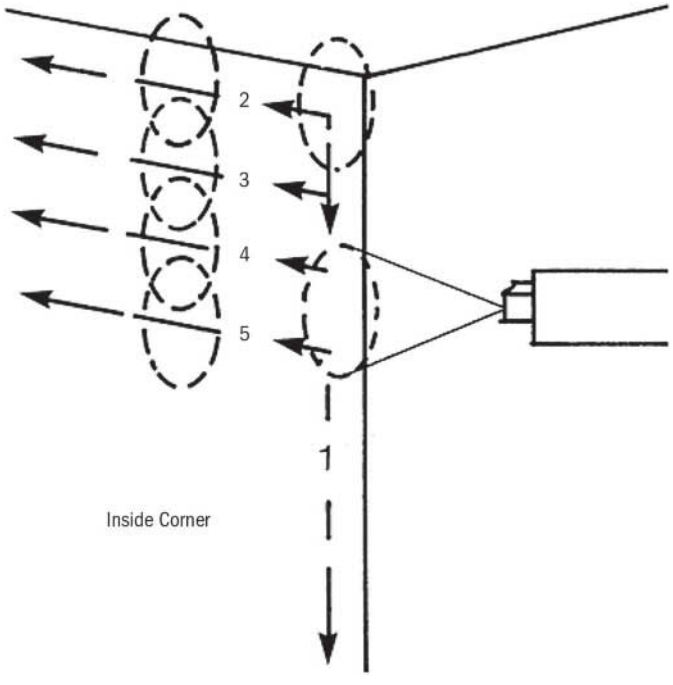


FIGURE 10.27: Spraying directly into the corner gives an uneven coating but is satisfactory for most work. Source: *Industrial Maintenance Painting* (Houston, TX: NACE, 1973), p. 88.



10.28: Spraying each side of the corner separately gives and even coating. Use a vertical spray patter. Source: *Industrial Maintenance Painting* (Houston, TX: NACE, 1973), p. 88.



FIGURE 10.29: Coating an H-beam using air spray.

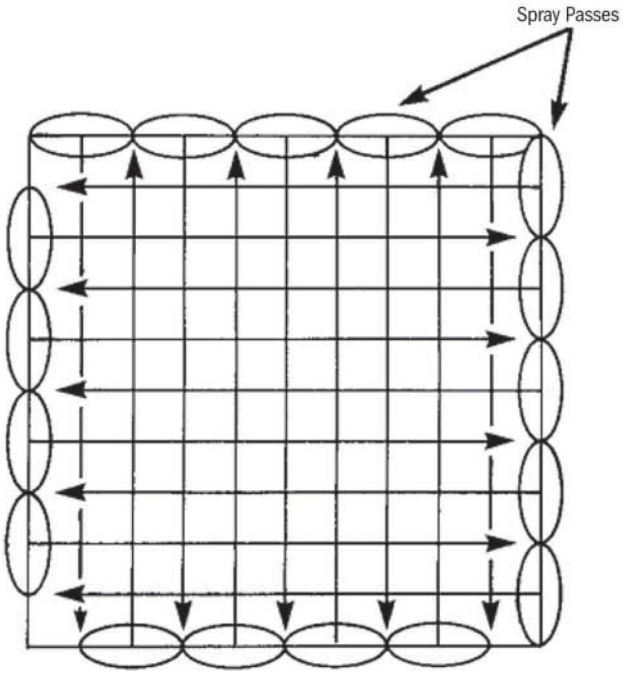


FIGURE 10.30: Cross spraying a blocked-out area with spray passes at right angles.

In either case, the spray passes that are used for the adjacent area to the corner should be triggered at the corner, carrying the coating into the previously coated area of the corner.

Spraying of a corner, followed by spraying of the flat area adjacent to the corner, is shown in Figure 10.29. In this photograph, an H-beam is being coated. Note the first pass of coating in the corner, with the second on the flat area overlapping the original corner spray. Such a procedure ensures full coverage of the area.

Cross Spraying

Cross spraying (cross hatching) is a technique used by many applicators to obtain a coating with an even thickness and no holidays. The procedure involves applying a relatively thin spray pass over a blocked-out area, as described earlier, and then applying a second pass over the same area at right angles to the first pass. Each pass should be properly lapped (50% overlap) and should fully cover the blocked-out area. It can easily be seen that when the second pass is applied at right angles, a full, even coverage of the area results (Figure 10.30). Cross spraying is a good technique to use with high-performance coatings, since continuous holiday-free films are necessary for full corrosion protection. A properly applied cross-spray coat will result in an even film that is not necessarily overly thick.

Round Work

It is generally assumed that cylindrical objects (e.g., pipe or tanks), are the easiest type of surface to coat because they are planar surfaces with no sharp edges or corners. While this is true for large tanks, it is not necessarily true for smaller surfaces. For instance, small-diameter pipe usually must be sprayed in a linear fashion, overlapping each pass at least 50%. This is necessary because a considerable amount of the spray is tangent to the round surface, and therefore, either passes out into the air or does not impact the surface directly (Figure 10.31). It is these areas that cause holidays and thin spots in the coating, and they are the reason why care must be taken in overlapping each spray pass.

Lack of proper overlapping of each spray pass is the cause of many coating failures on pipe. The holidays are usually linear with the pipe, indicating that the coating had not been overlapped sufficiently during application. Such a holiday is shown in Figure 10.32. The

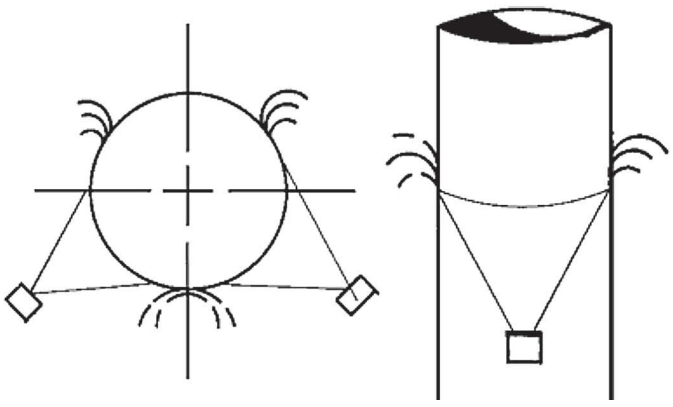


FIGURE 10.31: Tangent spray can cause holidays in pipe coatings.

area of the holiday did not receive any direct spray, only coating applied at a very long angle or tangent to the pipe surface.

The diameter of the pipe will determine the number of passes necessary to fully cover it. It must be kept in mind, however, that even though the surface may appear covered, tangent spray is not a continuous film and corrosion will soon begin in these areas. Figure 10.33 shows the proper procedure for coating cylindrical objects.

The coating of handrails, uprights on handrail grills, and similar slender-type work is difficult at best. The rule in this case is to make sure the spray pattern fits the job, by the adjustment of the fan on the gun. The gun fan may be adjusted from a very slender, almost cylindrical pattern to a very wide one. A wide fan should not be used. The objective is to cover the narrow work without excessive overspray and loss of material. Such work can be done by the use of a brush; however, in most circumstances it is preferable to apply coatings to such work by spray because there is a better chance of fully covering the edges, corners, and similar areas than there is by other means. Figure 10.34 provides an example of the way such small work should be coated.

Open Grill Work

It is often necessary to apply coatings on open grill work (e.g., steps, platforms, and walkways) due to the failure of galvanizing in an industrial or marine atmosphere. This is a difficult job and must be done carefully if the coating is to be successful.

Figure 10.35 illustrates an open work step, which is typical of this type of application. Not only is the application of the coating difficult, but the surface preparation is difficult as well. Such a grill must be coated from at least eight different angles; that is, four from the top and four from the bottom, in order to fully cover the surface. Figure 10.36 shows an open work bridge deck that was coated with one coat of IOZ and showed no corrosion after 10 years of service.

Expanded metal is used extensively in industry and is also difficult to coat due to the many metal directions and sharp edges. In this case, coating applications must be made from several different directions. Figure 10.37 show expanded metal partially coated with a high-build vinyl. This example shows good coverage of the sharp edges and corners by the heavy-bodied material.

Figure 10.38 shows the spraying of two types of open work. Note the angles of the spray used to cover as much area as possible. The same surface must be coated from the opposite angle, as well as from two angles on the opposite side of the work. Note also the shield used to produce spray bounce-back and reduce overspray.

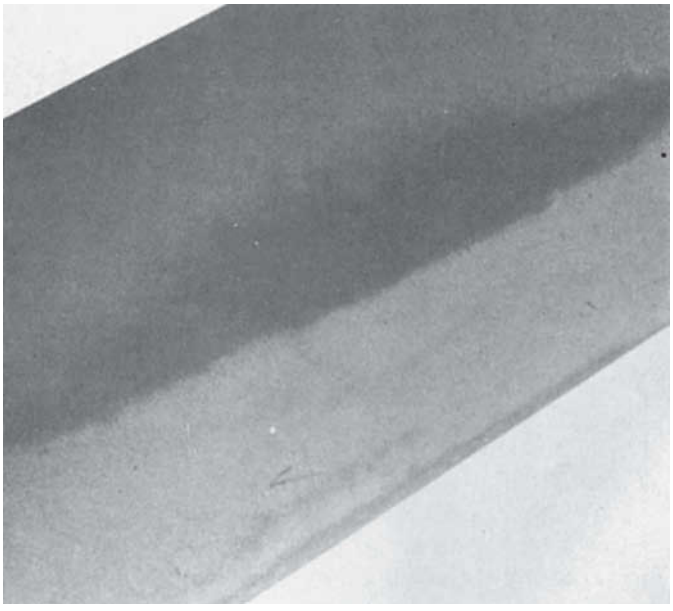


FIGURE 10.32: A holiday caused by improper overlapping of the spray pattern on a cylindrical surface.

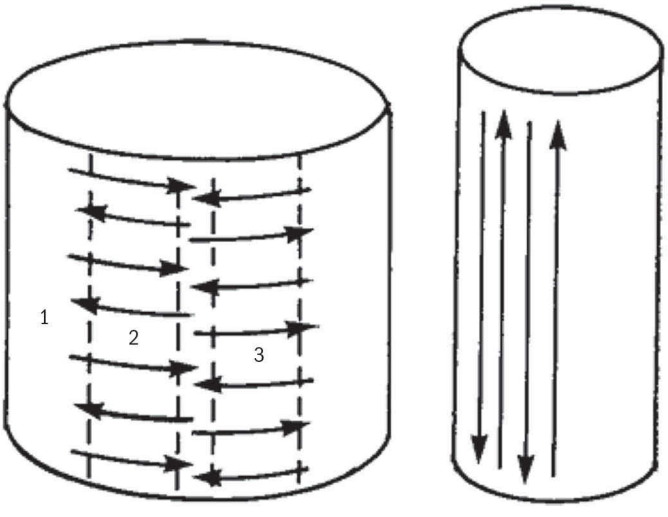


FIGURE 10.33: Round work should be treated to curve the strokes to conform with the surface. Source: *Industrial Maintenance Painting* (Houston, TX: NACE, 1973), p. 92.

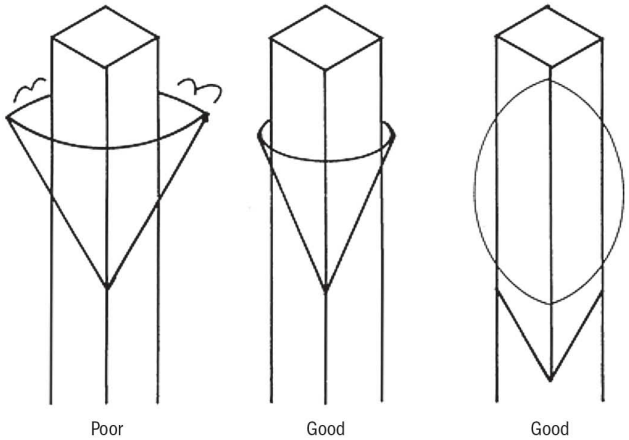


FIGURE 10.34: Procedure for coating slender surfaces. Avoid excessive overspray. Adjust the spray pattern to fit the job. The center illustration shows the best method for most work. Source: Industrial Maintenance Painting (Houston, TX: NACE, 1973), p. 91.

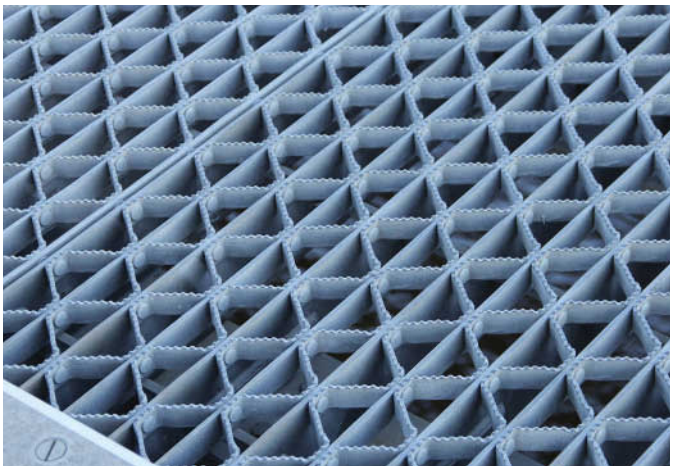


FIGURE 10.35: Typical open work grating step on an industrial structure. Note the depth of the grating and the difficulty of obtaining full coating coverage.



FIGURE 10.36: Open work grating used as bridge deck.

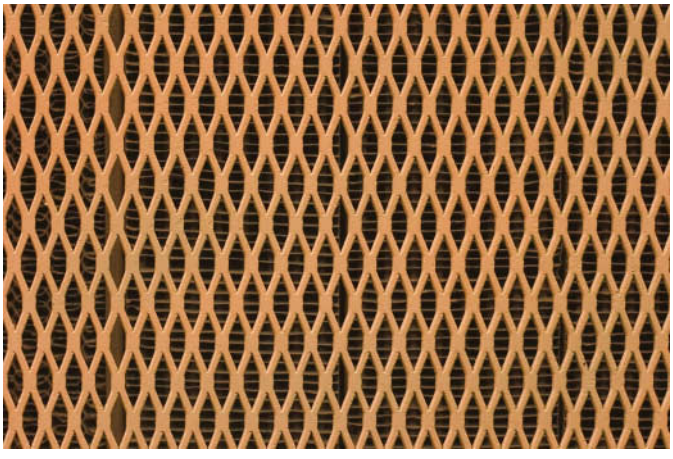


FIGURE 10.37: Expanded metal partially coated with a high build vinyl.

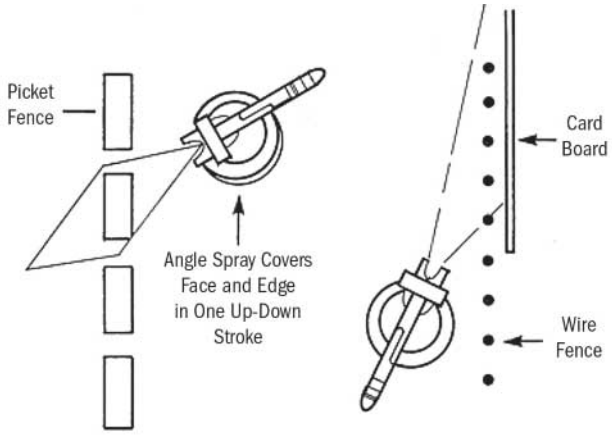


FIGURE 10.38: The spraying of two types of open work from four different angles (two on each side) to cover as much area as possible. Source: *Corrosion Prevention by Coatings,* Course 5 (Houston, TX: NACE).

Each application is unique, and the spray applicator must adjust his gun for each application in a way that will cover the work in the most efficient fashion, and in a way that will best eliminate pinholes, holidays, and coating loss due to overspray.

Spray Difficulties

There are a number of difficulties involved with an air-spray setup. The primary cause of most difficulties is dirty equipment and poor equipment maintenance. SSPC provides a list of many of the difficulties and their remedies, which is given in Table 10.5.

Airless (Hydraulic) Spray

The word airless is used in connection with this type of spray equipment since there is no air used in the atomization of the liquid coating. The liquid is forced through a very fine orifice by hydraulic pressure and forms a spray pattern as it expands into the atmosphere. The combination of the pressure and the small orifice breaks the liquid coating up into a very fine mist, which is forced onto the surface to be coated. In this way, its operation is similar to that of a garden sprayer. In a garden sprayer, the spray is of very low viscosity and therefore does not require much pressure. Pressure is built up within the container by a simple hand pump. The fan of the atomized liquid may be anything from a cone to a flat fan, depending on the orifice. The process is extremely simple and quite effective.

The gun for airless spraying is a simple device, consisting of not much more than a handle used to direct the spray in the proper direction. As previously mentioned, the fan is developed by the shape of the orifice through which the high-pressure liquid is directed. This is the most critical part of the airless spray gun, and the spray tips must be carefully made and machined to obtain the proper expansion of the liquid and the formation of the fan.

There are essentially no adjustments to be made on an airless spray gun. In order to change the fan size or shape, it is necessary to change the orifice tip. It is also necessary to change the orifice, depending on the type of coating that is being sprayed. Very thin liquid will require a very small orifice, while a heavy, viscous liquid will require a larger opening.

Because of the adjustments needed due to the use of different tips, a number of tips are essential. These vary from an approximately 0.010-in opening, up to one that may be over 0.040 in. The larger the orifice, the greater the flow of material, and the greater the speed and coverage that can be obtained. On the other hand, if a relatively large opening is used with a low-viscosity material, the rate of discharge may be such that it is impossible to keep up with the speed of the flow. As a general rule, the best orifice is the smallest orifice

TABLE 10.5: Air Spray Painting Faults and How to Remedy Them

Trouble	Possible Causes	Suggested Remedies
Sags	1. Dirty air cap and fluid tip (distorted spray pattern). 2. Gun stroked too close to the surface. 3. Trigger not released at end of stroke (when stroke does not go beyond object). 4. Gun stroked at wrong angle to surface. 5. Paint too cold. 6. Paint piled on too heavy. 7. Paint thinned out too much.	1. Remove air cap and clean tip and air cap carefully. 2. Stroke the gun 6 to 10 in. from surface. 3. Operator should release the trigger after every stroke. 4. Gun should be stroked at right angles to surface. 5. Heat paint in an approved paint heater. 6. Learn to calculate depth of wet film of paint. 7. Add the correct amount of solvent by measure.
Streaks	1. Dirty air cap and fluid tip (distorted spray pattern). 2. Insufficient or incorrect overlapping of strokes. 3. Gun stroked too rapidly ("dusting" of the paint). 4. Gun stroked at wrong angle to surface. 5. Stroking too far from surface. 6. Too much air pressure. 7. Split spray. 8. Paint too cold.	1. Remove air cap and clean tip and air cap carefully. 2. Follow the previous stroke accurately. Deposit a wet coat. 3. Avoid "whipping." Take deliberate slow stroke. 4. Gun should be stroked at right angles to surface. 5. Stroke 6 to 10 in. from surface. 6. Use least air pressure necessary. 7. Clean the fluid tip and air cap. 8. Heat paint to get good flow out.
"Orange-Peel"	1. Paint not thinned out sufficiently. 2. Paint too cold. 3. Not depositing a wet coat. 4. Gun stroked too rapidly ("dusting" the paint). 5. Insufficient air pressure. 6. Using wrong air cap or fluid nozzle. 7. Gun stroked too far from surface. 8. Overspray striking a previously sprayed surface.	1. Add the correct amount of solvent by measure. 2. Heat paint to get good flow out. 3. Check solvent. Use correct speed and overlap of stroke. 4. Avoid "whipping." Take deliberate slow strokes. 5. Increase air pressure or reduce fluid pressure. 6. Select correct air cap and nozzle for the material and feed. 7. Stroke the gun 6 to 10 in. from surface. 8. Spray detail parts first. End with a wet coat.
Excessive Paint Loss	1. Not "triggering" the gun at each stroke. 2. Stroking at wrong angle to surface. 3. Stroking gun too far from the surface. 4. Wrong air cap or fluid tip. 5. Depositing a paint film of irregular thickness. 6. Air pressure too high. 7. Fluid pressure too high. 8. Paint too cold.	1. It should be a habit to release trigger after every stroke. 2. Gun should be stroked at right angles to surface. 3. Stroke the gun 6 to 10 in. from the surface. 4. Ascertain and use correct setup. 5. Learn to calculate the depth of wet film of finish. 6. Use the least amount of air necessary. 7. Reduce pressure. If pressure keeps climbing, clean regulator on pressure tank. 8. Heat paint to reduce air pressure.
Excessive Spray Fog	1. Too high air pressure. 2. Spraying past surface of the product. 3. Wrong air cap or fluid tip. 4. Gun stroked too far from the surface. 5. Material thinned out too much. 6. Too little material at gun.	1. Use least amount of compressed air necessary. 2. Release trigger when gun passes target. 3. Ascertain and use correct setup. 4. Stroke the gun 6 to 10 in.from surface. 5. Add the correct amount of solvent by measure. 6. Adjust pot pressure or gun or both.
Paint Won't Come from Spray Gun	1. Out of paint (gun begins to sputter). 2. Settled, caked, pigment blocking gun tip. 3. Grit, dirt, paint skins, etc., blocking gun tip, fluid valve, or strainer.	1. Add paint, correctly thinned out and strained. 2. Remove obstruction; stir paint thoroughly. 3. Clean your spray gun thoroughly, and strain the paint. Always strain paint before using it.
Paint Won't Come from Pressure Tank	1. Lack of proper air pressure in the pressure tank. 2. Air intake opening, inside of pressure tank lid, clogged by dried-up paint. 3. Leaking gaskets on tank cover.	1. Check for leaks or lack of air entry. 2. This is a common problem. Clean the opening periodically. 3. Replace with a new gasket.
Paint Won't Come from Suction Cup	1. Dirty fluid tip and air cap. 2. Clogged air vent on cup cover. 3. You may be using the wrong air cap. 4. Leaky connections on fluid tube or nozzle.	1. Remove air cap and clean tip and air cap carefully. 2. Remove the obstruction. 3. Ascertain and use correct setup. 4. Check for leaks under water, and repair.
Gun Sputters Constantly	1. Fluid nozzle not tightened to spray gun. 2. Leaky connection on fluid tube or needle packing (suction gun). 3. Fluid pipe not tightened to the pressure tank lid.	1. Tighten securely, using a good gasket. 2. Tighten connections; lubricate packing. 3. Tighten.Check for defective threads.
Paint Leaks from Spray Gun	1. Fluid needle packing nut too tight. 2. Packing for fluid needle dry. 3. Foreign particle blocks fluid up. 4. Damaged fluid tip or needle.	1. Loosen nut, lubricate packing. 2. Lubricate this part daily. 3. Remove tip and clean. 4. Replace both tip and needle.

Source: *Steel Structures Painting Manual,* Vol. 1, "Good Painting Practice" (Pittsburgh, PA: SSPC, 1966), p. 106.

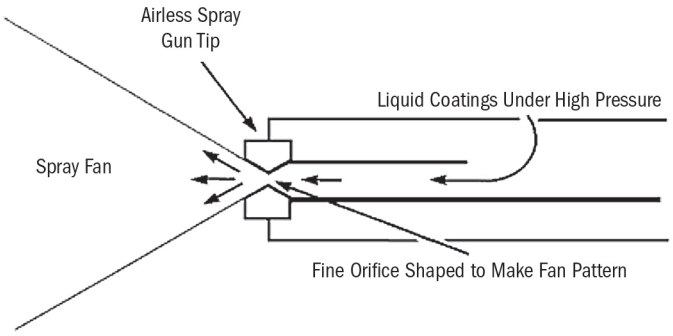


FIGURE 10.39: Operation of an airless spray gun tip.

that will allow the coating material to pass through without plugging.

As with the garden sprayer, a number of different spray patterns also can be obtained. These vary from almost cone-shaped patterns to fans with various widths. These can vary from approximately a 25-degree angle up to a 65-degree angle. The finer angles would be used for narrower work, such as in relatively small dimensional structural steel, while the wide patterns would be used for large, broad, flat surfaces. Figure 10.39 provides a schematic drawing of the airless spray gun tip and its operation.

Pressure Pumps

In order to supply the pressure on the liquid, hydraulic-type pressure pumps are used and may be operated by either air or an electric motor. A small gasoline-driven compressor can be used for portable operations. Most hydraulic pumps are actuated by an air cylinder. These have an air cylinder to hydraulic cylinder ratio of from 8:1 up to about 75:1. The hydraulic pressure can be regulated by the pressure on the air cylinder. Generally, it is better to have a pump with a higher ratio than required, rather than one with a ratio that is too low. This seems rather obvious, since too low a pressure would not provide the liquid dispersion required for proper application. On the other hand, the lowest air pressure into the pump that will produce the pressure required to form a uniform pattern is all that is required. Higher pressure is no advantage. Insufficient pressure causes streaks or fingers in the fan pattern. Adjustment of the air pressure usually eliminates these streaks or fingers. When the correct operating pressure for the particular coating liquid is obtained, the spray pattern evens out the smooth fan.



FIGURE 10.40: Airless spray application with proper spray width and gun distance from the surface.

A pump with a ratio of 20:1, 28:1, or higher is commonly used to apply the pressure required. With an air pressure of 100 psi, a 28:1 pump would provide a pressure on the liquid coating material of 2,800 psi. If the ratio was 20:1, an air pressure of approximately 50 psi would provide 1,000 psi pressure on the coating liquid. The pump pressure must be regulated to meet the application characteristics of the various materials, even as the fluid tip is selected for the material being applied.

Figure 10.40 demonstrates a properly adjusted airless spray gun. In this operation, a 100% solids epoxy coating was being sprayed. Note the even spray pattern with no fingers or streaks in the fan. Note also the distance of the spray gun from the surface (12 to 14 in) and the width of the fan. Both are optimum for the coating being sprayed.



FIGURE 10.41: A heavy duty airless pump on wheels.

The hydraulic pump used to pressurize the liquid is a mechanism with two cylinders. The air actuates the large cylinder and applies pressure to the smaller cylinder, which pumps the liquid coating under the higher pressure. The ratio of the air pressure to the fluid pressure is approximately the inverse ratio of the square of the respective cylinder diameters.

Hydraulic pumps vary in size from ones that can be used with a gallon of liquid, to those that can be used in very large, centralized coating areas, with the pumps operating out of 50-gal drums, or even larger, containers. Some pumps can fit directly on the top of a 5-gal can; others come equipped with wheels, so that a container of liquid is placed on the wheeled vehicle, with the hydraulic pump dropping down into the liquid. This makes for a very portable unit (Figure 10.41).

The spray gun and pump are the two most important items in airless spray equipment. The third is the high-pressure fluid line. The hose is usually fluorocarbon or nylon lined, which will withstand a working pressure of 2,500 psi or more. Fluid hose is usually a ¼- or 3/8-in ID hose, and if lined with a fluorocarbon, has a very low coefficient of friction. Generally, any air source may be used for actuating the hydraulic pumps. A small volume of air is required to operate the pump, and a ⅛- to ½-in hose is all that is required from the air compressor to the liquid pump. Table 10.6 provides a list of operating equipment sizes and conditions for two types of organic coatings.

An essential element in airless coatings is to have not only scrupulously clean equipment, but for the coating liquid completely free of any small particles that might clog the tiny spray gun orifice. The clogging of spray gun openings can cause a great deal of lost time and annoyance. Thus, any material used should be thoroughly screened or filtered to eliminate this kind of problem. It occurs often enough to make having several extra nozzles or tips on hand a good practice, so that they can be changed quickly when they become clogged. There are reversible tips, which can be turned around and cleaned by blowing the fluid through the tip in a reverse manner, forcing out the clogging material.

Cleaning the gun also can be hazardous due to the very high pressure of the liquid. If the spray gun is close to a person's body and is accidentally triggered, liquid coating can actually be forced into the flesh of the arm or hand. This has happened on some occasions. The safety precautions necessary for the operation of the gun may easily be forgotten while attempting to clean out small particles of contamination.

While the actual operation of an airless spray gun is similar to that of a conventional gun, there are some important differences. The principal one is that there is no air sprayed with the coating in airless spray equipment. The high pressure atomizes the coating, and

TABLE 10.6: Typical Airless Spray Equipment and Operating Conditions

	Fluid Pump	Gun Orifice Size	Foot Valve Filter	Fluid Pressure psi	Fluid Hose I.D.	Air Hose I.D.	Spray Pattern Width (inches)	Distance Gun from Surface (rushes)
High Viscosity Coatings	30–1	0.019 to 0.026	None to Course Mesh	2400 to 3200	¼ in.	½ in.	10–16	14–16
Low-Medium High-Viscosity Coatings	30–1	0.015 to 0.026	h	2400 to 3200	¼ in.	½ in.	10–16	12–14

there is no compressed air involved to cause air rebound from the surface to which the coating is applied. This aids materially in coating the interior of corners, corrosion pits, angles, and many other complex areas found where structural steel is fabricated. Since there is no compressed air to cause a cushion in these areas, the coating tends not to rebound, but stays on the surface.

This is a decided advantage, since a properly operated airless spray gun can apply the coating without bubbles or pinholes and yet obtain a smooth, wet film. In order to do this, however, the spray gun must be held some distance from the surface (i.e., several inches farther from the surface than conventional spray guns) so that the coating is applied to the surface with maximum dispersion. If the airless spray gun is held too close to the surface, too much liquid coating is applied, causing runs and, in many cases, bubbling and pinholing. The distance may vary with the coating being applied; however, it generally should be approximately 14 to 16 in (Figure 10.40).

Overspray is also reduced with airless spray, since there is no air intermixed with the coating as it is being applied. The volume of coating applied to the surface also can be somewhat greater with airless spray equipment. The spray is designed for the production application of coatings to large areas, so that a higher liquid flow is an advantage. For large surfaces, airless spray is generally faster, cleaner, and more economical than conventional air spray.

Figures 10.42 and 10.43 show the advantages of airless spray (e.g., a high volume of materials going on a very large surface). These figures also demonstrate poor coating technique. The gun is too far from the surface, with most of the coating never reaching the surface and falling onto the dock. Even though the application was improper, this project could not have been done at all without airless spray equipment.

While most coating materials can be applied by either air or airless spray, some coating materials are specially formulated for airless application.

In airless spray, more coating generally is applied to the surface and less lost into the surrounding air. Solvent consumption is also generally reduced because higher viscosity coating materials can be applied by airless spray. These usually are high solids content materials with a reduced amount of solvent as compared with conventional air-spray materials. In many cases, thicker film builds can be obtained by airless application. This depends on the material being applied. However, if the coating does not run readily, heavy single-pass applications can be made by airless spray. Table 10.7 provides a comparison of the two application methods, indicating the positive characteristics of each.

Heated Spray

Heating the coating liquid prior to application has been used with both air and airless spray applications. This is accomplished through the use of an in-line heater, which heats the liquid prior to the time that it passes through the spray gun. The increased temperature of the liquid generally reduces viscosity, allowing the coatings to be applied more readily and at a somewhat faster speed. It also has the reverse advantage. As the coating is propelled into the air, it is cooled rapidly and increases in viscosity shortly after it hits the surface. This

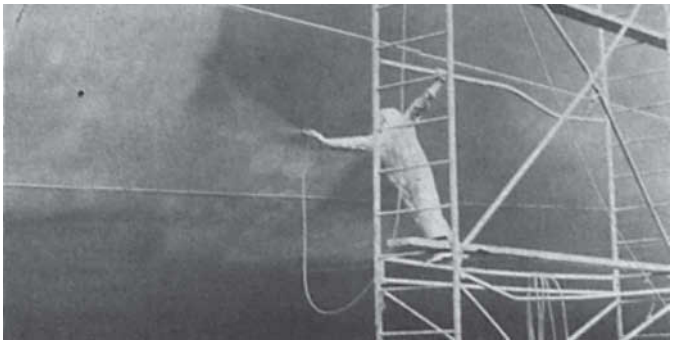


FIGURE 10.42: Airless spraying of an epoxy hull coating at an excessive distance from the surface, using poor application techniques.

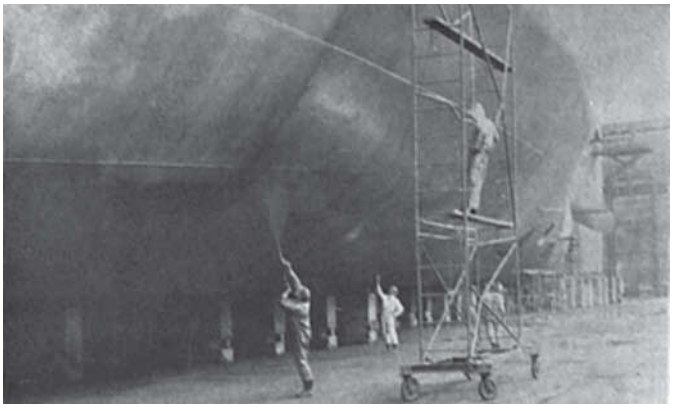


FIGURE 10.43: Coating by airless spray using poor application procedures.

TABLE 10.7: Airless vs. Conventional Spray

	Conventional	Airless
Overspray	10-30%	Below 10%
Pinholing	Possible	Unusual
Material Loss on Application	Considerable	Up to 35% less
Penetration of Corners/Voids	Fair	Good
Paint Clogging Problems	Slight	Considerable
Safety During Cleaning	Excellent	Fair
Coating Contamination From Air Source	Possible	None
Wind Loss	Considerable	Negligible
Gun Distance from Surface	6-10 in	14-16 in
Film Build per Coat	Lower	Higher
Versatility	More	Less
Thinning Before Spray	Usual	Sometimes
Hoses to Spray Gun	2	1
Compressors	Large	Small
Portability	Fair	Excellent
Masking	Considerable	Moderate
Coverage 1,000/ft^2/day	4-8	8-12

helps the coating remain in place and reduces the chance of sags and curtains, generally making a smoother, more uniform film.

The low-boiling solvents in a coating liquid tend to evaporate readily between the gun and the surface. This leaves a higher quantity of the higher boiling solvents in the material to aid in leveling the coating and providing a smooth, even film. Heating a coating formulated for hot application also allows higher solids and higher viscosity materials to be sprayed, which permits more material to be applied per coat without the danger of runs or sags. Heating of the coating liquid not only lowers the viscosity, but also tends to provide a more uniform viscosity material for application.

There are a number of suppliers of coating heaters, which come in various sizes, shapes, and forms. They generally preheat the coating from 120 °F (50 °C) to possibly 180 to 200 °F (77 to 93 °C). Many of the heaters are portable and attach to the applicator's belt. They are heated with electricity and therefore require an electric cord to the heater. This, along with the weight of the heater itself, makes the equipment somewhat more cumbersome for the applicator. The coating also may pass through a stationary heater between the pump and the gun. There can be considerable heat loss using this method, depending on the length of the hose after the position of the heater in the line.

As mentioned previously, heated coatings can be applied by either airless or air spray, and the benefits are approximately the same for both. Many product finish application units use airless spray and in-line heaters as a standard procedure. This equipment is less commonly used on large structural steel units, offshore rigs, large storage tanks, and so on.

Some of the advantages of heated spray are as follows.

1. The coating tends to have a more uniform viscosity.
2. Even coverage reduces runs and sags.
3. Drying time is often reduced.
4. Faster applications are possible due to the lower viscosity.
5. Coatings can be sprayed readily at lower ambient temperatures.
6. There is less overspray and bounce back from corners or enclosed areas.
7. There are less solvent fumes because of no added solvents.
8. There may be an increased thickness of coating applied per coat.
9. There is finer atomization with lower application pressures.
10. With reduced viscosity, there is the possibility of improved coating adhesion.
11. Better through cure can be achieved, resulting in denser films.

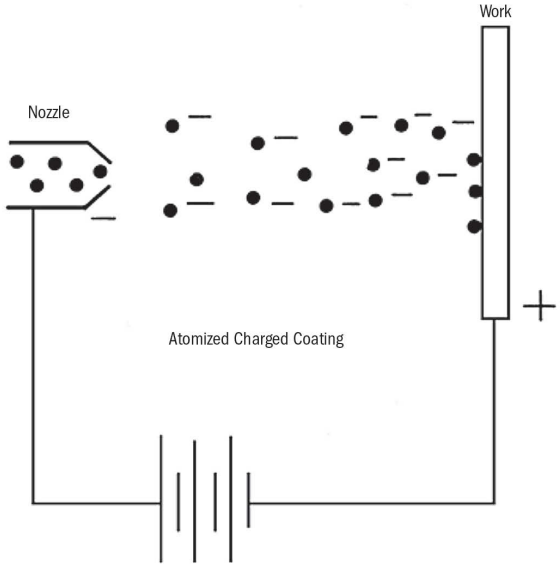


FIGURE 10.44: A high voltage DC power supply. Source: *Corrosion Control Principles and Methods*, Section 7. Ameron, Inc., Monterey Park, CA.

The advantages of electrostatic airless spray are:

1. Complete coverage of odd shapes
2. Complete use of the liquid coating
3. Almost no coating loss
4. Reduction in overspray to almost zero
5. Very uniform film build.

Electrostatic Spray

Electrostatic spray may be used with either air or airless spray equipment. Airless spray equipment undoubtedly has some considerable advantages where electrostatic procedures are used. The objective of electrostatic spraying is to apply a rather high electrostatic charge to the coating particles as they pass away from the spray gun. An 80,000-V static charge may be applied to the coating particles, with the object to be coated having an opposite charge. Generally, the particles are negatively charged and the object to be coated is positively charged or positively grounded. When the coating passes through the spray gun and into the air, the opposite charges attract each other, and the finely divided coating liquid is attracted to all sides, edges, corners, and some recesses of the object to be coated. The opposite side of the object also may be coated, provided the distance to be traveled is reasonable.

The principle of electrostatic spraying is shown in Figure 10.44. In this case, the coating particles pick up the negative charge as they evolve from the gun and carry the charge to the positively grounded surface. Almost all of the coating to be applied arrives on the surface to be coated with very little loss.

There is portable electrostatic spray equipment available, although for the most part this method of coating is used for product finish operations. One of the most common uses for portable electrostatic spray is on fencing (Figure 10.45).

There are also some substantial disadvantages in the use of electrostatic spray.

1. Not all coatings can be applied by electrostatic means.
2. The formulation of each coating is critical; that is, the coating must be designed for electrostatic spray.
3. The electrostatic procedure cannot be used on a nonconductive surface; it can only be used on bare metal or conductive coatings.
4. Only one coat of the material can be applied, because of the insulating characteristics of the original material.
5. Because of the very high voltage used, there is some hazard of electric shock during application.
6. The equipment is considerably more expensive than either air or airless spray setups.

The electrostatic method also can be used for dry powder coatings. In this case, the particles of the powder are negatively charged and the object to which they are to be applied is positively charged. The same electrostatic action draws the powder particles to the article to be coated, and a uniform layer of the powder is applied to the metal surface. The powder can then be fused in place, in a normal powder coating procedure.

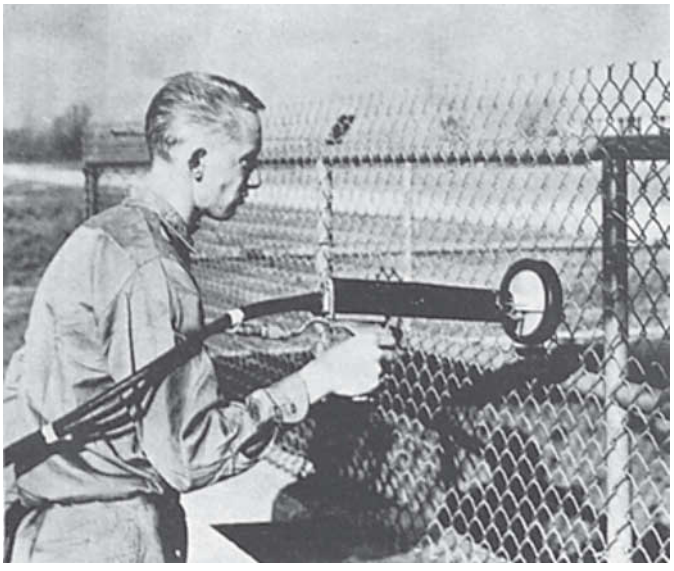


FIGURE 10.45: Electrostatic spray gun used to coat industrial fence. Photo courtesy of Ransburg Electro-Coating Corp., Indianapolis, IN.

Powder Coating

The powder coating procedure is generally an in-plant production-line procedure where a finely divided coating material is applied to a metal substrate in a fluidized bed (or by electrostatic spray, as discussed previously). The coating particles are dry and are completely formulated, including pigment. In a fluidized bed, they are floated in an air stream so that they are in constant movement. The object to be coated is usually heated to the fusion temperature of the coating and dipped into the fluidized bed, so that the coating particles fuse on the surface. The thickness of the coating can be controlled by both the heat and the time of exposure in the fluidized bed. After it is removed from the fluidized bed, the coated object then goes into a heating oven where the coating is further fused to the object until it flows into a continuous film.

Due to environmental restrictions, mainly on solvents, more coating applications are being made in this manner wherever such a procedure is practical. Many different types of coatings can be applied, including the thermoplastic materials (e.g., vinyls and acrylics) and epoxies. All powder coatings must be specially formulated for this procedure. Up to the present time, high-performance coatings have not been developed for practical electrostatic application to existing or new large structural steel objects.

Dip Coating

Dip coating is another method of application that in many ways is similar to powder coating. However, in the dipping procedure, the coating is in a liquid form and the part to be coated is dipped into the fluid bath. Again, the coating material must be properly formulated to provide an even thickness film over all parts of the object to be coated. In dip coating, one of the principal requirements is to remove the part from the bath at exactly the same speed as the coating flows from the surface. In this way, an even coating is formed without drips, tears, or heavy coating accumulation on the lower part of the work.

Dip coating and powder coating procedures usually are used where only one coat is applied. However, there is nothing to prevent additional dip coats from being applied to the object using the same procedure. Dip coating is an in-plant procedure and is usually part of a production line for the application of product finishes to fairly complicated parts or ones that will receive only one coat. The process is not applicable to high-performance, multiple-coat coating systems.

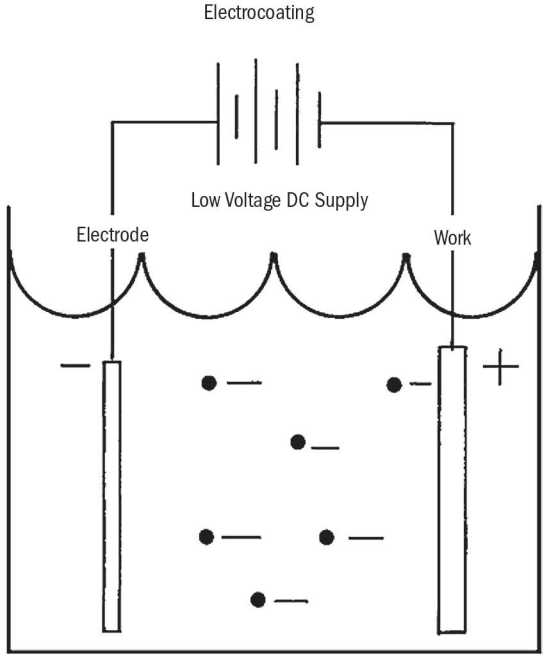


FIGURE 10.46: A schematic illustration of the electrocoating process. Source: *Corrosion Prevention by Coatings*, Course 5 (Houston, TX: NACE).

Electrocoating

Electrocoating is a modified dipping procedure where a low-voltage current is passed from a negative electrode to the part to be coated, which is the positive electrode. Very little active current is used in electrocoating, making the process similar to electroplating in character (Figure 10.46). The coating must be carefully and specially formulated for use in this process since the liquid coating must be conductive. The parts to be coated are usually on a conveyor line passing through the electrocoating bath. The coating is partially precipitated on the part in a uniform coat. Automotive frames and similar parts have been primed in this manner. This is a specialized process and can only be used on parts that are coated in-plant.

Application of Multiple-Component Systems

With the increased emphasis on 100% solids coatings and high-solids coatings, the use of fast-acting catalyst coating systems has been considered, and some successful ones have been developed. In multiple-component systems, the procedure is to mix the reactive components of the coating within minutes, or even a few seconds, of their application. To do this, special equipment is required so that the exact amount of each coating component can be mixed and then quickly applied to the surface.

One of the first of the multiple-component systems was the catalyzed polyester. These coatings were glass reinforced and applied to the interior of many tank bottoms. In this case, the catalyst and the polyester were mixed at the tip of the gun, applied to the surface, and within a matter of seconds were reacting in place. From this relatively crude beginning, more systems came into existence, along with the proportioning equipment and mixing equipment to go along with them. The general procedure is described by Donald J. Wisdorf in *Modern Paint and Coatings*,[1] as follows.

Proportioning base and catalyst are proportioned by air operated piston pump, a gear pump or a diaphragm pump. Piston and diaphragm pumps tend to be more widely used, partially because they are less complicated, have proved to be effective and are well known. The positive displacement principle tends to insure greater accuracy. Gear pumps tend to be sensitive to changes in viscosity so that speed adjustment is necessary. Slippage or leakage is common because of the metal-to-metal interface.

The proportioning pump meters the base and catalyst in the prescribed ratio (one to one, ten to one, or other) within whatever accuracy is judged appropriate for the application.

Pot life or reaction time of the material will significantly influence the design of the system. Pot lives of one to five minutes and longer will require one type of equipment. A five-second pot life will require a different, somewhat more elaborate design. For example, five seconds will require a manual or automatic flush for the unit to stay in operation. Short pot life coatings can be accommodated in existing equipment.100% solid plural component coatings have been mixed and sprayed successfully for more than ten years in shipyards, aircraft manufacturing and in the petrochemical industry.[1]

Once the proportioning of the ingredients has been accomplished, the actual application of the coating can be done by conventional, airless, or electrostatic spray. The key is to mix the catalysts and the components thoroughly, just prior to their being applied. More and more of this type of equipment is being developed as more and more 100% solids and very high-solids coatings are being used. Multiple-component polyurethane coatings are being used on aircraft, epoxy materials are being used on the interior of tankers, and polyester/vinyl ester materials are being applied to the interior of tanks and similar equipment.

The advantages of this multiple-component procedure are obvious. They involve fast-curing coatings, with high solids and therefore, a low solvent base with little air contamination. Also, heavy coating thicknesses can be applied in one coat. The multiple-component system generally is not used for maintenance coatings in plants where corrosion engineers are most involved. On the other hand, sophisticated computerized equipment is being developed, which will allow broader use of this type of system.

Drying or Curing

The drying or curing of a coating after application may be as important as the application itself, depending on the use of the coating.

Exterior Applications

The curing of coatings on the exterior of structural steel, tanks, and similar surfaces is considerably less critical than where the coating is applied in areas of splash or spray of chemicals or where the coating is used as a lining for the interior of a tank. Nevertheless, curing is important. Oil-based coatings and medium-oil or long-oil alkyds require a longer period of drying time than do some of the other high-performance coatings. Because of this, weather conditions can create problems, particularly where such coatings would be applied to tank tops and similar areas, where water can accumulate from either rain or heavy dew. If the coating is exposed to water prior to its taking at least its initial set, which may be 3 or 4 hours, coating problems can occur.

Lacquer-type coatings are undoubtedly the easiest materials to handle on exterior surfaces. This is because they dry rapidly (i.e., within a matter of minutes), and exposure to rain at that point is not detrimental. The same is true for chemical fumes or chemical splash and spray. Lacquer-type coatings are considerably more resistant once the solvents have been removed from the film. Nevertheless, the coating is substantially resistant to the environment after the initial evaporation of the solvents.

Even though cold temperatures reduce the evaporation rate of the solvents from lacquer-type coatings, the initial drying of the coating usually takes place within 30 minutes. Epoxies and polyurethanes, since they are internally cured (particularly those used for corrosion resistance), are very sensitive to temperature. This must be taken into consideration during application. Polyurethanes are much less sensitive to temperature than the epoxies; nevertheless, the chemical reactivity is temperature sensitive. Epoxies, including coal tar epoxies, can cure rather rapidly at temperatures above 70 °F (21 °C). However, if the temperature goes below 70 °F, the curing time increases substantially, even to the point that the coating may remain tacky for from 12 to 24 hours.

Curing is difficult under these conditions, and both atmospheric conditions and chemical fumes, splash, or spray can damage the coating prior to proper cure. Polyurethane coatings, particularly those that react with moisture, act rather well even though the temperature is cool, as long as the humidity is sufficiently high to supply moisture for curing the coating. On the other hand, hot, dry conditions can retard the cure of moisture-cure polyurethanes, making them susceptible to solvent and chemical action.

Water-based coatings cure by the evaporation of water, and subsequently, by the coalescence of the coating particles that were dispersed in the water. Proper coalescence of the water-dispersed resin particles is essential for the proper life of water-based materials. If the atmosphere is hot and dry, the coating may dry sufficiently rapidly so that the particles never are able to properly coalesce. If atmospheric conditions are cold and damp, the water may evaporate sufficiently slowly so that the resin particles agglomerate without proper coalescence. Again, the coating is improperly cured and will not be effective.

Temperature and weather conditions for the proper cure of water-based materials are somewhere between 50 and 80 °F (10 and 47 °C), with a relative humidity in the median range (i.e., 30% to 60%). Under these conditions, the water evaporates sufficiently slowly so that the resin particles are moved in place in the film in such a way that the particles coalesce and form a solid film. Exterior exposure may not be as critical from a total resistance standpoint for exterior coatings as for immersion coatings. On the other hand, curing is important, and unless it takes place within a reasonable time, coating problems can be expected.

Curing of all of the previously discussed coatings is much easier under controlled drying conditions, such as those that exist in product finishing operations or where the coating is done under controlled interior conditions. In product finishing operations, there is usually a forced drying or curing part of the total coating application process. If this is the case, proper curing conditions are established, and the maximum resistance of the coatings can be quickly obtained.

Interior Coating Applications

Coatings applied to the interior of tanks and similar areas where the coating will be subject to immersion, water, or chemicals, are in a much more critical situation from a curing standpoint. In this case, the optimum curing conditions must exist for the coating to be fully resistant.

Vinyl coatings and some other lacquer-type materials are known to retain solvents. This is caused by a mutual solubility of the solvents and resins. While the resins are soluble in the solvents, the solvents are soluble in the resins, which is where solvent retention comes in. With the solvents dissolved in the resins, it is much more difficult for them to evaporate. Many are held for long periods of time and can almost be considered plasticizers. Unless it is force-dried, 2% to 4% of the solvent can be retained in the coating film almost permanently. Force drying increases the vapor pressure of the solvent to the point where it escapes from the resin retaining it.

There have been instances with vinyl coatings where the solvent retention in the coating lasted for many months or a year or more. Inclusion of solvents in the coating, even though it is hard and abrasion resistant, tends to reduce the resistance of the coating for immersion conditions. In order to remove the remaining solvent from within the vinyl coating, it is necessary to increase the temperature and provide good air movement to carry the solvent away from the surface. Without the air movement, it is possible for the solvent in the air and in the coating to come to equilibrium when in a closed space. This would result in solvent remaining in the coating.

Force-drying does not mean that the coatings would be baked, but that the temperature would be raised for a period of time from 130 to 160 °F (55 to 70 °C) in order to drive the residual solvents out of the coating. This may take a number of hours, during which the hot air is circulated in order to remove the solvents from the area. Such treatment can make a measurable difference in the resistance of vinyl coatings used for immersion purposes.

Chlorinated rubber coatings, even though they are lacquer-type coatings, do not have strong solvent retention. The chlorinated rubber resin does not have the same mutual solubility characteristics as the vinyls, and these coatings are known to "through dry" rather quickly.

Epoxy coatings also react well to force drying conditions. Although the epoxy coatings are internally cured, the chemical reaction of the cure proceeds at a much more rapid pace at elevated temperatures. In the same temperature range as used for force-drying vinyls, curing takes place more rapidly and more completely, making the epoxy coatings that much more solvent and chemical resistant.

Epoxy phenolic coatings often require some additional heat to reach their maximum cure and resistance. Generally, they are slower to react than the unmodified epoxy coatings, and some measure of force curing improves their resistance. This is also true of phenolic coatings, which require a high bake in order to develop their resistance to water and chemicals. In this case, the heat curing is part of the coating process and is necessary to develop the properties of the coating. It is believed that force curing tends to improve almost all coatings, by increasing their adhesion and chemical and solvent resistance, and by reducing the chance of chemical contamination of the film prior to its reaching a full cure.

All coatings can be over cured to the point where their properties are diminished. In many cases, it is better to have a somewhat over cured condition than to have an under cured condition; that is, over curing to a point just before the coating begins to break down. The coating will then have its maximum properties in terms of adhesion and resistance. In the case of the thermosetting coatings, however, under curing leads to poor adhesion, poor water resistance, and poor resistance to solvents and chemicals. Therefore, a somewhat over cured coating is preferable.

This is particularly true where coatings are to be used for immersion, for areas of heavy condensation, or where they are subject to constant chemical contact. Even some of the water-based organic coatings are improved by heat treatment. The original IOZ coatings based on a high alkali silicate were cured by heat at around 350 to 400 °F (180 to 205 °C). The coatings reached their maximum resistance within approximately one hour and maintained these properties over a period of many years. Even now, while the heating process generally is not used for such coatings, if a rapid cure is required, heating of the water-based inorganic coating can substantially increase the speed of cure for quick handling and exposure

Weather Conditions

Weather conditions can have a substantial effect on coating application. Weather conditions are less critical where coatings are applied to interior surfaces, although even in this case, problems can occur. The ideal conditions for applying almost all coatings include a temperature of 70 °F, little or no wind, and humidity within 50% to 60%. All coatings respond well to such conditions. Moving away from the ideal, problems can occur which have a decided effect on the resistance of the coating.

Humidity

Humidity is one of the weather conditions that are an almost universal problem. This is because humidity may change rapidly from relatively low to very high during a single working day. It is the consensus of most coating authorities that coatings should be applied at temperatures no lower than 5 °F (3 °C) above the dew point. This may be difficult for the actual applicator to determine, since condensation is difficult to see. Wherever high humidity is encountered, particularly in coastal and marine areas, coating application must be carefully controlled as the temperature of the substrate approaches the dew point. Coatings applied over a surface covered with even a light film of condensation are almost always doomed to failure.

Table 10.8 shows the percent relative humidity above which moisture will condense on metal surfaces that are not insulated. This chart provides good guidelines as to when coating applications should be restricted. For example, if the metal temperature is 60 °F (15 °C) and the surrounding air temperature is 70 °F (which are reasonably normal conditions), there is a good chance of surface condensation if the humidity is 56% or above.

Table 10.9 shows how to determine the dew point if the air temperature and relative humidity are known. Both of these charts are helpful in assuring proper application conditions.

Hot, Dry Weather

Hot and dry weather conditions may or may not be good coating conditions. Under hot, dry conditions, overspray is much more of a problem, and coatings tend to dry much faster, often resulting in dry spray. For example, unless lacquer-type coatings are properly formulated for hot, dry conditions, excessive overspray can result when applied under such conditions. This is even more likely where there is even a mild wind condition. Dry spray also may result during the application of ethyl silicate-based inorganic coatings. Also, because these coatings require moisture to cure, they may not cure satisfactorily under such conditions. The solvents in epoxies may even dry so rapidly that the coating develops an uneven, orange peel-type surface. Moisture-cured polyurethanes also may not cure

TABLE 10.8: Percent Relative Humidity Above Which Moisture Will Condense on Metal Surfaces Not Insulated

Metal Surface Temp.	4 °C 40 °F	7 °C 45 °F	10 °C 50 °F	13 °C 55 °F	15 °C 60 °F	18 °C 65 °F	21 °C 70 °F	24 °C 75 °F	27 °C 80 °F	30 °C 85 °F	32 °C 90 °F	35 °C 95 °F	38 °C 100 °F	40 °C 105 °F	43 °C 110 °F	46 °C 115 °F	49 °C 120 °F
1 °C 35 °F	60	33	11														
4 °C 40 °F		69	39	20	8												
7 °C 45 °F			69	45	27	14											
10 °C 50 °FF				71	49	32	20	11									
13 °C 55 °F					73	53	38	26									
15 °C 60 °F						75	56	41	17	9							
18 °C 65 °F							78	59	30	21	14	9					
21 °C 70 °F								79	45	34	25	18	13				
24 °C 75 °F									61	48	37	29	22	16	13		
27 °C 80 °F									80	64	50	40	32	25	20	15	
30 °C 85 °F										81	66	53	43	35	29	22	16
32 °C 90 °F											81	68	55	46	37	30	25
35 °C 95F												82	69	58	49	40	32
38C 100F										83	70	58	50	40			
40 °C 105 °F											84	70	61	50			
43 °C 110 °F												85	71	61			
46 °C 115 °F													85	72			
49 °C 120 °F														86			

Source: *Corrosion Control Principles and Methods*, Section 7, Ameron Co., Pasadena, CA.

TABLE 10.9: Dew Point Determination

Air Temp. °C	Dew Points (°C) at Various Relative Humidity %							
	30%	40%	50%	60%	70%	80%	90%	100%
−1	—	—	—	—	−6.5	−4	−2	−1
4	—	−6.5	−4	−2	0.5	1.5	3.5	4.5
10	−6.5	−3.5	0.5	2	3.5	5.5	8.5	10
15.5	0	2	4	8	10	11.5	14	15.5
21	3	6.5	10	13	15	18	19.5	21
26.5	7	12	15.5	19	21	23.5	25	26.5
32	13	16.5	20.5	24	25.5	28.5	30.5	32
38	18	22	25.5	29	31	33.5	36	38

Note: It is essential to ensure that no condensation occurs on blasted steel or between coats during painting. Air at a given temperature can only contain a certain (maximum) amount of water vapor. This proportion is lower at lower temperatures. The dew point is the temperature of a given air-water vapor mixture at which condensation starts, since at that temperature its maximum water content (saturation) is reached. In practice a safety margin must be kept, whereby the substrate temperature is at least 3 °C above dew point.

TABLE 10.10: Theoretical Yield for a Unit Volume of 100% Solid Coating at Specified Unit of Film Thickness

Measuring System	Unit Volume	Unit Dry Film Thickness	Area
Metric	1 Liter	100 µm	10 m^2
U.S.	1 U.S. gallon	0.001 in	1,604 ft^2
British	1 Imperial Gallon	.0001 in	1,925 ft^2

properly under such conditions. In addition, water-based water emulsion coatings may dry so rapidly under these conditions that the coating does not properly coalesce, but may mud crack or craze, thereby resulting in an unsatisfactory coating.

Hot, Humid Weather

Hot, humid weather presents another set of conditions to be considered. High humidity can create condensation problems, particularly as the late afternoon or evening approaches. This means that a constant check of the surface is necessary to make sure that coatings are not being applied over such condensation.

Warm, moist conditions are good for moisture-cured coatings such as ethyl silicate inorganics and moisture-cured polyurethanes. However, they are not as satisfactory for vinyls, since many solvents evaporate rapidly due to the temperature and, because of the rapid evaporation, the temperature of the coating may be reduced below the dew point so that progressive blushing can easily occur. This is also a problem with most lacquer-type coatings under humid conditions. Blushing is the condensation of moisture on the surface of the semiliquid coating, causing it to whiten. This blushing is caused by the precipitation of the coating resin on the surface due to the water, and it remains even after the coating is dry. A blushed coating is not satisfactory from either an appearance or resistance standpoint.

Cool, Dry Weather

Cool or cool, dry conditions (i.e., above 40 °F [5 °C]) are usually good conditions for the application of lacquer-type or water-based coatings such as water-based inorganics, acrylics, or similar products. Under these conditions, the water dries from the coating relatively slowly, allowing the coating to make a good strong film. Silicate dispersion and lithium silicate-type IOZ coatings are particularly good under such conditions. On the other hand, moisture-cured inorganics may not cure for a long period of time under conditions that are cold and dry. This also may be true of moisture-cured urethanes.

Cold, Humid Weather

Cold, humid conditions are more satisfactory for moisture-cured coatings such as the ethyl silicate-base inorganics and moisture-cured polyurethanes. They are not as satisfactory for water-based coatings such as alkali-based inorganics or the water-based organics. It can be so cold and humid that the water will not evaporate from the coating over a period of many hours. Under such conditions, neither the water-based inorganics nor the organic water-based products will make a proper film on the surface. A poor coating with little resistance to corrosive conditions results. Epoxy coatings are particularly subject to poor curing during cold conditions. Increased humidity may be reactive with amine type curing agents, causing further coating resistance problems.

Weather conditions are critical to the application of coatings. In fact, it often is necessary to select the type of coating that may be applied under the particular weather conditions that exist at the time.

Coating Coverage

Coating coverage can be defined in a number of ways. It can be the area that a gallon/liter of coating will cover, the thickness of the film covering the surface, or the amount of coating required for a given area at a given thickness. Coverage, as it normally is described, is considered in a NACE Technical Committee Report entitled, "Determination of Theoretical Coverage Rates of Inorganic and Organic Protective Coatings."2

> The "coverage rate" of a coating is defined as the area of a surface that can be covered at a uniform specified DFT by a specified unit volume of a coating. In metric units, the coverage rate is expressed in sq. meters/litre at a DFT of 100 microns (0.1 mm). In U.S. units, the coverage rate is expressed in sq. ft/U.S. gallon at a DFT of 1 mil. In British units, the coverage rate is expressed in sq. ft/Imperial gallon.
>
> The following table (Table 10.10) is presented as an example of the theoretical yield of a 100% solid (no volatiles) coating spread at a specified unit film thickness assuming 100% utilization. In this example, the area covered by one litre of 100% solid coating at a thickness of 100 microns is 10 sq. meters.[2]

Since coverage is an important factor in any application, the above description indicates only theoretical coverage. A more detailed discussion of coverage is given in Koppers Protective Coatings Technical Data Sheet.[3]

A gallon measure contains 231 cubic inches which when spread out covers an area of 231 sq. inches one inch thick (231 sq. in. equals 1,604 sq. ft.) Since one mil is $^1/_{100}$ of an inch, one gallon of solid material, not containing any volatiles will cover a thousand times 1,604[5] or 1,604 square feet one mil thick. For simplicity we drop 4 square feet and state one gallon of solid material of any kind will produce a one mil thickness on 1,600 square feet. This is strictly a question of volume and has nothing to do with the weight of the gallon or the kind of material contained in the gallon. If more than one mil is needed the coverage will of course be proportionally less and it is easy to see that one gallon will produce 2 mils on 800 square feet. (½ of 1,600 square feet), 3 mils on 533 square feet (¼ of 1,600 square feet), 4 mils on 499 square feet (of 1,600 square feet), and so on. On these facts all the following computations are based.

If all coatings would contain only solid material, all coating regardless of type would give the same mil thickness per square foot. Most paints, however, contain solvents to make application possible. The amount of solvent used is governed by the method of application, and the inherent viscosity of the solid content of the paint, and it may vary greatly. These solvents go out of the paint film after application and do not contribute to the final dry mil thickness of the coating. They do contribute however to the wet mil thickness.

For example: one gallon of paint containing 50% solid material by volume (also called nonvolatile by volume), and 50% solvent by

volume will cover 1,600 square feet 1 mil wet or 800 square feet 1 mil dry. Dry thickness is less because one half of the volume is made up by solvent that will leave the film and dissipate. Expressed differently one gallon of paint having 50% nonvolatile volume will cover 800 square feet one mil dry. All mil thicknesses mentioned will be dry mil thicknesses if not otherwise stated. Mathematically if you multiply 1600 by the nonvolatile volume percentage of the paint you get the coverage at one mil dry thickness.

$$1{,}600 \times 50/100 = 800 \text{ square feet 1 mil thick} \qquad 3$$

While theoretical coverage rates are never attainable in actual practice, since they do not take into account additional solvent evaporation, application losses, wastage, surface complexities, and other variables, they can be used in an important way. Applicators can make appropriate deductions from the theoretical values to compute estimated practical coverage rates. The factors that must be taken into consideration include non-uniform DFT; application wastage (e.g., overspray); material retained in containers, spray pots, and lines; surface profile developed by surface preparation procedures; and the effect of pitted or irregular surfaces.

These elements of material loss and increased consumption are beyond the control of the coating manufacturer. Consequently, manufacturers cannot be held accountable for the practical coverage rates obtained at the job site. However, they can be held accountable for total volume solids and theoretical coverage rates of products as furnished.

When all factors are taken into consideration, the practical coverage amounts to considerably less than the theoretical coverage. The average reduction in coverage is from 10% to 30%. The practical coverage may become even lower on heavily pitted steel, rough concrete, or while spraying in the wind.

It is not possible for even the best applicator to hit the mil thickness right on the nose; thus, there should be a reasonable leeway. The unavoidable error, however, lies on the high side of the required thickness, since most specifications call for a minimum mil thickness. Wet thickness gauges are commercially available and easy to use.

Mild atmospheric conditions call for a thickness of at least 3.5 mils. In industrial environments, where the conditions are more severe, 5 mils are recommended. Submerged surfaces need a thickness of from 5 to 15 mils, depending on the corrosiveness of the liquid and the coating system used. Heavy bituminous coatings are best applied in 18 to 20-mil thicknesses, and in some instances as high as $^{1}/_{32}$ of an inch.

As stated previously, coating coverage and thickness are closely related and are both important in obtaining proper coating performance. The importance of film thickness is discussed by John D. Keane in a paper entitled, Minimum Paint Film Thickness for Economical Protection of Hot-Rolled Steel Against Corrosion.[4]

> A ten-year paint exposure study was conducted to determine whether or not there is a minimum or optimum paint film thickness, such as 5 mils, for the economical protection of hot- rolled steel. In all work to date, each additional mil of paint thickness has been accompanied by an increase of about 20 months in paint life.
>
> It was shown that there was indeed an economic initial paint film thickness above which long-term protection was afforded throughout the entire study period. This minimum effectual thick- ness, however, was not a constant, being thinner for the more durable and less permeable paints. In addition, this thickness tended to be lower in milder environments, and to an unexpectedly limited extent, lower on well-prepared surfaces. It was found far more economical to apply sufficiently heavy films at the beginning rather than to undertake more frequent subsequent maintenance painting.[4]

Coverage also implies coating continuity. In any application of any high-performance coating to prevent corrosion, coating continuity is extremely important. Without continuity, the coverage (i.e., coating thickness) means very little. Continuity, on the other hand, should mean that the coating is applied evenly over the entire surface with no coating defects. This concept is important when using any anticorrosive coating, but it is even more important where coatings are applied to the interior of containers to protect against corrosion or to protect the contents against contamination.

In order to assure a proper coating job, it is essential that quality controls are enforced during and following the application. Each coat of a coating application should be carefully inspected (hold point) before the succeeding coating is applied. Overspray or dust should be removed by light sanding and dusting; loose brush hairs in the prime coating should be removed; and any holidays should be re-primed.

Thickness and continuity are two of the most important items that should be considered in application quality control checks. One procedure that is recommended by most manufacturers is to assure proper coverage by alternating the color of each succeeding coat. If the prime coat is red, the second coat may be black or gray, the third coat an alternate of the black or gray, and the final coat can be whatever is selected as being in harmony with the rest of the structure. Alternating colors between coats not only helps in the inspection of the coating during the application, but also aids in obtaining the proper thickness and continuity of the coating. It also aids the applicator in being able to visually determine when an area has been thoroughly covered. In any tank lining job, visibility is less than ideal and alternating the color of each coat helps assure good judgments.

Inspection

Specifications for the finished coating system usually call for a minimum film thickness. A variety of instruments are available for such measurements. The simplest and least accurate of these is the wet film gauge. By sinking this instrument into the wet coating film, a reading can be obtained. Naturally, coating thickness will diminish as the solvent in the coating evaporates. Therefore, the wet film gauge will nearly always indicate a greater film thickness than that which actually exists. This is why it is important to take a reading immediately after coating application. A second drawback in the use of this instrument is the inability to measure total film thickness in a multiple-coat application, since only wet coat readings are obtainable. A third problem is when lacquers are measured. Since the previous coat is soluble in the following one, the wet film gauge will sink into the previous coating, giving a greater-than-actual reading for the second coat.

At best, the wet film gauge can give the inspector or better yet, the applicator, a rough idea of the thickness of each coat as it is being applied. Its areas of greatest use are in spot checking the coating film as it is being sprayed, which allows the applicator to immediately

correct any application defects. It is also possible with this instrument to measure coating films that are being applied over smooth concrete and wooden surfaces.

DFT readings over steel are usually taken with nondestructive gauges of two types. Type I is the pull-off type that operate by permanent magnet-calibrated spring mechanisms giving readings on a graduated scale. Type 2 fixed probe types operate on electromagnetic principles and give digital readouts. Electronic gauges using the eddy current principal are effective on nonferrous metals. The newest of the electronic gauges can measure DFT on nonmagnetic surfaces such as concrete, wood, and plastic using ultra-sonic principles. Several manufacturers make these different instruments, including the more popular models from Mikrotest,† Elcometer,† and Positest†. Most of these instruments are small enough to be carried in a pocket, and should be readily available to every inspector.

A hand microscope device, the Tooke Gauge†, requires cutting the film and can be used for DFT measurements over nonferrous substrates. It is also useful over steel, particularly in measuring the thickness of each coat in a system. A calibrated reticule inside the microscope chamber serves as a measuring device by reading the amount of lines within each different colored coat of paint.

It is extremely important that the dried coating film contain no bare spots or holidays. Such areas often are too small to be noticed with the naked eye. Therefore, to ensure 100% coverage, holiday detectors are provided. These battery or electrically operated instruments are capable of detecting any pinholes or bare areas in the coating and may be used to inspect any nonconductive coatings applied over a conductive surface. One example of such a device would consist of a rod, which is electrically connected to a power supply, holding a wet sponge. This power supply also is connected to the metallic surface over which the coating is applied. The coating film acts as an insulating barrier, thereby preventing completion of the electrical circuit. If, however, there is a holiday in the coating, the circuit will be completed, current will flow, and some type of signaling device such as a bell or buzzer will alert the inspector. This type is accurate over films up to 20 mils DFT. Another type uses either AC or DC electrical current and a brass or graphite wand in place of the wet sponge. When a holiday is detected a spark appears, usually charring a ring around the holiday or pinhole. These must be calibrated according to the thickness of the coating being inspected, normally using 100 volts of electricity per mil of coating.

It should be remembered that holiday detection of any type may be misleading once the coating has been placed in immersion service as the coating retains some of the liquid media and interferes with electrical currents.

This method of inspection is extremely important where the coating is to be continuously immersed in a highly corrosive solution or used to prevent liquid contamination. Holidays, if not patched, will become focal points for corrosion, thereby resulting in deep pitting of the underlying surfaces.

The completed coating should also be inspected for runs, overspray, and roughness. Any areas that show these or other signs of improper application should be repaired or recoated.

Cleaning

An important part of any application job is the cleaning of the equipment upon completion of a day's work. Dirty or improperly cleaned equipment can cause more downtime and coating difficulties than almost any other part of the application procedure. The cleaning of the coating tools should be done immediately after use before the coating can become hard, because once it reaches this state, many of the high-performance coatings are insoluble and extremely difficult to remove from either interior or exterior surfaces.

The first step in the cleaning procedure is to remove as much of the liquid coating as possible from brushes, rollers, paint pots, pumps, air lines, and guns, and clean these tools at least two and perhaps three times in the correct solvent until no coating is noticeable in the last cleaning. If possible, the solvent should be somewhat stronger than the solvent within the coating itself, in order to ensure that the coating is dissolved from the interior of brushes, hoses, spray guns, and other areas. The brushes, pots, and coating containers should be washed and then wiped thoroughly dry.

After solvent cleaning, brushes and rollers should be flushed with a good detergent and warm water. Household dishwashing or clothes washing detergent is good for this purpose. It is surprising, even after using the solvent, how much additional material can be removed through the use of a detergent and warm water. The brushes and rollers should then be rinsed in clear water, the excess water removed, and in the case of brushes, the bristles should be brushed straight with a short-fiber wire brush. This not only helps to straighten the bristles out, but also tends to remove any of the coating that may have dried on the outside bristles adjacent to the handle of the brush. Any coating in this area should be removed to prevent the brush from becoming stiff and unusable in a short period of time. Rollers should be stood on end and allowed to dry. Brushes should be laid flat so the bristles will not warp or become fuzzy during the drying period.

Also, use extreme caution when cleaning airless spray guns. The high pressures involved can be very hazardous, particularly when the spray head is removed. The airless spray must be pointed away from any person or part of the body. The high pressure can drive the solvent or coating into the flesh, making a wound difficult to heal. With good care, all coating tools and equipment will last much longer and will always be in proper condition for additional use. Clean equipment is also insurance against contamination of the applied coating.

Application Problem Areas

Chapter 7, on structural design, indicated some of the coating problems that exist with much of the structural design that is common today. Since most of these are application problem areas, they will be discussed in greater length in the following sections.

Edges and Corners

The coating of sharp edges and exterior corners has been discussed previously in this chapter. However, due to the importance of these areas, this application should be stressed. Figure 10.47 provides a good example of sharp edges and corners that often exist. The photograph is a view of the interior of a block section showing the bottom reinforcing members in a large tanker. While this is a complex area, all of the edges and corners shown must be thoroughly coated in order to provide the corrosion protection required. Such areas should be double coated, with the first coating applied directly at the corner edge and the second application overlapping

†Trade name.

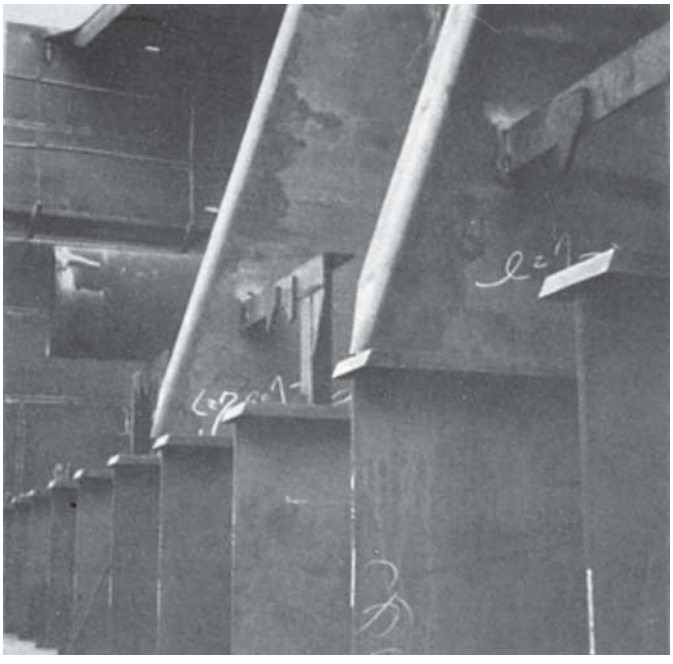


FIGURE 10.47: A block section of the bottom of a tanker tank showing the many sharp edges that require special attention.

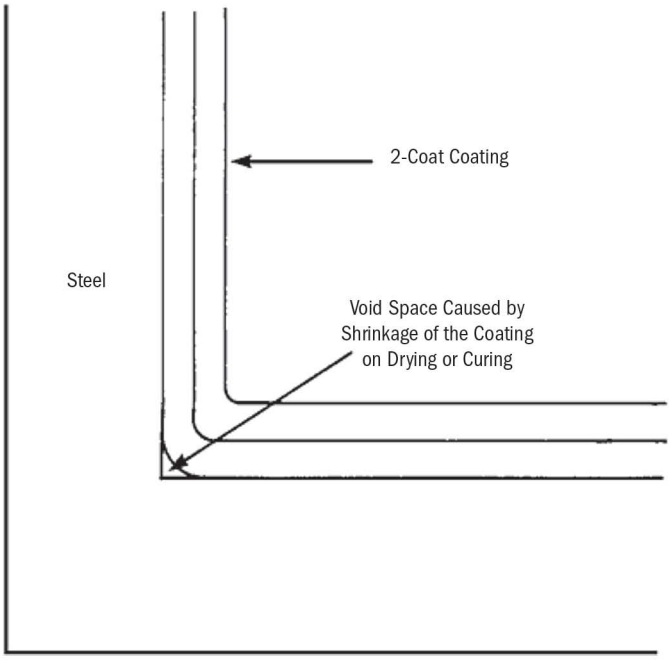


FIGURE 10.48: Bridging of the coating in a square corner.

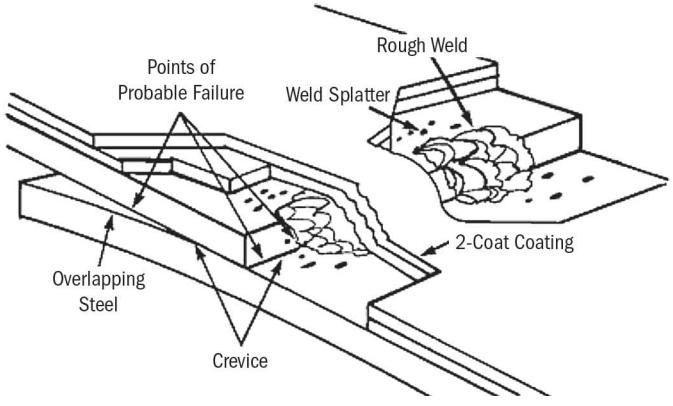


FIGURE 10.49: Coating difficulties on welded plates.

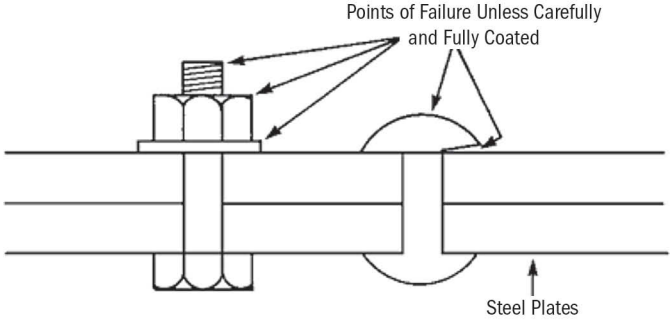


FIGURE 10.50: Coating difficulties on bolts, nuts, threads, and rivets.

the corner or edge in the flat area. Where possible, it is best to stripe the corners and edges by brush, flowing the coating out over the sharp edges in order to build up maximum coating.

Figure 10.47 also shows the number of inside corners that are common in such structures. In this case, the first coating may be directed into the corner, followed by additional passes on the flat area adjacent to the corner, and carrying the spray pattern into the corner each time. In coating inside corners, there is the problem of applying too much coating under certain conditions. Since coatings tend to shrink, if too much coating is applied into a corner (particularly where drying of the coating is relatively slow), the coating may shrink away from the inside corner. This causes a void underneath the coating, as shown in Figure 10.48.

Thus, sufficient coating must be applied to thoroughly cover the inside corner with coating thickness. However, the coating should not be applied so thickly that a void occurs in the corner upon shrinking. This can only be accomplished through extreme care on the part of the coating applicator, since only he or she can control the coating thickness. Coating of the inside corner also may be complicated by welds in that area. In this case, additional care must be taken to ensure application of the proper coating thickness over the weld and corner area.

Welds

Welds nearly always represent an application problem, since they usually are rougher than the adjacent steel surfaces (Figure 10.49). The coating must be applied over such a weld so that all of the rough areas, pits, undercutting, and sharp areas are thoroughly coated. In this case, it is always good practice to apply at least the first coat over the weld by brush as opposed to spray. Using a brush, the coating can be worked into the rough areas to make sure that they are properly filled and without holidays.

If spraying of such areas is required, it is recommended that welds be striped with a coat before coating any adjacent areas. When the adjacent areas are coated, the coating should be carried out over the weld area, providing a double coat. Where this is properly done, the weld areas normally will outlast the flat areas in a corrosive atmosphere. This is due to the additional coating thickness, along with the extra care taken during the application.

Bolts, Nuts, and Rivets

While bolts, nuts, and rivets provide the most common way of fastening structural steel besides welding, they pose obvious coating difficulties. In this case, it also is good coating practice to brush coat these areas prior to coating the flat area. With the brush, the coating can be worked into all crevice and corner areas, building the coating up and making sure that no holidays remain (Figure 10.50).

Figure 10.51 shows the effect of spraying a riveted area. While the entire area may have seemed to be covered during the spray operation, it can be seen that after some exposure, the left-hand area of the rivet is rusty, while the remainder of the rivet is well protected. This is caused by the applicator spraying from one direction only, with the surface away from the spray being shaded from the coating (Figure 10.52).

Such application deficiencies are common on steel structures. Rivets or bolts should be sprayed from at least four different angles to prevent holidays from occurring adjacent to the rivets or bolts. Rivet and bolt areas should be sprayed first and thoroughly covered, and then recoated during the coating application to the adjacent flat areas.

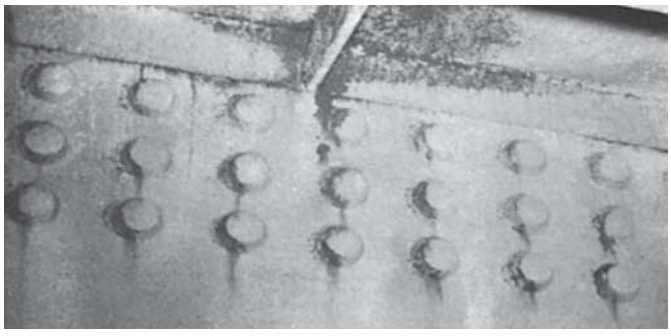


FIGURE 10.51: Corrosion resulting from spraying rivets from only one direction.

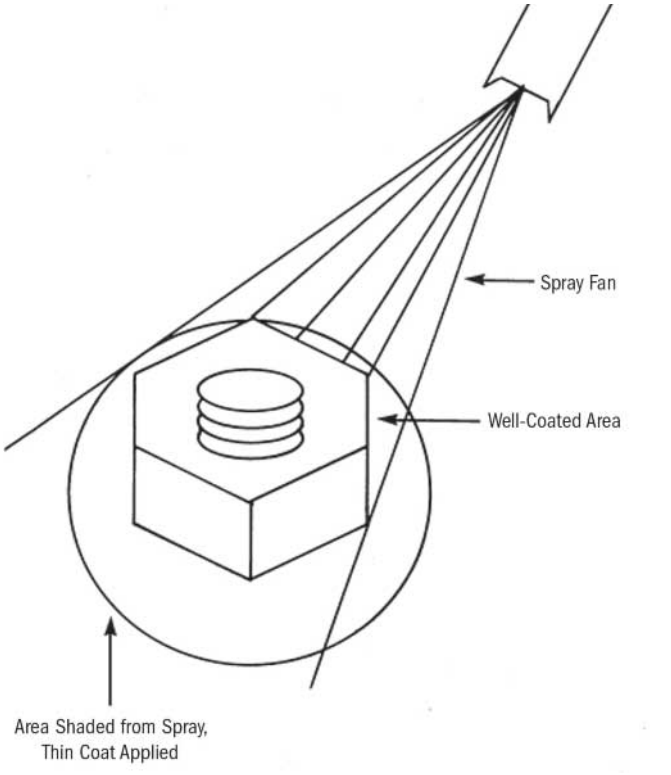


FIGURE 10.52 Incorrect spraying procedure from only one direction leaves a shaded area of thin coating.

Coating Difficulties

There are many coating difficulties that are commonly encountered during application. While most of these are under the control of the applicator, anyone supervising an application job should be on the look out for them.

Brush Marks

Brush marks pose a common problem in brushing operations, particularly when using many of the more thixotropic formulations that are available in the heavier bodied coatings. A coating that flows very well tends not to have brush marks, since the marks will flow out to a smooth film. With the heavier coatings, however, the coating should be thoroughly brushed to cover the area, making sure that full coverage is obtained. Following this, very light strokes of the brush should be applied all in one direction to minimize any heavy brush marks that might be left in the original pass (Figure 10.53). The light stroking of the brush as the area is completed vastly improves the problem of brush marks with heavier materials.

Stippling or Orange Peel

A stippling or orange peel type of surface is common when using thixotropic coatings with a roller, particularly a roller with a heavy nap. In many ways, the orange peel is similar to the brush marks in a coating in that there are heavy and light areas, even though the film may be continuous. They are more common where the roller is pressed heavily against the surface and rolled rapidly. While they cannot be completely overcome in thixotropic coatings, they can be improved considerably by a light slow rolling of the surface once the entire area has been covered. This light rolling should be in all one direction in order to provide a uniform texture. Coatings that have considerable flow-out are much less of a problem in this way, and usually a thinner film is applied to the surface.

Orange peel also can result from the spraying process. Again, it is more prevalent with a thixotropic-type coating and usually results when the spray gun is not adjusted properly for maximum dispersion in the spray. Where this is a problem, the spray should be adjusted so that it is as fine as possible without causing overspray.

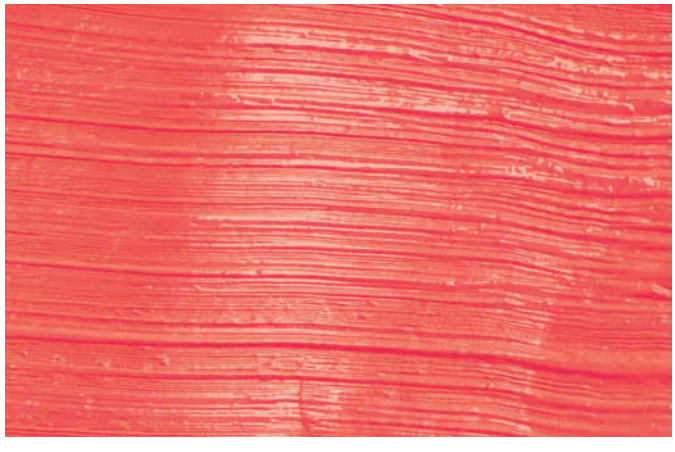


FIGURE 10.53: Typical brush marks in a heavy-bodied coating. Photo: Thinkstock.

Overspray

Overspray usually is caused by gun adjustment, although there are some coatings that have a greater tendency to overspray than others. Chlorinated rubbers and vinyls are examples of these. Some ethyl silicate IOZ coatings also tend to overspray more than others. The problem is caused by the fast drying coating losing sufficient solvent from the time that it leaves the gun until it hits the surface, so that a nearly dry particle of coating sticks to the surface (Figure 10.54). This often is the case where one area of coating overlaps another, or at the end of the spray pass.



FIGURE 10.54: A typical overspray condition on a coating.

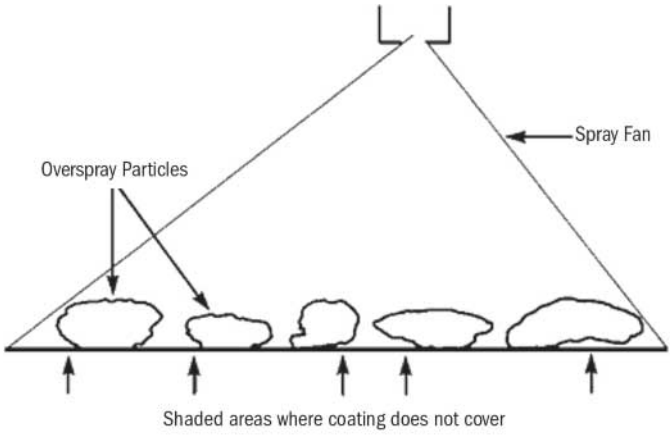


FIGURE 10.55: Pinhole corrosion due to non-uniform coverage of overspray.



FIGURE 10.56: Typical example of overspray and the resulting pinpoint corrosion that can result. Photo: Thinkstock.

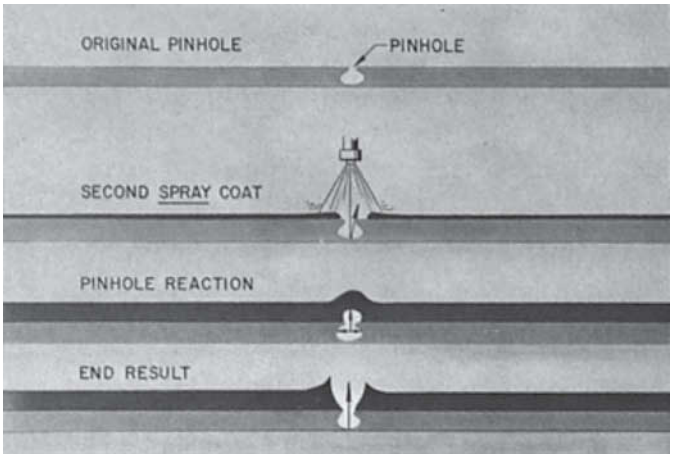


FIGURE 10.57: The mechanism of pinhole formation.

The gun adjustment that causes most overspray is where there is too little material passing through the gun or where there is an excessive amount of air and increasing the pressure on the liquid, so that both are optimum, will reduce overspray to a minimum. Holding the spray gun too far away from the surface is also another cause of overspray. Tilting the gun when spraying either high or low can cause excessive overspray. For instance, during the spraying of some tanks, the applicator tried to spray above and below a scaffold platform, with excessive overspray in both areas. These areas failed quickly and were extremely costly to repair. Thus, care should be taken to ensure that the coating is applied to the surface as a good, wet film without excessive dry spray at the edges of the fan.

Overspray can cause coating failure by creating areas of pinholes surrounding the dry spray that sticks to the surface. If overspray occurs on the surface, it should be removed by a light sanding of the surface prior to the application of additional coats. Figure 10.55 shows the reason why corrosion may begin where a coating is applied over overspray. The overspray particles actually create a shadow for additional spray over the surface, creating a small bare spot in and around the shaded side of the overspray particle. This is a common occurrence and should not be overlooked during an application. Once these bare areas around the overspray particles exist, it is extremely difficult to obtain a continuous coating over the area, and pinpoint corrosion begins very quickly (Figure 10.56).

Overspray is more commonly associated with the standard air spray equipment than it is with airless spray. Since no air is incorporated into the coating during the airless spraying process, this problem is largely eliminated.

Pinholing

Pinholing is another problem that can be caused by improper gun adjustment. This usually occurs where there is too much pressure on the coating liquid and too little air pressure to disperse the coating. The pinholes usually occur in the center of the fan where the coating is heavy and where air has been blown into the coating. These small bubbles break and cause the pinhole in the coating. Coatings with excellent flow-out often flow sufficiently well so the pinholes are removed. On the other hand, most of the high-performance coatings are sufficiently heavy bodied so that the pinhole, once formed, tends to remain.

Once formed in a coating, pinholes are extremely difficult to remove since a second coat usually will not cover the pinhole, as indicated in Figure 10.57. In this case, the pinhole is formed in the original coating, and when the second spray coat is applied, it covers the pinhole, leaving a small bubble underneath the coating. The solvent vapor pressure in the bubble tends to cause it to expand and break, again leaving a hole clear through the entire coating.

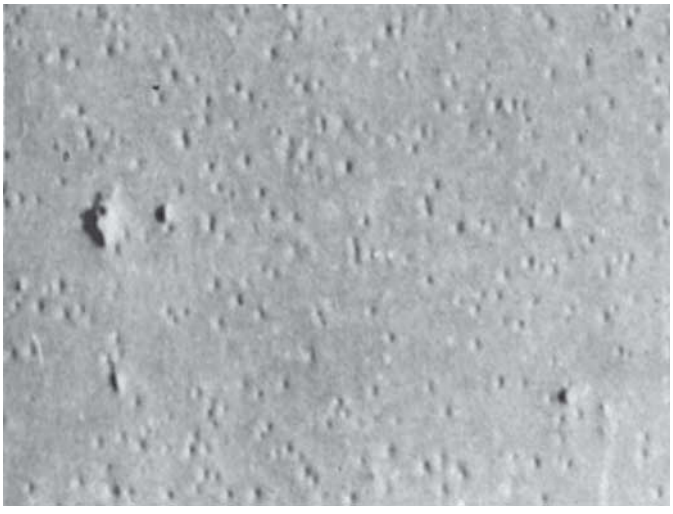


FIGURE 10.58: A pinholed coating.

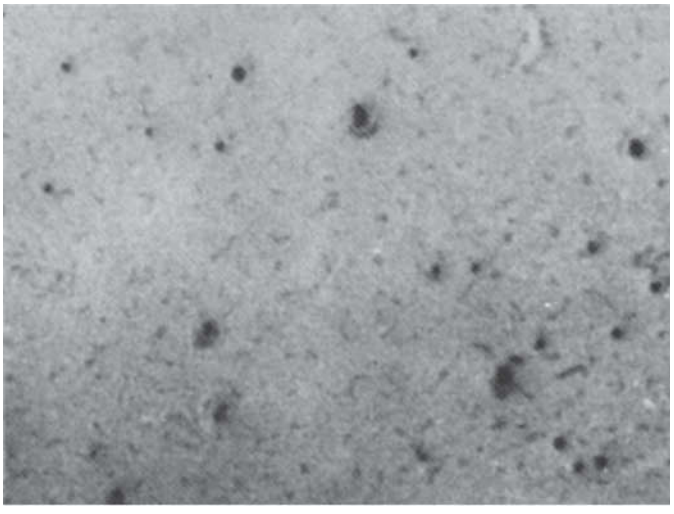


FIGURE 10.59: A pinholed coating magnified to demonstrate actual pinhole openings. Source: *Steel Structures Painting Manual*, vol. 1, "Good Painting Practice" (Pittsburgh, PA: Steel Structures Painting Council, 1966), p. 106.

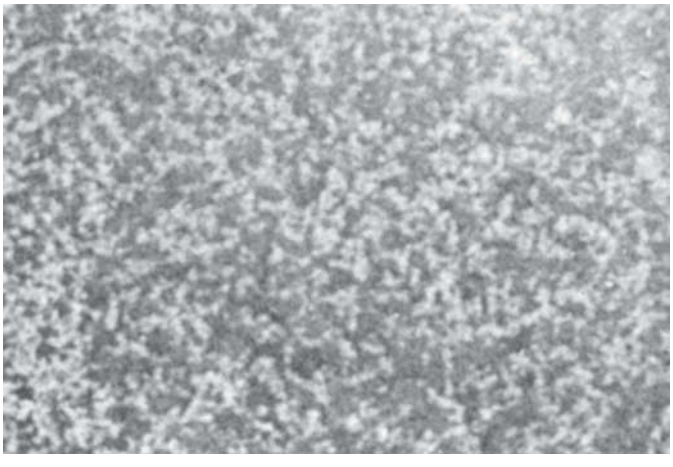


FIGURE 10.60: Spattercoating.

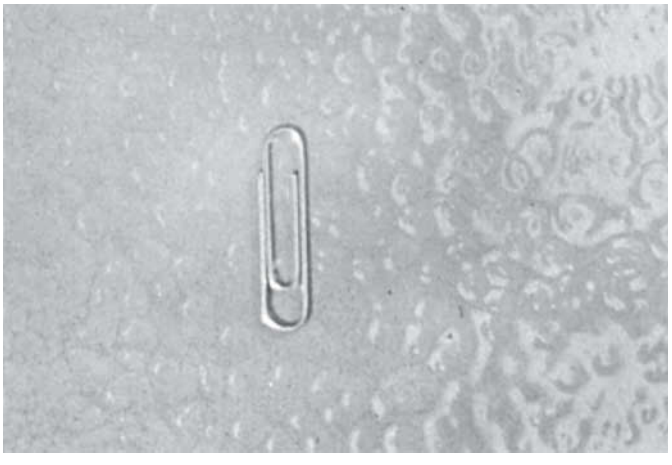


FIGURE 10.61: Typical cratering or "bug-eyeing" of a coating.

Pinholing can be a serious problem wherever corrosion-resistant coatings occur. Gun adjustment must be watched very carefully to see that this is not the cause of the trouble. Pinholing can also occur because the gun is held too close to the surface, not allowing the coating to be sufficiently broken up before it hits the surface.

Pinholing may not be as prevalent with airless spray as it is with air spray, although it can occur with airless spray as well. In this case, it usually occurs where the gun is held too close to the surface, creating bubbles in the coating. The airless spray should be held a sufficient distance from the surface so that the spray is entirely broken up and as fine as possible as it hits the surface. A wet, even film is the answer to the problem.

Figure 10.58 shows a typical surface with fine pinholes throughout. Figure 10.59 illustrates a pinholed coating magnified to show the actual openings in the film.

Spatter Coat

Spatter coat is a condition that can occur at the end of a spray stroke or where each pass of the spray is not sufficiently overlapped. Spatter coat is where the individual particles of coating from the spray hit the surface, but the coating is not continuous. There is a small area between the individual coating droplets that is bare, even though during the application the applicator may think the surface is covered. Spatter coat is a major cause of holidays in a coating. The area may look as though it is fully covered because of an even coloration; however, insufficient coating has been applied to create a continuous coating of even thickness (Figure 10.60).

Cratering

Cratering is also called fish-eyeing, or bug-eyeing. There are a number of causes for this kind of coating difficulty. It is usually associated with phenolic or epoxy coatings, and, in some cases, can be traced back to improper coating formulation. The solvent balance within the coating can create this condition. A typical example is shown in Figure 10.61.

Cratering also can be caused by very fine oil droplets in the air used to spray the coating. In this case, the coating does not properly wet the surface and tends to pull away from the fine droplet of oil. It also can be caused by oil in the sandblast air, which is left in a small spot on the surface. These are extremely fine droplets and ordinarily cannot be seen on the sandblasted surface.

Polyurethane coatings applied over oil spots commonly fish-eye.

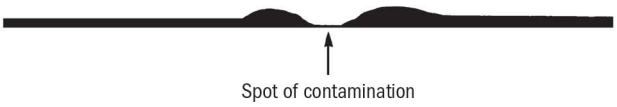


FIGURE 10.62: Cratering due to the static condition of the particle of contamination, which causes the coating to be repelled from that area.



FIGURE 10.63: Runs in a coating.



FIGURE 10.64: A coating sag.



FIGURE 10.65: Solvent blistering. Source: *Steel Structures Painting Manual,* vol. 1, "Good Painting Practice: (Pittsburgh, PA: Steel Structures Painting Council, 1966), p. 106.

Another cause of this problem is particles from the air that have the same charge as the coating. The static condition of the particle causes the coating to be repelled from that area, causing a small crater (Figure 10.62). Since this problem usually is caused by contamination, the solution to the problem is to eliminate the contamination. This should be done as soon as there is evidence that the coating is tending to crawl or crater. If the coating is applied and cured in this condition, it is usually very difficult to apply a second coat over such a surface. Contamination still exists and the cratering or bug-eyeing often recurs at the same spot. If the coating has dried in this condition, it is necessary to hand or power sand the surface thoroughly prior to applying the second coat.

If the cratering condition is caused by improper solvent balance, there is little the applicator can do to aid the situation. In this case, the coating supplier should be called in to overcome the problem.

Runs or Sags

Runs or sags are also called curtains, and generally are caused by the heavy application of a coating in a certain area, so that, on a vertical surface, the weight of the coating causes it to run down the surface and create runs or curtains (Figures 10.63 and 10.64). This often leaves a thin area above the run or sag. The area above the sag also may contain pinholes. The sag or run itself also may contain bubbles, which can break, causing voids in the coating.

Runs and sags usually are in the direct control of the applicator. If the gun accidentally goes too close to the surface and a run or sag is formed, it should be removed from the area before the coating is dry and the coating reapplied at that point. Where they are left on the surface and the coating dries, these areas should be thoroughly sanded to level out the coating and remove voids or pinholes. Coating should then be reapplied to the area.

Solvent Blistering

Solvent blistering is a condition that can occur in almost any coating that contains a solvent. It may occur more readily with lacquer-type coatings, which tend to dry on the surface rapidly and trap solvent underneath. This does not necessarily mean that it cannot occur with epoxies and other similar coatings that contain solvent and which also may dry on the surface faster than the solvent evaporates from the body of the coating. Solvent blistering usually occurs in areas where the sun hits the coating during the application, causing the surface to become quite warm and evaporating the solvent rapidly. It often occurs with heavy-bodied coatings because of the greater coating thickness.

Should solvent blistering become a problem, one answer to the situation is to apply the coating in the afternoon, after the sun has ceased to create such hot, drying conditions. If this is impossible, the coating should be applied in several thinner coats rather than in one thick coat, since the solvent can evaporate more readily out of the thin coating. This requires additional passes over the surface in order to obtain the proper coating thickness. However, it can eliminate the problem of solvent blistering and the creation of a weak

spot in the coating at that point. An example of solvent blistering is shown in Figure 10.65.

Blistering of this type can also occur over inorganic coatings, which contain some porosity. In this case, the solvent expands within the porous inorganic coating, causing sufficient pressure to cause blistering of the topcoat. There are many formulations of topcoats available that do not tend to blister over inorganics. These materials usually contain higher boiling solvents, which lessen the problem unless the coating is applied on a very hot surface. Again, if this is a problem, coating in the afternoon can often overcome it. Thin coats and more coats can also help in this situation.

The same condition can also exist over concrete. Even when hard-troweled, concrete is sufficiently porous that coatings applied over it in the sun may tend to solvent blister. The reason for the difficulty is solvent expansion in the porosity of the concrete, creating a pressure that is sufficient to raise a blister. Coating late in the day, or in several thin coats, can also remedy this condition.

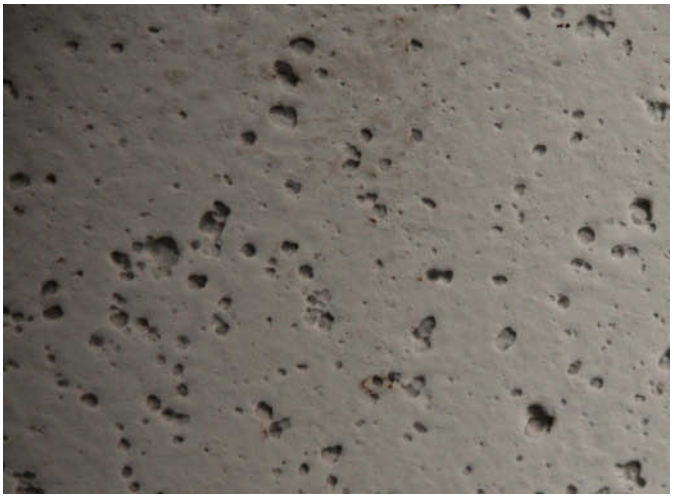


FIGURE 10.66: Airborne contaminants in a coating.

Pigment Separation

Pigment separation is not a common problem. However, one of the areas where it has been noted is where water-based IOZ coatings are applied under cold conditions (i.e., sufficiently cold so that the water does not evaporate from the coating rapidly). If the coating is applied on a vertical surface, the weight of the zinc in the coating tends to separate from the liquid in the coating, causing small curtains where the pigment is concentrated. This leaves areas without pigment, which can then corrode.

Lead containing coatings applied heavily under slow drying conditions can also have pigment separation. This situation also can be caused by improper solvent balance. It is usually caused by thinning the coating with a marginal solvent that causes the pigment to agglomerate. When this occurs, the coating has an uneven appearance, with streaks of the pigment occurring as the coating dries.

In the case of the coating applied where the temperature is too cold, this can be overcome by warming the surface or by waiting for changing weather conditions. In the case of the improper solvent balance, a change in the thinning procedure should be started as soon as it is noticed.

Bleeding

Bleeding is a condition that usually exists in lacquer-type coatings where the first coat is one color and the second coat a different color. If the primer is red and the second coat is gray, and if the coating is brushed or rolled, the red pigment in the first coat may bleed into the second. This is usually less of a problem where the coatings are sprayed.

Bleeding can also occur where a dye has been used as a pigment in one coat, followed by a second coat that has a solvent that will attack the dye and dissolve it. In this case, the dye then bleeds into the second coat, causing discoloration. In the latter case, there have been all types of remedies suggested for a bleeding surface prior to the application of another coat. These include a coat of aluminum pigmented coating, a coat of a material dissolved in alcohol (e.g., shellac), or a coat of a thermoset type coating.

These remedies are usually satisfactory for decorative-type paints. In working with high-performance and corrosion-resistant coatings, such procedures are not recommended since they change the nature of the coating system and may cause failure after a period of time. Such pigment types usually are not used in corrosion-resistant coatings, and therefore there is a limited chance of it occurring. On the other hand, vinyls and chlorinated rubbers are standard for corrosion-resistant coatings and the first situation mentioned can easily occur.

In order to overcome the problem, spraying of the second coat is recommended. A light film should be applied so that the solvent in the second coat does not have time to partially dissolve into the first coat and allow the pigment to bleed through to the surface. Once the light second coat is applied, and is dry, a full coat can then be applied over the surface, usually without additional difficulty.

Dirt in the Film

The problem of dirt in the film is not at all uncommon. Applicators have actually been known to coat over a pile of sand on a deck. This is strictly the result of a lack of attention, care, and good application procedures. Dirt and contamination is a problem in many corners and in side angles, and extra care needs to be taken to remove the dirt and contamination before the coating is applied (Figure 10.66). If the coating is applied over such contamination, rapid corrosion may occur since the coating will not be continuous. Where such contamination is overcoated and the coating dried, the area should be scraped and sanded smooth prior to applying additional coats.

Lifting of Previous Coatings

The lifting of previous coatings usually occurs during coating repair and where one coating is applied over a previously dried coating. The previous coating may be corroded or damaged, and if a coating of a different type is applied (particularly one that has a rather strong solvent base), it may swell the previous coating around the break and cause it to lift and curl. The application of a coating with a strong solvent over an oil-based material is often the cause of this difficulty. In this case, the second coat should be thoroughly compatible with the first so that swelling does not occur. The coating with the strong solvent usually causes the undercoating to swell and curl. This also can occur where the first coating is the same as the repair coat. In this case, solvents in the repair coat soften the first coat, causing it to swell and lift from the surface.

The answer to these situations is to thoroughly sand the coating smooth around the damaged area, feathering the broken edge sufficiently far from the damaged area so that the coating adhesion is sound. Apply a thin coating so that it can dry quickly. This can be

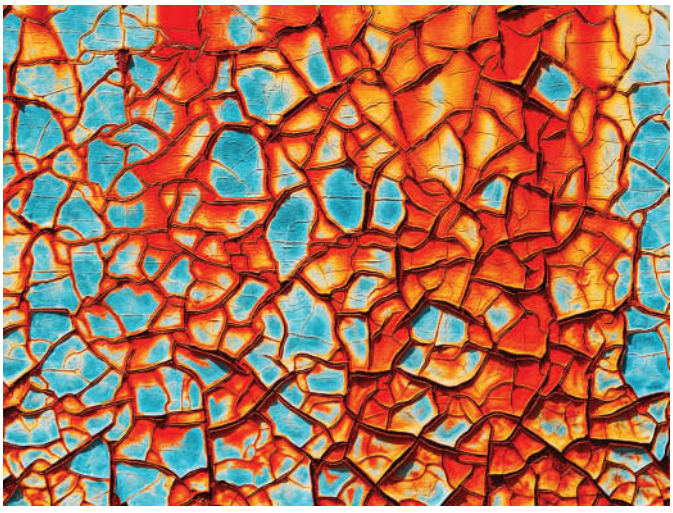


FIGURE 10.67: Mud cracking of a coating. Photo: Thinkstock.

followed by several other thin coats, each well dried before another is applied, to build up the required thickness. Thick coats can cause the undercoat to wrinkle and swell and generally lose adhesion to the surface,

There also is a possible related reaction. When one coat is applied over another after a considerable period of time (months or years), there may be a tendency for the first coat to lose adhesion, although not to the extent of swelling, wrinkling, or peeling from the surface. Nevertheless, the adhesion is weakened, and, if used for immersion or in a critical corrosion service, blistering or other failure can occur. This often happens in repair areas and where an overall refresher coat is applied. Under immersion conditions, the area surrounding the repair often fails due to the loss of adhesion of the initial coating. This has occurred when vinyl and other water immersion coatings have been repaired. It is related to the effect of the solvent in the latest coat on the original material. Some swelling and softening will undoubtedly occur, causing a physical strain on the original bond. This causes some degree of adhesion re- lease of the original coating, which later results in coating failure.

Not all coatings are affected in this manner. Oil-based coatings, alkyds, and so on, are less affected since they are strongly cross-linked and their solvents are very mild. High-performance coatings, however, particularly when used for immersion or when constantly wet, can react in this manner. When high-performance coatings are to be repaired and have been used for immersion, it is best to test the adhesion of the original coating before and after it is overcoated. A small patch is usually enough to determine any adhesion change. If there is some change for the worse, it may be more cost-effective to remove all of the old coating and start anew, than to repair and risk an additional failure.

Mud Cracking

Mud cracking is a problem that is more common with IOZ coatings than with organic coatings. On the other hand, it does occur with water-based coatings that have a high pigment loading. Mud cracking is usually the result of the coating being applied too heavily so that, as the coating dries, it shrinks sufficiently to cause the coating to crack (Figure 10.67). This generally occurs where there is a high pigment loading in the coating or where there is a rapid drying of the coating in addition to its being applied in a thick film. The usual answer to the problem is to apply the coating under less rapid drying conditions and in thinner coats, allowing the thin coats to dry before applying an additional coat.

Cost of Application

Since the beginning of their widespread use in the 1930s, there has been continuing discussion on the cost of the application of high-performance coatings. All kinds of analyses have been made to justify the cost of high-performance coatings, and, under almost all conditions, the analyses have indicated that high-performance coatings will do the job, last longer, and be more economical than conventional coatings under corrosive conditions. Nevertheless, in the context of this book, it is difficult to establish any specific costs for application, since every application has its unique problems and requirements. No two applications of protective coatings are the same, unless they are being applied to a piece of equipment on a production-line basis. In general, anticorrosive coatings or maintenance coatings are specific for the particular job on which they are being applied. The exterior of a tank, for example, is a large, broad, generally flat area and therefore the application costs involved are probably at a minimum. On the other hand, the cost of applying a coating to a structural steel installation would be quite different, due to the many edges, corners, bolts, and other complex areas that require coating. Therefore, there is no rule of thumb as to the application cost on any particular job.

Also, when considering inflation, there is no way of calculating exact costs that would be applicable today and for a few months in the future. Percentages, however, can provide some continuing basis for application costs. Sol T. Sprayer, in an article entitled, Smart Money Painting,5 gives some interesting information from an industry standpoint.

> The chemical industry alone is said to spend more than $600 million a year to fight plant and equipment deterioration resulting from corrosion. On the average, annual painting costs for a chemical plant are said to approximate 0.5% of the capital investment.
>
> Thus, the annual cost of painting a $10 million plant is calculated at around $50,000 per year.
>
> It is interesting to note that the relationship of cost of maintenance painting to capital investment varies with the industry involved. In the heavy chemicals industry, as already noted, the average cost of painting is 0.5% of the capital investment. In the plastics industry it is somewhat lower, 0.42%. The pharmaceutical industry spends the same amount as the plastics industry, whereas the metallurgical industry spends the very low figure of 0.21%.
>
> On the other hand, plants manufacturing organic intermediates spend 0.77% per year of their capital investment for painting, whereas the corresponding figure for the petrochemical industry is 0.62%.[5]

TABLE 10.11: Cost of Three Major Components of a Coating Application.

	IOZ and 2 coats	3-Coat Alkyd	3-Coat Organic High Performance	Average
Surface Preparation	42.6%	40%	49%	44%
Labor	32.0%	46%	33%	36%
Material	25.4%	14%	19%	20%

To be somewhat more specific, Table 10.11 provides some percentage costs of the three major components of a coating application. These figures are derived from three different types of coatings, ranging from a three-coat alkyd to an IOZ coat and two coats of high-performance topcoat. The average of the costs for the three different types of coatings was 44% for surface preparation, 36% for application labor, and 20% for materials. While the figures for each of these three components vary for each coating, as is shown in the table, the average figures are indicative of the range of costs for each one of the items. Figures for lead based paint removal projects would include a significant percentage for containment and debris disposal, which would make the materials percentage even lower.

Probably the most important point in the average is the relatively low cost for the material in an overall application. It only averages 20% for three different coatings shown in Table 10.11. The cost of material, therefore, is small compared with the other costs involved in an application. The importance of this is that even the best coating, or coating system, is still only a fraction of the cost of the surface preparation and application labor. Thus, it should be emphasized that the cost of material is secondary to the other costs involved and that the best possible material is low-cost insurance for the longtime corrosion protection of a valuable structure.

The material cost is even lower when the total cost of the application is considered. These three major components do not include the other miscellaneous items (e.g., scaffolding, cleanup materials, general overhead, and profit) that would be included in an overall contract. When considering the material in relation to the entire cost, it is an even less significant factor than when comparing these three major components of an application.

There are a number of hidden costs in maintenance coatings, which generally do not occur at the time of the application, but are obscured by one, two, three, or more layers of coating and that require time to develop to a point of failure. These are such items as contamination left during surface preparation, exterior contamination of the surface prior to the application of coatings, the character of the underlying surface itself, and imperfections in the application of the coating (e.g., holidays, pinholes, brush marks, or overspray).

These often are not recognized or even a cause of concern until the point of failure is reached. At this time, the solution or elimination of the problem is often much more costly than the original application. For example, if the original application cost is $1/ft2, the repair of a failed coating due to some of the hidden deficiencies could cost $2, $3, $5, or even $10/ft2, depending on the complexity of the structure and its location. Lead paint removal jobs commonly cost from $6 to $12/ft2. The economics of maintenance coatings and their application are, therefore, extremely complex.

While the variables involved are innumerable, they are, however, primarily people-oriented. If an improper coating is selected, if the character of the surface is disregarded, if the design of the structure for corrosion resistance is improper, if the specifications have been written in a vague manner, if the applicator applies the coating to minimum specification, and if the inspection on the overall application job is cursory, it is generally too late for the management of a company to do anything but live with less than the job they paid for. On the other hand, since these variables are all people-oriented, proper management and supervision can overcome many of the costly application problems. This is particularly true when management is aware of the problems and has the help of corrosion engineers who can intelligently recognize and appraise the various factors involved in the application of a coating.

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4. J.D. Keane, W. Wettack, W. Bosch, "Minimum Paint Film Thickness for Economical Protection of Hot Rolled Steel," *J. of Paint Technology* 41, 533 (June 1969).
5. S.T. Sprayer, "Smart Money Paint."

ANNEX 10A

Training and Certification of Application Specialists

Historically, the training and certification of painters (applicators) has been part and parcel of industrial trade organizations and councils. For example, Australia has a four-year trade course to become a tradesman industrial painter. There are similar schemes in other countries. For those countries where such a training and certification scheme is not available, a very good alternative that owners and contractors can use to help them select the best qualified candidates for a particular job or as a permanent contractor employee is the NACE No. 13/SSPC-ACS 1 Applicator Certification Standard No. 1.

The following information has been excerpted from this standard to illustrate the value of such a training and certification program. Any current NACE or SSPC member can download the program without charge. Nonmembers can download it for a fee.

Applicable parts of this Standard are:

- General
- Definitions
- Body of Knowledge
- Qualification Levels for Application Specialists
- Requirements for Each Qualification level
- Examination Requirements for Level II Core and Specialty Qualifications
- Certification Program Requirements
- Requirements for Maintaining Qualifications

The appendix Sections to this standard contain the mandatory "Body of Knowledge," the mandatory "Knowledge and Skills Requirement," and a "Non-Mandatory Skills Assessment Program."

Section 3 contains the core areas of the Body of Knowledge:

1 Environmental, safety, and health;
2 Process control: specifications, codes and standards, quality assurance, and quality control;
3. Materials: consumables; surface preparation materials; coating materials; material properties, characteristics, and use; material safety data sheets (MSDS);
4 Surface preparation: the purpose of surface preparation, chemical cleaning, hand and power tools, waterjetting (WJ), abrasive blasting, surface preparation standards, environmental controls, substrate repairs, and surface contaminants; and
5 Application: storage, mixing, environmental conditions and controls, conventional spray, airless spray, thermal spray, trowel, brush, roller, tapes, heat shrinkable coatings, powder coatings, plural component spray, curing, recoat and overcoat, defects, and repairs.

The specialty areas of the Body of Knowledge include:

1 Installation of polymer coatings and linings on concrete floors and secondary containment;
2 High-pressure water cleaning (HPWC) and ultrahigh-pressure waterjetting (UHPWJ);
3 Electrostatic spray;
4 Plural-component spray;
5 Powder coatings;
6 Specialty pipeline coatings; and
7 Thermal spray coatings.

Section 4 of this standard sets forth requirements for three basic qualification levels—Level I, Level II, and Level III—for an Application Specialist. In addition, requirements are set forth to attain specialty qualifications for Level II.

Level I qualification is intended for entry-level Application Specialists. Level I Application Specialists customarily work with and under the supervision of Level II and Level III Application Specialists.

Level II qualification is intended for experienced Application Specialists able to work independently.

Level III qualification is intended for Application Specialists responsible for planning, oversight, evaluation, and supervision of industrial coating and lining of complex industrial structures.

Section 5 of this standard contains the Requirements for each Qualification Level.

5.1 Application Specialist Qualification Requirements—Level I
- 5.1.1 Successful completion of a skills assessment program measuring essential employability skills: text reading, document use, and numeracy (see Appendix C);
- 5.1.2 Successful completion of examinations and skills test on the Body of Knowledge (see Appendix A); and
- 5.1.3 Successful demonstration of the ability to read, write, and communicate in the language of the workplace location (e.g., English in the United States, United Kingdom, and Canada; French in Quebec; Spanish in Mexico).

5.2 Application Specialist Qualification Requirements—Level II
- 5.2.1 Successful completion of all Level I requirements;
- 5.2.2 Qualify to take Level II examinations by one of the following methods:
  - 5.2.2.1 Successful completion of a three-year apprenticeship program that includes a minimum of 3,000 hours of verifiable work experience and a minimum of 450 hours of coating-related technical training (training to be dispersed evenly throughout the experience phase); or
  - 5.2.2.2 Five years (minimum) of related work experience that includes a minimum of 5,000 hours of verifiable work experience and a minimum of 450 hours of coating-related technical training (training to be dispersed evenly throughout the experience phase); or
  - 5.3.1.2 Five years (minimum) of verifiable work experience in inspection or supervision of coating related work for complex industrial structures after completion of the requirements included in Paragraph 5.2.2; and
- 5.3.2 Successful completion of Level III examination.

Section 6 of this standard contains the requirements for both written and practical examinations on such subjects as Coating of Concrete, High Pressure Water Cleaning (HPWC), Ultra High Pressure Water Jetting (UHPWJ), Electrostatic Spray, Plural Component Spray, Powder Coatings, Specialty Pipeline Coatings, and Thermal Spray Coatings.

Section 7 of this standard contains the Certification Program Requirements:

7.1 Certification programs operated under this standard shall be developed and operated in accordance with ISO(2) 17024.[1]

7.2 Certification examinations shall be based on the competency requirements in the Body of Knowledge for the qualification level that the candidate is striving to achieve.

7.3 Practical examinations for Level II shall require the candidate to prepare and coat a test panel or test apparatus that mimics the efforts required to prepare and coat complex industrial structures. The examination and test panel or test apparatus shall test the candidate on his/her ability to:
- 7.3.1 Plan steps and procedures;
- 7.3.2 Set up and start abrasive blasting equipment;
- 7.3.3 Abrasive blast the test panel or test apparatus to a specific level of cleanliness and surface profile;
- 7.3.4 Inspect, assess, measure, and document the specified surface preparation;
- 7.3.5 Mix and thin liquid coating materials;
- 7.3.6 Set up and start coating application equipment;
- 7.3.7 Set up and start spray, brush, or roller application, as appropriate;
- 7.3.8 Brush, roll, and/or spray coat the test panel or test apparatus;
- 7.3.9 Inspect, assess, measure, and document the coating application (each coat and total coating system); and
- 7.3.10 Clean up and dispose of waste.

7.4 The test panel shall be in accordance with ASTM(3) D4228[2] or appropriate equivalent.

7.5 The coating systems shall be specified at the time of testing. A variety of coating materials, surface preparation methods, and means of application shall be used to test the candidate's ability to handle various types of coatings and their surface preparation and application issues.

7.6 Inspection and documentation of surface preparation and coating application shall be in accordance with ASTM D5161.[3]

Section 8 of this standard contains the Requirements for Maintaining Qualification:

8.1 Qualifications shall be valid for no more than three years. Qualifications shall be maintained by one of the following methods:
- 8.1.1 Successful completion of a minimum of 40 hours per year of training; or
- 8.1.2 Successful completion of the qualification examination(s) for the qualification level (core or specialty) being maintained.

References

1. ISO 17024—ISO/IEC 17024 (latest revision), "Conformity assessment—General requirements for bodies operating certification of persons" (Geneva, Switzerland: ISO).
2. ASTM D4228 (latest revision), "Standard Practice for Qualification of Coating Applicators for Application of Coatings to Steel Surfaces" (West Conshohocken, PA: ASTM).
3. ASTM D5161, "Standard Guide for Specifying Inspection Requirements for Coatings and Lining Work (Metal Substrates)" (West Conshohocken, PA: ASTM).

11 Coatings for Concrete

Introduction

Concrete may provide the largest surface area of all construction materials. While major emphasis has been placed on the use of steel as a surface for corrosion-resistant coatings, it is believed that the total area of concrete surfaces is even greater, although there is a substantial portion of concrete surfaces that do not require coatings. Concrete in itself is considered a corrosion-resistant substance and is often applied over steel to prevent its corrosion. In fact, where concrete is well placed and dense, it is one of the best corrosion-resistant coatings available for steel. It provides a thick, dense, water-resistant barrier, as well as creating an inhibitive atmosphere that retards steel from corroding.

Most of the major water lines around the world are either reinforced concrete, cast iron, or steel-lined with a cement mortar coating. This concrete coating has maintained its properties and prevented steel from corroding under water pipe operating conditions for up to 100 years. There are few other coatings that can make an equivalent claim. Concrete provides the best protection when exposed to fresh water and to the atmosphere. Unfortunately, because of its reactive characteristics, concrete requires protection from many common conditions found in industrial and marine areas throughout the world. Thus, coatings are needed to provide this protection.

Concrete has been in use in one form or another since the time of the Romans, some 2,000 years ago. Some of the aqueducts of this ancient period are still in use. Many concrete structures that are hundreds of years old include dams, canals, buildings, wharfs, and bridges. This type of durability is one reason for its wide range. The following are some of the properties that lend concrete its durability.

Properties of Concrete

Concrete is inorganic and therefore essentially a rock. Very few organisms, such as fungi or bacteria, attack it as they do organic materials. It does not "rot," in the common sense of the term. It is generally unaffected by sunlight, weather, moisture, dryness, or other similar conditions.

Concrete is also hard and does not wear away easily. Its abrasion resistance is determined by the aggregate used. The use of hard, durable granitic aggregate makes it very abrasion resistant, even though hydrated cement alone is not a highly abrasion-resistant material.

Concrete has good compressive strength, which is its most outstanding property. Few normally occurring conditions, except earthquakes, can cause it to fail in compression.

Concrete also improves with age. Crystallization takes place under water over a long period, thus increasing its hardness and compressive strength. In many cases, such crystallization will actually heal minor cracks in a concrete structure. Since concrete originally contains considerable lime, it reacts with carbon dioxide (CO_2) from the air to form calcium carbonate ($CaCO_3$) or limestone. This also increases its hardness and compressive strength.

Concrete has proven a durable building material under most common environmental conditions. However, it also is a very reactive material to many chemical exposures, primarily acidic ones. Even pure flowing water will dissolve concrete under certain conditions. Thus, many concrete deionized water tanks have been lined to prevent water contamination by calcium or other ions.

Composition of Concrete

In order to better understand the requirements for a coating used for concrete, the basic chemical composition of cement should be discussed. Portland cement consists principally of tricalcium silicate ($3CaO{\cdot}SiO_2$) and beta dicalcium silicate (B-$2CaO{\cdot}SiO_2$), together with lesser and variable quantities of tricalcium aluminate ($3CaO{\cdot}Al_2O_2$), tetracalcium alumino ferrite ($4CaO{\cdot}Al_2O_3{\cdot}Fe_2O$), or some solid solution of the iron phase, periclase (MgO), free lime (CaO), and trace amounts of many other compounds.1

To produce concrete from Portland cement, hydration is required. The chemical reactions that result in the formation of the hard, durable concrete surfaces are shown in Table 11.1. The structural strength of concrete depends on the conversion of the anhydrous calcium silicates to hydrated calcium silicates, as shown in the table. It will be noted in the hydration reaction of dicalcium and tricalcium silicates that a sizable amount of lime is formed, up to as much as 20% of the hydrated product. It is largely this lime content that gives rise to the high alkalinity in concrete, which can be in the neighborhood of a pH of 13 when concrete is saturated with water.

This high alkalinity provides the corrosion resistance to steel that is coated with concrete. Steel is passivated at an alkalinity of approximately 11.5. Saturated concrete, then, provides a good media for the encapsulation of steel and for maintaining the steel in a corrosion-resistant state as long as chloride salts do not reach the steel. However, this strong alkaline condition can also cause problems with the coatings applied over a concrete surface.

TABLE 11.1: Hydration Reaction of Portland Cement

$$2(3CaO\text{–}SiO_2) + 6\,H_2O \rightarrow 3\,CaO \cdot 2SiO_2 \cdot 3H_2O + 3Ca(OH)_2$$
(Tricalcium Silicate) (Tobermorite Gel) (Lime)

$$2(2CaO \cdot SiO_2) + 4H_2O \rightarrow 3CaO \cdot 2SiO_2 \cdot 3H_2O + Ca(OH)_2$$
(Di Calcium Silicate) (Tobermorite Gel) (Lime)

$$4CaO \cdot Al_2O_3 \cdot Fe_2O3 + 10H_2O + Ca(OH)_2 \rightarrow 6CaO \cdot Al_2O_3 \cdot Fe_2O_3 \cdot 12H_2O$$
(Tetra Calcium Alumino Ferrite) (Calcium Alumino Ferrite Hydrate)

$$3CaO \cdot Al_2O_3 + 12H_2O + Ca(OH)_2 \rightarrow 3CaO \cdot Al_2O_3 \cdot CA(OH)_2 \cdot 12H_2O$$
(Tricalcium Aluminate) (Tetracalcium Aluminate Hydrate)

$$3CaO \cdot Al_2O_3 + 10H_2O + CaSO_4 \cdot 2H_2O \rightarrow 3CaO \cdot Al_2O_3 \cdot CaSO_4 \cdot 12H_2O$$
(Tricalcium Aluminate) (Calcium Mono Sulfo Aluminate)

Source: J.E. Ilaria, *Coatings for Concrete and Other Masonry Substrates*, 12th Annual Liberty Bell Corrosion Course (Philadelphia, PA: 1974).

The hydration of the concrete or cement particles or the curing of concrete can require some period of time. As a matter of fact, cement continues to cure or continues the hydration process for many years. However, it does develop its primary physical properties within 28 days, if the concrete is maintained with the proper moisture content. Twenty-eight days is the time usually used by engineers to indicate that the concrete has cured to its proper physical state. Note that this is the normal ambient temperature and relative humidity required for the concrete to achieve its designed compressive strength and should not be confused with the time required for the concrete to reach a paintable state, which will be explained later in this chapter. The most common method of testing compressive strength of concrete (and indirectly, degree of cure) in the United States is to cast concrete test specimens in the field in accordance with ASTM C31,[2] then cure and crush these specimens in a laboratory in accordance with ASTM C39[3] to determine the compressive strength.

This process may be speeded up to a considerable extent by steam-curing concrete. In this process, the concrete is heated to 140 to 160 °F in a steam atmosphere, which increases the chemical reactions, and in a few hours the cement will be fully hydrated and the concrete will reach its full strength. Many manufactured products, such as cement-asbestos pipe or concrete pipe, have been treated in this manner to speed the curing process. Such treatment is difficult in the field and therefore, seldom used.

The hydration process is one that definitely bears on the ability of concrete to be coated properly. In addition to the air and water pockets that have been discussed in Chapter 9, the cement particles and their curing reactions also create porosity. This is well explained in an article entitled, "Coatings for Concrete and Other Masonry Substrates," by Joseph E. Ilaria.4 His explanation is as follows.

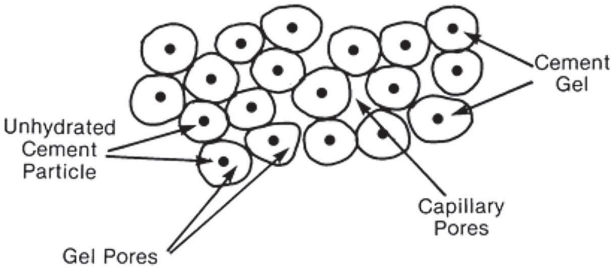


FIGURE 11.1: Physical aspects of cement hydration. Source: J.E. Ilaria, *Coatings for Concrete and Other Masonry Substrates*, 12th Annual Liberty Bell Corrosion Course (Philadelphia, PA: 1974).

The amount of mixing water added is usually at least two times that needed to satisfy the anhydrous cement. However, this excess water is needed especially in poured in-place concrete to make the mix workable and allow it to take the shape of its mold. The excess water evaporates off, in time, giving rise to voids or air spaces within the cement gel.

Figure 11.1 illustrates the physical aspects of cement hydration. The dark centers of the grain are surrounded by cement gel in which the hydrates precipitate. When the excess water evaporates off, there is within the gel, pores known as gel pores. These pores may be of any shape but assuming them to be rectangular slits, their size would be in the 2 × 4 micron range. The excess water between grains, due to its relatively low specific gravity compared to the cement compound (1.0 vs. 2.5), will also have a tendency to migrate, giving rise to channels within the mass. These channels are called capillary hardening pores. Keeping in mind the relative sizes in the cement-hardening process (if we magnified one hydrated particle to one inch, a piece of sand of the same scale would have a 10 foot diameter). You can probably visualize the amount of free void space in a hydrated dry cement product. Absorption measurements on high strength concrete (5-600 lb cement/cubic yard) which is a measure of the % weight of water a pre-dried (212 °F) concrete specimen will hold can vary between 4 and 6% weight which converts to 10-15% by volume.

The total porosity of cementiferous materials depends on the efficiency of the mix (the sand, stone, cement and water), the type product, the method of curing and the use of certain chemical admixtures.[4]

Much of the detail of cement porosity, pinholes, and water and air pockets, as well as the general character of concrete, is covered in Chapter 9 under "Surface Preparation of Concrete." Proper surface preparation is vital to the effectiveness of a coating, and concrete preparation is much more critical than that of steel. While that information will not be reiterated here, reference should be made to Chapter 9 whenever concrete is to be coated in order to develop the best method of preparing the concrete surface. In this chapter's discussions, all concrete surfaces will be assumed to have been properly prepared in accordance with Chapter 9.

There are numerous types of concrete that may be used with coatings. Some of these were cement-asbestos products such as transite board, cement-asbestos shingles, corrugated cement, asbestos roofing or siding, in addition to the more conventional non-reinforced concrete, reinforced concrete, prestressed concrete, gunited concrete, and centrifugally cast concrete. Asbestos can no longer be used as a reinforcing material due to its link to asbestosis in humans. Mineral fibers of various types have been used successfully as a replacement for asbestos fibers. Concretes may be made with all types of aggregate, ranging from river sand to granitic aggregates, limestone aggregates, and various fibrous types of aggregates such as glass and asbestos. Each of the types of concrete and the different aggregate mixes may present a different surface over which a coating is to be applied, which affects the selection of a coating.

Problems in Coating Concrete

There are some physical and chemical properties of concrete that have a direct bearing on coatings. Concrete performs best when under compression, and it has a relatively high compressive strength (i.e., 2,000 to 6,000 psi). In this state, it resists cracking and checking, and the surface does not appreciably change, even with time. This makes a good, constant surface over which to apply coatings. Unfortunately, the opposite property—tensile strength—is low, so that concrete in tension can crack, making the surface difficult to protect. Cracks can occur due to foundation settling, earth movement (as in the joints of concrete pipe), the vibration of machinery, and many other reasons. Whenever concrete changes from a state of compression to one of tension, cracks appear. Concrete is also brittle, which adds to the cracking problem and often causes spalling.

One of the ways in which cracking is reduced is to prestress concrete or place it in permanent compression. Many concrete tanks, both above and below ground, are of a prestress design, which means that the reinforcement is in sufficient tension to maintain the concrete under compression. Cracking, however, is not completely eliminated, as some prestressed cylindrical tanks, which are wound with high tensile wire, may develop a few cracks parallel to the reinforcing wire. Much concrete pressure pipe is also made using a prestressed design. Each of these physical conditions can create coating problems where concrete is used under corrosive conditions.

Moisture Vapor Transmission

As discussed previously, concrete is porous. It also contains a permanent amount of free moisture that can evaporate or be absorbed, depending on the humidity to which the concrete is exposed. Concrete is saturated when immersed in water, while the moisture content goes down when exposed to low humidity and increases rapidly when the humidity rises above 80%. Concrete can be formed in such a way that it will not transmit liquid water; on the other hand, concrete is not impervious to moisture vapor or moisture vapor transfer, as indicated by its change in moisture content due to humidity.

The fact that water, in the form of vapor, can readily pass through the concrete structure is extremely important to any coating that is applied. For example, in a coated concrete vault that is kept at a constant humidity of 50%, if there is no waterproofing on the exterior, and the earth around the vault is damp, there is a constant positive vapor pressure on the concrete side of the coating. Unless the coating has excellent adhesion, blistering and coating failure will occur. This is not an isolated example. Subterranean structures, basements, subways, and electrical vaults all have problems of this sort. The cause is the vapor pressure passing through the concrete and constantly pushing on the back of the coating. This may be the most important problem encountered in obtaining a proper coating over a concrete surface.

It is difficult to apply a coating on the interior of a concrete surface when the exterior is subject to moisture conditions, and to maintain the interior of the structure free of moisture. During World War II, there were literally hundreds of large underground tanks built to contain petroleum products. Most were of a prestressed design to reduce cracking; however, most did not have any exterior water barrier. They were coated on the interior with a petroleum-resistant coating and many coating blistering problems as well as actual leaks developed. The coating was applied to a generally dry surface, while well points kept the groundwater down. Once the well points were removed, it was obvious that the moisture was against the back of the coating. Wherever coatings are to be applied to underground concrete structures, there should be an exterior waterproofing membrane applied. ACI 515.1R-79, "A Guide to the Use of Waterproofing, Dampproofing, Protective and Decorative Barrier Systems for Concrete,"[5] is recommended to anyone faced with preventing moisture vapor transfer through a concrete structure.

The alkalinity of concrete also comes into play under such conditions where the moisture is being transferred from the exterior of a structure to the interior. The alkaline salts within the cement can be brought to the concrete surface where the CaO then reacts with CO_2 in the air to form rather voluminous white crystalline deposits. In many cases, where somewhat porous coatings are applied, these are actually pushed off of the surface by the formation of the calcium salts, which are brought to the cement surface from the interior of the wall. Any time that moisture conditions such as these exist, it is very difficult, without the very best penetration and adhesion, to obtain coatings that will satisfactorily adhere over long periods of time.

In summary, the properties of concrete structures that are made with Portland cement are generally as follows.

1. The compressive strength is relatively high, from 2,000 to 6,000 psi.
2. The product has a relatively low tensile strength, in the neighborhood of 500 psi.
3. The concrete is alkaline, developing a pH of from 12 to 13.
4. Concrete is porous; when dry, its free volume can vary from 10% to 25%.
5. Concrete contains free moisture and holds it within the structure even under severe drying conditions. The amount of free moisture in a cured concrete structure depends on the relative humidity in which the structure exists.
6. A concrete structure can prevent liquid water from transferring through the concrete. On the other hand, concrete is porous to moisture vapor and will transfer moisture vapor through a concrete structure from a side of high humidity to one of lower humidity.

There are a number of other difficulties or problems that are associated with concrete structures, several of which have a direct bearing on the application of coatings to concrete surfaces.

Cracking

One characteristic of concrete is that it may crack in various ways. Cracks are the result of the low tensile strength of concrete, and may be due to the shrinkage of concrete during the curing process.

Shrinkage Cracks

In general, there are two types of cracking. The first is the cracking caused by shrinkage; such cracks are normally found during the initial curing period of the concrete and many of them are only surface cracks. These cracks are not working cracks and are only subject to stress as the concrete is subject to temperature expansion and contraction. Shrinkage cracks, for the most part, can be mended during the surface preparation procedure. Large shrinkage cracks can be filled; small surface shrinkage cracks can be opened sufficiently to allow the coating to penetrate and seal the crack.

Figure 11.2 shows shrinkage cracks in hand-troweled, sidewalk-finished concrete. They are only surface cracks and thus do not

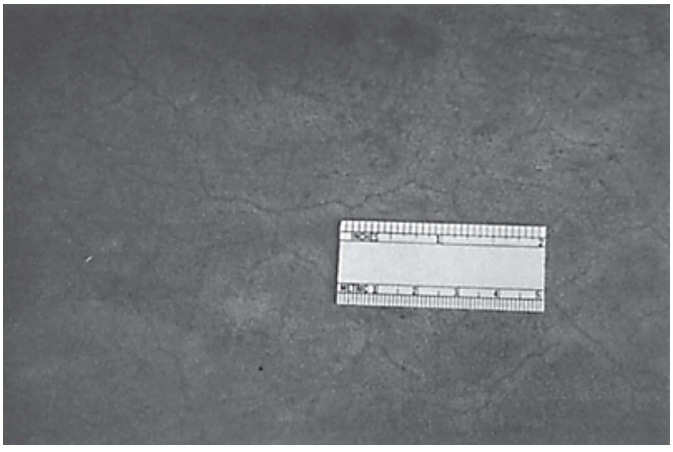


FIGURE 11.2: Typical shrinkage cracks in troweled concrete.

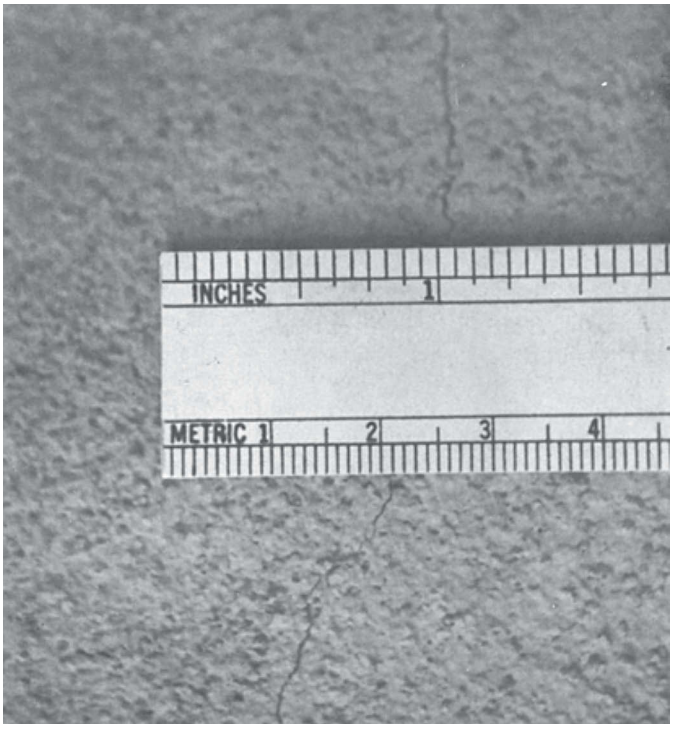


FIGURE 11.3: Shrinkage crack in cement-plastered wall.

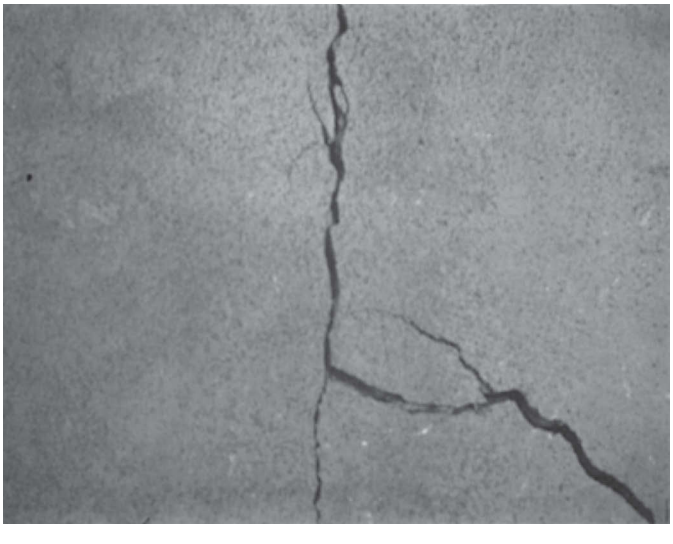


FIGURE 11.4: Typical structural crack in a concrete foundation resulting from earth movement.

penetrate deeply. Nevertheless, they do represent weaknesses in the surface, which can allow water to be absorbed more readily than into a solid surface, and which must be filled during surface preparation or by the coating.

Figure 11.3 is another type of shrinkage crack. Such cracks often form on walls and similar areas that are plastered with cement plaster. Many times such areas require a high-performance coating, and cracks such as this can cause difficulties such as blistering, lack of coating penetration, and so forth. If the coating penetrates readily and fills the crack, the area is usually stronger than without the coating. These usually are not working cracks, and proper filling during surface preparation or coating makes a satisfactory surface. One method of restoring monolithic form to a structure with static shrinkage cracks involves the injection of low-viscosity epoxy resins into the cracks and sealing the tops of the cracks using a two-component epoxy putty.

Structural or Working Cracks

Structural or working cracks are those that form due to movement in the structure, ground movement, earthquakes, and similar causes. They can appear at almost any time during the life of the structure. Such cracks often take place in areas where the structure changes direction, such as on inside corners. They may also be diagonal across a structure wall due to a slight shift in the foundation. Such cracks are working cracks, which means that as the structure moves, the cracks expand and contract.

Figure 11.4 shows a structural crack in a concrete foundation due to ground movement. It is a working crack and thus moves periodically. Structural (working) cracks usually are much wider and longer than shrinkage cracks, and spalled concrete may exist along the crack proper, as is the case in Figure 11.4.

If a coating has been applied over a structure where a working crack develops, this will crack the coating and will cause corrosion or other difficulties at that spot. Once these cracks have developed, it is difficult to seal them with coating since they periodically move. When this takes place, the coating will tend to crack along with the structure.

Engineers often talk about coatings that will bridge cracks, and many kinds of highly flexible and extensible materials have been tried. Generally, however, there are few materials that adhere tightly enough to concrete to bridge a working crack. The reason for this is that when the coating is applied over the surface of the structure and cracking occurs, there is infinite expansion at the crack almost irrespective of the size of the crack. The crack starts from a point of zero and then expands to $1/32$, $1/8$, $1/16$ in or more. Even in a $1/32$-in crack, the stress applied on the coating at the pint of the crack is much more than the tensile strength and extensibility of most materials (Figure 11.5).

One procedure used to repair cracks is to vee them out and fill the "V" with additional mortar or similar materials. If this is a working crack, sooner or later the area will crack again, and if coated over, will crack the coating as well.

There are some coatings that have a better chance than others of bridging very small cracks. These are coatings with appreciable thickness, usually 20 to 40 mils or more, as well as some extensibility. In this case, the stress is spread over the total thickness of the coating, which allows the coating closest to the surface to be subject to considerably less stress. Heavy rubber linings $1/8$ in or so in thickness, which are tightly adherent to the surface, can accommodate some cracking. On the other hand, because of the stress put into the coating across the crack, it is a weak area in the coating film, and while it may not crack immediately, it can do so on aging.

Another procedure is the use of a fairly heavy extensible primer, followed by a strong, tough coating. When cracking, the major stress is accepted by the rubbery primer and is not transmit-

ted to the stronger topcoat (Figure 11.6). It must be stressed, however, that such coatings can only bridge small, narrow cracks or checks and not cracks of any major proportion.

Another method of repairing structural cracks involves saw-cutting the crack into an expansion joint, then placing a polyethylene foam backer rod into the expansion joint, followed by placement of an elastomeric joint material up to the level of the coated surface. A polyethylene tape is then placed directly over the joint material followed by a rubber strip, which extends beyond the polyethylene tape. The protective coating system is then bridged over the entire joint system.

From the previous examples, it becomes obvious that thin coatings are not satisfactory to bridge cracks. This is only possible through use of thick coatings and then only for small, so-called "hair" cracks. Coatings to bridge cracks are largely a myth where even mild corrosive environments exist.

Cracking of concrete is a serious problem and one that can cause severe corrosion to either the concrete or to the reinforcing within the concrete. A tightly adherent coating does not provide complete protection. Only a material that will spread the strain over a considerable area is practical.

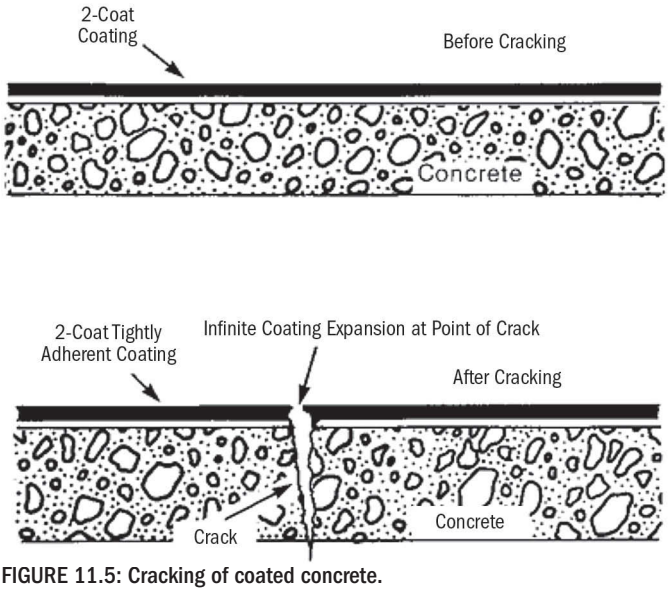


FIGURE 11.5: Cracking of coated concrete.

One type of lining material has been designed to resist strong corrosive solutions and to overcome possible cracking problems in a concrete structure. This is a plasticized PVC sheet that has "T" extensions on the back. The sheet is placed on the concrete form with the T extensions facing into the concrete. The concrete is then cast around the T's as the plastic sheet is held against the concrete form. In this case, the T's are spaced at 50-mm (2-in) to 63-mm (2.5-in) intervals and there is no adhesive holding the sheet tightly against the concrete surface. The principle of this lining material is shown in Figure 11.7. Newer materials include polyethylene sheets with similar protruding extensions on the concrete side of the sheet.

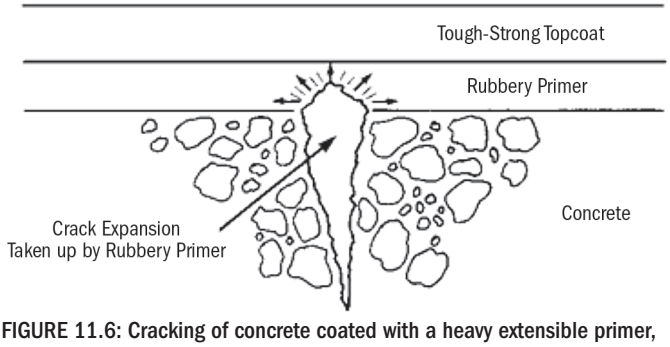


FIGURE 11.6: Cracking of concrete coated with a heavy extensible primer, followed by a strong topcoat.

Should a crack occur; the sheet lining is only tied down at intervals and is free from the surface of the concrete in between the intervals. This allows the extension of the concrete at the crack to be taken up by the 63 mm (2.5 in.) of sheet between the tees. This places little strain on the lining and it remains intact over the cracked area. This type of lining has been in service for 40 to 45 years in many highly corrosive areas such as sewers, copper leaching tanks, and ferric chloride tanks, without any break due to cracks in the concrete structure.

For protection of existing concrete structures, both PVC and polyethylene sheets can be adhered to the concrete by specially formulated mastic adhesives.

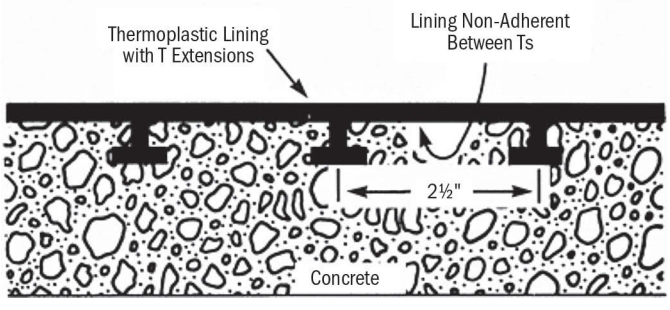


FIGURE 11.7: A cast-in-place lining for concrete structures.

An engineering design made to overcome thermal expansion and contraction and shrinkage cracking is the use of expansion joints. Expansion joints have proven to be satisfactory under many conditions. However, where there is concrete movement, cracking between expansion joints can also take place. From a coating standpoint, there are also many problems in making expansion joints completely corrosion-free, so that each installation requires an individual solution.

Alkalinity

The alkalinity of concrete is an inherent problem, particularly where coatings are concerned. Any coating that is not thoroughly alkali-resistant will eventually break down and be destroyed by the alkali content in the concrete. There is a substantial amount of alkali in concrete, which is particularly available whenever moisture is present. When a coating is applied over the surface of concrete, it seals the surface to the internal moisture, and a pH of 12 to 13 is available at the moist concrete/coating interface.

One action of the alkalinity in concrete has already been mentioned (i.e., the formation of efflorescence or a white crystalline deposit on the concrete). This is caused by the moisture passing through the concrete, and carrying the soluble concrete salts with it to the surface. The moisture evaporates, leaving the alkaline salts (primarily calcium hydroxide [$Ca(OH)_2$]) on the surface. This reacts with CO_2 from the air, creating a fluffy, white crystalline deposit on the concrete surface.

When coatings are somewhat porous to moisture or porous to CO_2, this reaction can take place underneath the coating, causing it to blister, with the white, crystalline deposit pushing the coating off the surface. At the same time, some of the concrete surface may also be softened and destroyed by the crystal action. This is not an isolated problem, but takes place wherever there is a source of moisture in the concrete, such as ground water, or moisture coming from cracks, waterproofing, flashing, and similar structural areas.



FIGURE 11.8: Moisture-developed efflorescence, g causing damage to both the concrete and the coating.

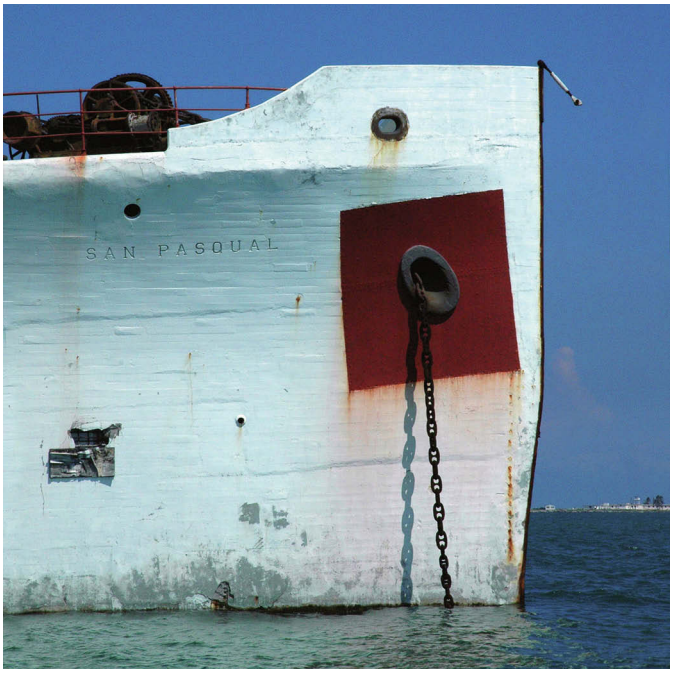


FIGURE 11.9: The vinyl coating applied to the hull of this concrete ship has protected the surface from salt penetration for over 25 years.

Figure 11.8 demonstrates the formation of the white salts underneath a coating applied over a concrete block building. In this case, the moisture was coming from a crack in the roofing of the building, getting into the concrete block, and coming to the surface in the area shown.

The alkalinity in concrete is also a primary cause for the chemical activity of concrete. Being highly alkaline, it is subject to attack by any material that is even slightly acidic. In the case of a material like hydrochloric acid (HCl), the calcium salts and hydration products that make up the concrete are attacked and become soluble. These can easily be washed away, leaving the aggregate without any binder.

In the case of sulfuric acid (H_2SO_4) attack, such as would be the case in a chemical plant, a concrete sewer outfall, or a sewage treatment plant, the acid again attacks the calcium products in the concrete, creating calcium sulfate ($CaSO_4$). The $CaSO_4$ is not soluble like the calcium chloride ($CaCl_2$); however, its volume is several times that of the original hydrated cement. As the reaction takes place, the $CaSO_4$ increases in volume. It is a soft product, but because of the expansion in volume, it tends to spall and break the concrete. It pushes off the coatings, and in sewers, the expansion has been strong enough to push cast-in-place, tile lining off the surface, and crack the tile lining. In this case, it is a combination of both a chemical and a strong physical attack. Even very slightly acidic products, such as pure water, will attack the calcium compounds in concrete and dissolve them. Concrete flumes bringing pure snow water from the mountains have been found corroded to a depth of an inch or more, purely by the solvent action of the snow water.

Concrete, in spite of its durability to ordinary atmospheric conditions, is a reactive material to many chemical products. This must be taken into consideration when coatings are selected for concrete surfaces.

Freezing and Thawing

The moisture content within concrete can be responsible for a catastrophic concrete failure where concrete is subject to freezing and thawing. During the freezing cycle, the ice that is formed from the moisture in the concrete expands approximately 10%, causing a tremendous physical pressure within the concrete. Because of the relatively low tensile strength of the concrete, it cracks and spalls. This is a major problem with all types of concrete structures that are located within areas where freezing weather can occur. The structures subject to such damage are bridges, buildings, foundations, concrete pipelines, highways, sidewalks, and similar areas. One of the answers to this problem is a proper coating (i.e., one that will seal the concrete against absorption of moisture from the surface and keep the humidity within the concrete as low as possible).

Porosity and Soluble Salts

Concrete is porous to moisture, various gases, and chemical products. Some of these are the various soluble chloride salts. These occur in seawater, in deicing salts, and wherever the concrete might be subject to sodium chloride (NaCl). NaCl and $CaCl_2$, which are the two common soluble chloride salts, are very soluble in water and can be carried into the concrete by the water on the surface and the moisture within the concrete itself.

These salts do not necessarily leave, but are held within the concrete. When the concrete dries, the salts form crystals and spalling of the concrete can occur. When the concrete is re-exposed to moisture, the salts redissolve and then recrystallize on drying, thus starting the disintegration all over again. This cycle of dissolving and recrystalling can be quite damaging to concrete and is a common phenomenon on concrete highways and bridges where deicing salts are used. The problem is also common in chemical plants and is quite prevalent in areas where concrete piers are used to cross salt marshes. The concrete spalls readily and rapidly at the marsh-concrete interface.

The sealing of concrete surfaces against salt penetration is not as easy as it appears. It requires a careful and uniform application of a coating, usually of some thickness, in order to prevent pinholes or imperfections from allowing the salt to penetrate and crystallize. Many different kinds of coatings have been used to prevent such ionic penetration, from the vinyls, epoxy, coal tar epoxy and coal tar cutbacks, elastomeric polyurethanes, elastomeric polyureas, and acrylics.

Corrosion of Steel in Concrete

More of a problem than crystallizing and spalling, is the problem of chloride and sulfate ions and oxygen reaching the reinforcing within reinforced concrete structures and setting up a corrosion cell. When this occurs, the steel corrodes, forming a voluminous rust

scale, which expands several times over the original steel volume. With the relatively low tensile strength of the concrete, this expansion creates internal pressure, rupturing the concrete at the point of the salt penetration.

Some such rupturing can be seen in Figure 11.9 on the upper area of the bow where the original wooden bumper was located (part of the bumper still hangs on the surface). The concrete in these concrete ships was extremely dense and very heavily reinforced. The concrete was a minimum depth over the reinforcing, so that any salt penetration would have caused extensive damage.

A similar problem is shown in Figure 11.10 where a reinforced concrete pipe was located in a difficult soil condition. After 15 years, there was sufficient ion and oxygen penetration to set up a corrosion cell, as shown. The concrete over the reinforcing broke away because of the internal pressure of the iron oxide formed due to the corrosion cell.



FIGURE 11.10: Corrosion of reinforcing in a concrete pipe subject to corrosive soil conditions.

The more porous the concrete, the more readily this reaction takes place. This is particularly damaging to concrete used for pipe, piling, roadways, bridges, and similar structures. The action of chloride salts combined with freeze-thaw conditions, create a serious, continuing problem with any concrete structure.

As indicated in the previous section, coatings placed on concrete subject to salt crystallization can help eliminate the corrosion problems of concrete coated steel or reinforced concrete. Coatings can prevent chloride and other ions from penetrating into concrete of high porosity. Coatings, however, cannot prevent chlorides from penetrating into exposed, cracked areas of the concrete. Cracks make easy access both to water and to the chlorides, creating substantial corrosion problems.

Reactive Aggregates

In certain areas, there are concrete aggregates that react with the moisture and alkali in the concrete to cause disruption of the concrete. Normally, the total aggregate is not reactive, since aggregates are usually closely examined for incorporation into a concrete structure. On the other hand, pieces of the reactive aggregate can get into the structure, and areas have been seen where the aggregate has expanded, spalling the concrete, and rising above the surface between ¼ and ½ in. The expanded aggregate actually extended beyond the concrete surface by that amount.

The possibility of reactive aggregate should be kept in mind wherever there is a critical concrete structure to be coated. The aggregate should be thoroughly examined prior to use in the structure. There is little that can be done if reactive aggregate is present, except to physically remove the aggregate and to repair the concrete in the area. Such aggregate will push coatings off of the concrete wherever the reaction occurs.

Properties Required for Coatings Used on Concrete

There are a number of properties needed by a coating to be effective on a concrete surface. The following are some of the most pertinent.

Coating Penetration of Concrete

The surface preparation of concrete surfaces has been well covered in Chapter 9, and the general application of coatings has been covered in Chapter 10. While these subjects need not be reiterated in this chapter, there is one point worth covering. An area where concrete is quite different from steel is in the penetration of the concrete surface by the coating. When applying a coating to concrete, penetration of the surface is extremely important for the best adhesion and for the best resistance and life of the coating.

Penetration is to concrete what surface profile is to steel. In both cases, maximum adhesion is the goal. Coatings that penetrate concrete have much improved adhesion and increased longtime performance as compared with those that remain on the surface and rely on adhesion alone. One good example of this is the penetration of some liquid epoxy coatings into a well-prepared troweled concrete surface. There are instances where the resin has penetrated as much as 1/4 in below the concrete surface. This not only makes for maximum adhesion, but increases the density of the concrete surface as well. Not all epoxy coatings will do this. Those based on higher molecular weight solid resins will only penetrate as far as the solvent will carry the resin into the surface. While this penetration is very limited, the less viscous the coating, the greater the penetration.

Penetration is limited by the molecular size of the resin. Some liquid epoxies have a sufficiently low molecular weight and an excellent concrete wetting characteristic so that in-depth penetration is achieved. This penetration is also aided by highly wetting solvents. In this case, the epoxy actually impregnates the surface and then reacts to a solid, making the penetrated area much stronger than the remainder of the concrete. If the concrete is shattered, the penetrated area will usually remain with the coating.

Figure 11.11 is a photo of a cross section of concrete with a liquid epoxy primer (unpigmented) applied to the surface. Note in this case that the primer has primarily penetrated into the concrete, with little of the primer remaining on the surface. The concrete was sawed to provide the cross section. The sawn surface was etched with acid to bring out the depth of penetration of the primer. The penetration in this case was approximately 3 mm (1/8 in). Both halves of the concrete are shown in the figure; the upper half has not been acid etched and the lower half has been etched. The penetration can be seen in both sections; however, it is more obvious on the lower section.

It is this penetration principle that has been used for many of the epoxy coatings that have been developed especially for concrete. Many of both the spray-applied coatings and the trowel-applied coatings, heavy-bodied coatings for nuclear power plant reactor areas have been designed to penetrate, and have thus reduced to a minimum blistering due to deionized water immersion and design basic

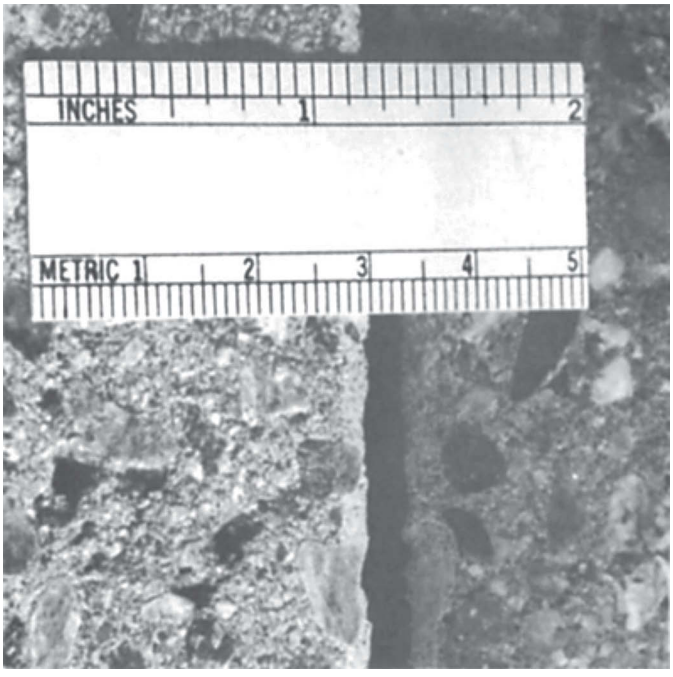


FIGURE 11.11: A concrete surface penetrated by an epoxy primer.

accident (DBA) testing. The DBA test is a combination of steam, high-temperature, pressure, and vacuum and is a very difficult test of coating adhesion.6 Coatings with a strong penetrating quality perform best under such test conditions and on continuous immersion.

Vinyl coatings were the first of the high-performance coatings for concrete, and penetration of the vinyl polymer was the initial method of obtaining adequate adhesion. Vinyl coatings are good concrete coatings because of their chemical properties, and a small penetration can be obtained by applying the vinyl primer as a very dilute solution. On a well-etched concrete surface, the dilute primer will penetrate to some degree (not nearly to the extent of a liquid epoxy) and will improve the vinyl coating adhesion to a marked degree.

Other types of generic types of penetrating coatings with specialty uses over concrete are acrylics, silanes, silicones, siloxanes, silicates, methyl methacrylates, chlorinated rubbers, asphalt emulsions, and polyurethanes.

The surface of concrete that is best for penetration is a surface that has been either abrasive or water blasted, or acid etched to a fine sandpaper finish. In this case, all of the concrete laitance is removed from the surface, thus allowing for maximum wetting and maximum penetration of the coating into the concrete. All of the small hair cracks, checks, and pores are opened by this surface preparation, and there is usually easy penetration of the coating into these areas. Following the penetrating coat (primer), the surface should be fully sealed by the application of additional coats.

A recommended application procedure for almost any coating on concrete is to dilute the first coat and apply a very wet film. The coating should not run or curtain, but should be as heavy as possible, short of running, to allow the liquid to penetrate the surface. The application can be by brush, roller, or spray, as long as a sufficient amount of the liquid coating is applied and allowed to penetrate.

Penetration of the concrete surface provides physical adhesion while the reactive sites on metal substrates provide chemical or polar adhesion. In both cases, substantial improvement in adhesion results.

Low Molecular Weight

Low molecular weight is an extremely important property of any coating that must be highly penetrating. The molecular size of the resin molecules should be sufficiently low so that there is easy penetration between sand grains and cement pores, as well as into the various minor cracks, checks, and openings in a concrete surface. This allows the coating to penetrate as deeply as possible beneath the concrete surface.

There are many low molecular weight materials. Many of the oils have a relatively low molecular weight and are very penetrating. On the other hand, the oils are soon turned to soap because of the high alkalinity of the concrete, and therefore, they are not satisfactory for this purpose. Many low molecular weight materials also remain liquid and therefore cannot develop into a strong binder. Some of the vinyl and chlorinated rubber coatings contain relatively low molecular weight additive resins, which aid in the penetration of concrete surfaces and help to bind the higher molecular weight vinyl and chlorinated molecules into the surface. Polyester resins can begin as low molecular weight materials and solidify on curing. On the other hand, these materials are subject to attack by alkali, and, while more resistant than the drying oils, would still be somewhat questionable where strong corrosion-resistant surfaces are required.

Of all the materials that fit this category, the catalyzed liquid epoxies are undoubtedly the most effective. Even with the epoxies, there are materials with lower molecular weight and greater penetrating power than others. The liquid epoxy resins combined with liquid curing agents and strongly penetrating solvents provide the best answer. Newer epoxy primers and sealers utilize very low viscosity resins without any pigmentation to achieve penetration with essentially 100% solids epoxies.

Wetting the Surface

In many ways, the property of wetting goes along with the low molecular weight. Generally, most low molecular weight materials will also wet the concrete surface well and will penetrate. To properly wet a surface, the coating should not bead or stand up on the surface, but should readily flow out over the surface, spreading itself. If a drop is applied to the concrete surface, the drop should spread out over the surface without any additional physical effort required. Many solvents aid in this. It is preferable to use somewhat slower evaporating solvents rather than fast drying materials to develop the maximum wetting of the concrete surface. The liquid epoxy coatings, because of their excellent compatibility with cement and their resistance to alkali, wet concrete surfaces very well.

Alkali Resistance

Any coating that is to be applied over a concrete surface must have good chemical resistance, particularly on the alkaline side. With a possible pH of 12 to 13, any tendency to react with alkali will create a deficiency in the adhesion of the coating. In many cases, lack of alkali resistance can go beyond adhesion to the point of actually saponifying the coating and causing it to disintegrate.

The two best known alkali-resistant coatings are those based on vinyl and epoxy resins, and both make good coatings for concrete. The vinyl coatings have broader weather and general chemical resistance than the epoxies, while the epoxies have the properties of penetration and wetting, which gives them maximum adhesion.

Increased Density of the Surface

Increased density is a result of the penetration and wetting of the coating. There is only one coating type that really improves the density of a concrete surface, and that is the catalyzed liquid epoxy coating. Even without over coating, the penetration of the liquid resin can flow into checks, cracks, and between sand grains and increase the density to a point where there is little water absorption or chemical activity. Figure 11.11 demonstrates this property, showing the depth of the penetration into the concrete porosity on the surface. This not only improves the adhesion of whatever coatings are applied over the top, but it increases the resistance of the surface to both chemical and physical attack as well.

Appreciable Thickness

Coatings applied to concrete surfaces should have appreciable thickness. It is more important to have a thick coating over concrete than it is over a smooth steel surface. Not only should the coating penetrate the concrete, adding to its thickness, it should have a substantial thickness over the surface to cover any imperfections and irregularities of the concrete. Appreciable thickness also helps in the minor shrinkage cracks that take place on the concrete surface. Without some thickness, there is no resistance to stresses involved. As previously discussed, coatings highly adherent to concrete will not resist working cracks or even large shrinkage cracks. On the other hand, coatings in the 20- to 30-mil category should be capable of bridging hair cracks and checks, particularly if the cracks are in the concrete surface before the coating is applied. The connotation of bridging cracks is somewhat different than the application of coating over an existing crack. The term bridging, as used by engineers in a specification, means that if the concrete cracks after the coating has been applied, the coating will stretch over the crack and act as a solid bridge, preventing liquid penetration or corrosion from occurring. As mentioned, this is impossible with thin coatings, and very difficult, if not impossible, with coatings of some thickness. It is only the specially designed coatings and linings described previously that will perform satisfactorily under most cracking situations.

Resilience and Flexibility

Coatings for concrete need to have some resilience, flexibility, and extensibility. Coatings for steel do not require these properties to the same extent as those for concrete since steel is a relatively solid base. If the coatings have good adhesion, they need only slight resilience to perform well. Concrete, on the other hand, is a much softer and brittle base, so that coatings for concrete need to be somewhat resilient, extensible, and flexible in order to follow any shrinkage or expansion and resist the impact to which concrete is frequently subjected.

This is particularly true on floors subject to traffic. The coating should not be rubbery, but should be tough and resilient. When this property is combined with penetration into the surface so that strong adhesion results, the coating will have good wear resistance.

Adhesion

Adhesion is undoubtedly the primary property required for concrete coatings. It is one thing for the coating to have adhesion and to retain the adhesion when the concrete is dry; it is another problem when it is subject to moisture vapor pressure or even to liquid water within the concrete and directly underneath the coating. There are many cases where this condition prevails, particularly on subsurface structures such as basements, underground tanks, and similar areas. The coating should have the penetrating power described, and a thorough wetting characteristic for the concrete surface; it should retain the penetration and the adhesion, even though there is water within the concrete adjacent to the coating.

In addition to adhesion, the coating needs to have appreciable thickness and be physically strong in order to resist the back-pressure of the water. If it did not have this property, it would not be satisfactory for any area where water pressure can develop within the concrete and underneath the coating. This is a common problem, and blistering of coatings on concrete where such back-pressure exists or where the coating is immersed is also common. A coating can only maintain its integrity with a strong bond to the surface. The concrete also needs to be strong (in tension), since most coatings have a higher tensile strength than the concrete and with back-pressure can actually rupture the concrete surface in the blistering process. A weak concrete surface, or one containing concrete laitance, will easily blister.

Abrasion Resistance

All of the properties discussed in the previous section have a bearing on abrasion resistance. Abrasion resistance is important with most concrete coatings since most concrete surfaces are subject to hard usage, impact, and wear. This is especially true of floors where walking, sliding of heavy objects, and wheeled traffic are normal conditions. Any coating subject to these conditions should wear out rather than chip and peel. The coating systems that have the greatest abrasion resistance are liquid epoxy-type floor toppings, which contain hard abrasion-resistant aggregates, or a polyurethane coating system using a liquid epoxy primer for penetration and adhesion, followed by abrasion-resistant urethane topcoats.

Reasons for Coating Concrete

If concrete is such a durable material itself, then why should it be coated? Its various properties, which have been previously described, provide the reasons.

Decoration

Concrete is a rather drab, dull, gray material without much overall attraction other than its utilitarian aspect. Decoration, therefore, is the reason for coating the majority of concrete surfaces. Almost any alkali-resistant, weather durable, color coating can satisfy this requirement. The coatings used range from stucco color coats to many different vinyl and latex/acrylic water and solvent-base materials. These materials are usually not the high-performance coatings with which we are most familiar; however, this does not mean that the high-performance materials should not contribute to the decoration of the concrete structure in addition to their corrosion-resistant purposes.

Specially formulated 100% solid epoxy and polyurea coatings containing various colored pigments have achieved remarkable success on showroom floors, including those displaying restored antique cars.

Decontamination

The normal porosity of concrete allows it to absorb almost any contaminant that comes into contact with it. Within nuclear facilities, coatings for concrete must be easily decontaminated in case of radiation spills. Within schools and hospitals, coatings must render the concrete surface resistant to bacteria. Within food establishments, coatings must resist growth of algae or other slime-type growths that could contaminate the food being processed.

Conductivity

Hospital operating rooms, solvent storage facilities, and microchip manufacturing facilities are among the many areas where conductive fillers have to be used in conjunction with organic polymers to dissipate static electricity.

Waterproofing

The prevention of water penetration into concrete structures, either above or below ground, is also a major reason for coating concrete. Without coating or waterproofing, interior surfaces can be damp and efflorescent. With coatings that do not provide waterproofing, the surface can be peeled, blistered, or thoroughly disrupted by the moisture. Waterproof coatings can overcome these problems by preventing the water or moisture from passing through the concrete, and it is essential for most subterranean structures.

Chemical Resistance

Chemical resistance is another significant reason for coating concrete. Since concrete is such a reactive material, it is essential to keep it separated from other reactive materials, either to prevent corrosion to the concrete or to prevent contamination of the chemical solution. Most food processing plants coat their concrete surfaces, not only to prevent food acids from attacking the concrete, but to maintain sanitary conditions in the plant and to prevent food contamination. In areas where the acids are particularly aggressive, chemically resistant mortars, bricks, tiles or sheet membranes are more likely to be applied.

Corrosion Resistance

Corrosion resistance for concrete is another common reason that coatings are needed. Chemicals, acids, food acids, carbonic acid solutions, and pure water all can take their toll on uncoated concrete.

In order for a coating to provide full corrosion protection, it must form and maintain a continuous film over the entire surface and all its imperfections. Any lesser coating could only be used for decorative purposes.

Freeze-Thaw Cycles

Concrete, because of its moisture content, is susceptible to damage by continuing freeze-thaw conditions. The physical forces of ice are greater than the concrete's strength thus causing the concrete to spall and shatter. The only prevention method is to maintain the concrete with as little contained free water as possible, and coatings seem to be the only practical way to do this.

Reinforcing Steel

Reinforcing steel in all kinds of concrete structures can be seriously corroded if the concrete is porous to chloride, sulfate, other less common ions, or oxygen. Most of these materials, if left unchecked, will cause corrosion cells to form on the reinforcing steel, thus breaking and spalling the concrete in the corrosion cell area. High-performance coatings, being resistant to the passage of ions and oxygen, provide a practical answer for the protection of concrete and the reinforcing steel imbedded in it, particularly when combined with a properly designed impressed current cathodic protection system for the rebar.

Types of Coatings for Concrete

As previously outlined, the reasons for coating concrete are quite numerous. The concrete installations normally coated include floors, buried pipe, exteriors of structures and tanks, tank interiors, nuclear power contaminant vessels, interiors of sewer pipe, water reclamation equipment, and similar structures. These structures need protection against a variety of conditions, such as food products, food chemicals, fats, oils, sewage, corrosive soils, chemical plant waste and fumes, radioactive chemicals, brines, and even fungus and bacteria growth. The following are some of the more common coatings used for these purposes.

Bituminous Cutbacks

Bituminous cutback coatings are solvent solutions of coal tar or asphalt. The word bituminous includes both, and both have been extensively used on concrete. The coal tar cutbacks have better chemical resistance and better water impermeability than the asphalts. On the other hand, the asphalt cutbacks have better weather resistance and sunlight resistance than the coal tars. The coal tars tend to alligator and check when applied where they are unprotected from the weather. Asphalt cutbacks are used to line concrete water pipe and water storage tanks where no odor or taste can be tolerated. A thin coat is generally applied as a primer, followed by heavier coats over the surface to resist water penetration.

Heavy and rather thick-bodied coal tar cutbacks do an excellent job of protecting concrete from chemical attack and water absorption and aiding in the flow rate of concrete pipe. These materials generally wet concrete well, making for good adhesion without extensive surface preparation. Bacteria in the ground does not attack them. They have been used on concrete sewer pipe, catch basins, filter tanks, and underground storage basins, and they make excellent waterproofing for the exterior of foundations and structures. As a waterproofing for concrete structures, they may be applied as a single coat, although more often, they are installed as a built-up membrane of several coats, including fiberglass mat for reinforcing. Both coal tar and asphalt may be used in this way.

Some bituminous cutbacks are used as concrete penetrants. In this case, they are applied as a thin material and allowed to soak into the concrete, increasing the surface density and helping to minimize water penetration and concrete spalling due to freezing. Bituminous coatings are also available as water emulsions. These materials have many of the properties described above. However, they do not have the penetration characteristics of the coal tar cutback and they are not as effective for continuous immersion or wet conditions.

Their properties are better suited for spillage or spray, or for relatively dry areas where a black, reasonably chemical-resistant coating is satisfactory.

Prior to applying emulsions to concrete, the surface should be dampened, but not running wet or puddled. This effectively thins the material at the material-concrete interface, allowing deeper penetration and greater bond or adhesion. This also precludes the water in the emulsion from being "sucked" suddenly into a dry concrete "sponge." If this later occurs, there is a risk of "sucking" resin into the concrete, leaving a powdery, chalky layer of pigment on the surface. Later, subsequent coat adhesion problems could develop.

Emulsions cure by water evaporation and resin coalescence, leaving a breathing-type film. This film will allow moisture vapor to pass through without lifting the film, but will not permit water to pass because of surface tension. This characteristic is only important if the total coating system is emulsion based.

Chlorinated Rubber Coatings

Chlorinated rubber coatings have the water and chemical resistance, as well as the adhesion required for concrete coatings, including the all-important alkali resistance. They are lacquer-type and therefore, dry relatively rapidly to form a good resistant film on the surface. They have been used extensively for the coating of concrete water tanks and swimming pools, and, where properly and carefully applied, have done an excellent job. They can be supplied in many colors and offer excellent adhesion. They perform well under conditions of high humidity and they can be recoated with relative ease once the previous surface has been thoroughly cleaned. Good adhesion results from re-coating. Since these are solvent-sensitive coatings, the new coating tends to bite in and thus satisfactorily adhere to the previous coating.

Chlorinated rubber coatings are not satisfactory for sewer coatings or sewer linings, as they are not resistant to animal and vegetable oils and greases, and are rather quickly softened when these materials deposit on the surface. The chlorinated rubber coatings for use on concrete should not be modified with drying oils or alkyds, but with low molecular weight, chemical-resistant, permanently plasticizing-type resins. This is important, since the chemical resistance of chlorinated rubber is reduced by the amount of any oil-type modifiers.

Vinyl Coatings

Vinyl coatings have been used for many years as a coating for concrete of all types, from tank linings to nuclear energy chemical installations and concrete floors in food plants.

Figure 11.12 shows large keyed concrete sections used as radiation shields at a nuclear energy chemical extraction plant. The heavy vinyl coating was subject to heavy radiation densities, radioactive materials, and decontamination chemicals. Any penetration of chemicals into the concrete would have been both dangerous and damaging.

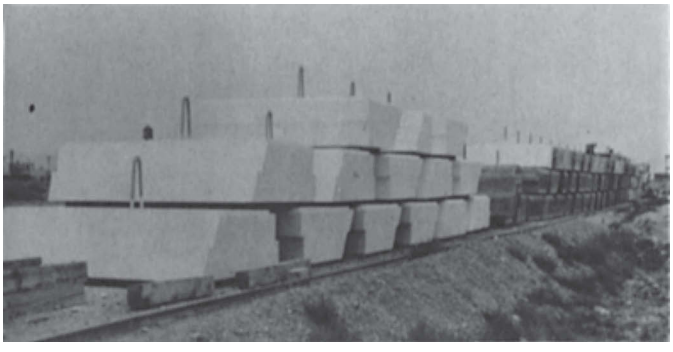


FIGURE 11.12: Keyed concrete radiation shields coated with a vinyl coating.

Vinyl coatings have excellent chemical resistance to both acids and alkalies as well as being resilient and flexible. Heavy-bodied, thick, viscous vinyl coatings, when combined with adequately thinned vinyl primers, have proven to have excellent resistance and adhesion over a period of many years. Vinyl coatings are lacquer-type materials, which dry rapidly. The primer should be applied as a heavy, wet coat in order to obtain maximum penetration into the concrete. Since they dry rapidly, additional coats often can be applied within minutes, which is considered an advantage. However, there are also disadvantages in this fast drying process. One is the possibility of overspray. The second is surface drying of the film while solvents remain within the pores of the concrete surface. These solvents are reasonably volatile, and if the concrete surface is warm, as from exposure to the sun, solvent blistering of the vinyl coating may occur. This can be avoided by application during a cooler time of day.

Vinyl coatings generally have relatively low solid content, and this may require additional coats in order to build the desired thickness. As a result they do not meet current volatile organic compound emissions regulations and usage is very limited.

Epoxy Coatings

Epoxy coatings have been well proven in concrete service. While all epoxy coatings adhere well to concrete surfaces, the ones that are outstanding are those formulated with liquid epoxy resins, liquid curing agents, and highly penetrating solvents. This combination allows the epoxy resins to penetrate deeply into the concrete surface, react, and increase the density as well as the strength of the surface of the concrete. There are many of these epoxy coatings available, and, where properly formulated, they will provide a coating with excellent chemical resistance and maximum adhesion to the concrete surface.

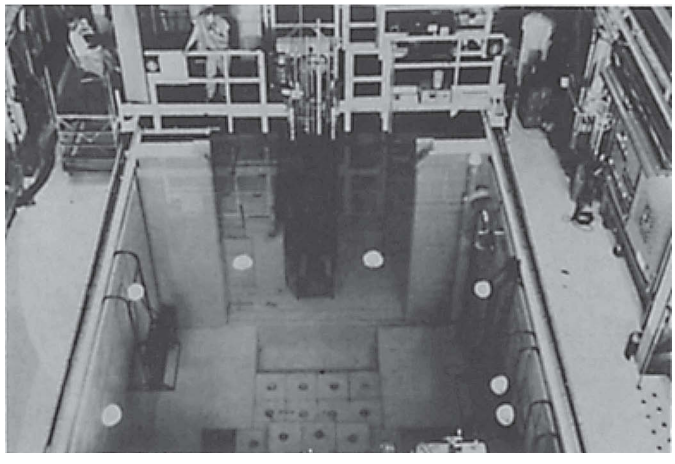


FIGURE 11.13: A concrete nuclear test reactor coated with a multiple-coat epoxy coating system.

Epoxy coatings have been used extensively throughout all industry as coatings for concrete areas such as floors, tank linings, pump bases, and so on, as well as in nuclear power plants. Here, they have been used as linings for the interior of chemical process areas, nuclear fuel storage areas, waste fuel storage areas, and many areas where coatings are not only subjected to high radiation chemicals, but to continuous immersion in ionized water. One such application is shown in Figure 11.13 where an epoxy coating was applied to the interior of a small concrete nuclear test reactor.

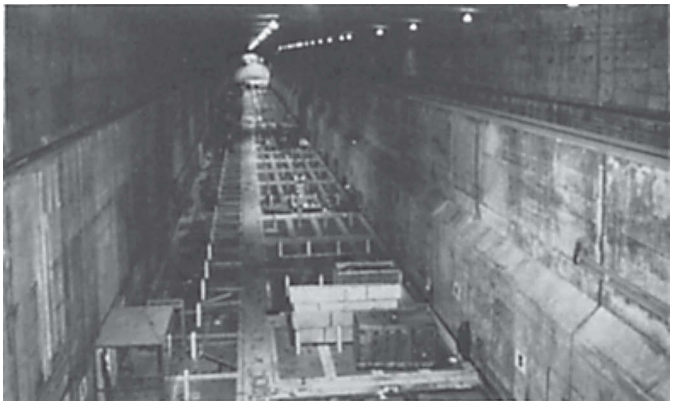


FIGURE 11.14: The interior of a nuclear chemical processing area prior to application of a conventional epoxy-type coating.

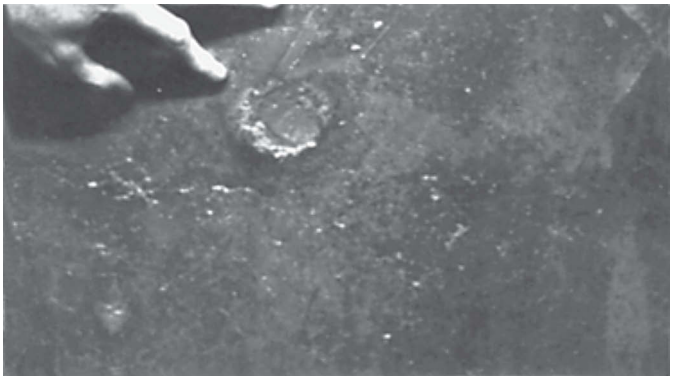


FIGURE 11.15: Poured concrete surface coated with a thixotropic base coat, which provides excellent filling and wet- ting of the surface, including the form tie hole in the center.

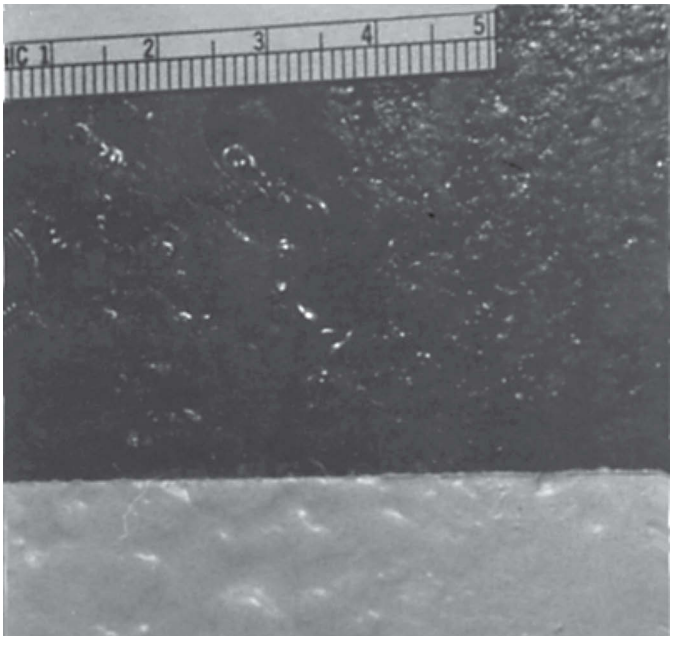


FIGURE 11.16: Poured concrete surface coated with the thixotropic epoxy base coat (top), followed by the conventional epoxy topcoat (bottom).

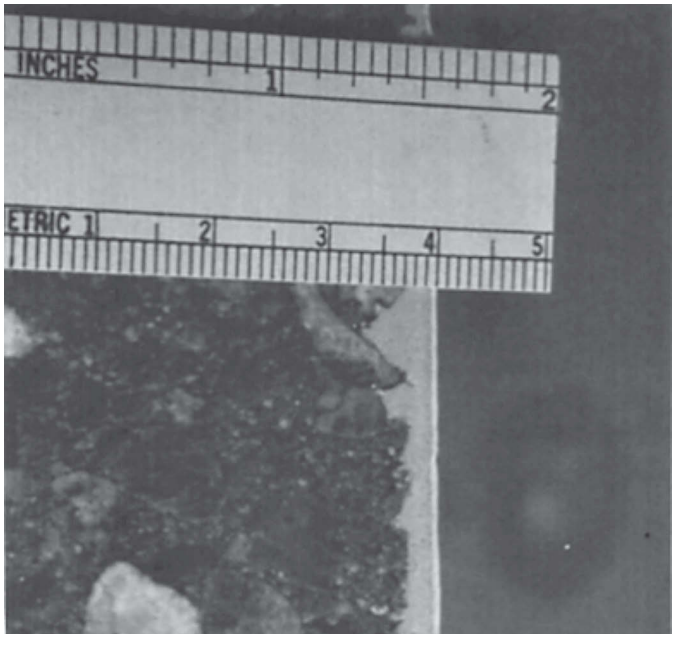


FIGURE 11.17: Cross section of concrete treated with an epoxy surfacer and coated with a conventional epoxy topcoat.

Another known application of an epoxy coating was on concrete surfaces in a chemical reaction area of a nuclear extraction plant. The coating was dry, but subject to high radiation. This concrete reaction chamber was broken into after 17 years of service, and the epoxy coating was completely intact, adherent, glossy, and, except for a slight yellowing, appeared to be entirely unchanged.

There are several types of epoxy formulations, each of which has its place in coating concrete.

1. Epoxy coatings, relatively thin, applied over concrete surfaces, which are prepared as outlined in Chapter 9. These are usually solvent-based epoxies using relatively high molecular weight resins and are quite similar, if not identical, to many epoxies used for steel.
2. Thin thixotropic liquid epoxy-based primers, which can be applied to the original concrete surface and provide both surface preparation and a base for other epoxy topcoats.
3. A thick epoxy surfacer applied by trowel, or a combination of spray and trowel. This is applied directly to a clean, but otherwise unprepared concrete surface. It also fills the concrete surface imperfections and can be used alone or with additional coats of conventional epoxy topcoats.
4. A system using an unpigmented clear 100% solids epoxy sealer followed by 100% solids epoxy pigmented topcoat provides both good penetration of the concrete and resistance to wear and chemicals on the surface.

These coatings may be either the amine-cured or polyamide-type epoxy and should be applied over smooth, filled concrete, which has been etched or blasted to a fine sandpaper finish. These are normally relatively thin coatings, 8 to 15 mils in thickness, and a smooth concrete surface is necessary to obtain a continuous film. They are used in chemical plants, food plants, paper plants, and nuclear plants as a general purpose, chemical-resistant coating. They are generally used in areas of fumes, chemical dusts, splash, or areas requiring possible decontamination, but not for immersion in difficult chemicals. Figure 11.14 is an example of a large concrete surface in a nuclear chemical processing plant that was being prepared for application of this type of epoxy coating.

The second type of epoxy coating is one that is a combination of a thin thixotropic base coat (primer) with the conventional epoxy topcoats described above. The base coat is a combination of liquid epoxy resins and highly penetrating solvents, which penetrate and have excellent adhesion to concrete. This may be applied by spray over a clean but otherwise unprepared concrete surface, and then



FIGURE 11.18: The spray application of a concrete surfacer to a chemical drainage trench in a plating plant.



FIGURE 11.19: The trowel application of an epoxy surfacer to a concrete wall.

squeegeed over the surface to fill all of the imperfections common to poured concrete or concrete block. As little as possible of the base material is left on the surface.

Figure 11.15 shows a concrete surface with the base material applied and with all of the normal concrete imperfections filled, including the form tie hole in the center. Notice also the dark color of the concrete, indicating the thorough wetting of the surface by the epoxy base coat.

Figure 11.16 is a closer view of a concrete surface, showing both the base coat and the conventional epoxy topcoat. These coatings are not exceptionally thick, but do provide a dense, impervious surface over even exceptionally rough concrete. Excellent adhesion to concrete is one of this coating system's primary properties.

Such concrete coating systems have been used to a considerable extent by the nuclear power industry in critical areas, which are exposed to radiation and which may require decontamination. Even concrete water storage areas and retention basins for used nuclear fuel have been coated. Such coatings may, however, be used on any concrete surface subject to water immersion, immersion in mild chemicals, or in areas of dusts, splash, or spray.

The third system is a combination of a relatively heavy concrete surfacing material, which may or may not be followed by conventional epoxy topcoats. The concrete surfacer is a mixture of liquid epoxy resins and catalysts with finely graded aggregate to form a material that may be applied by spray or trowel. There is sufficient liquid epoxy present so that it can effectively wet and penetrate the concrete surface to obtain maximum adhesion. The surfacer is applied to the surface in a sufficiently thick layer so that it not only fills the imperfection in the concrete surface; but provides a surface layer with a thickness of 1.6 mm (1/16 in) to 3 mm (1/8 in).

Figure 11.17 shows a cross section of with an epoxy surfacer, followed by a conventional epoxy topcoat. The surface imperfections in the concrete are well filled and the surface is smooth and dense.

Figure 11.18 shows the spray application of a concrete surfacer to a drainage trench in a plating plant. Such a trench is exposed to plating chemicals, including strong acids such as chromic and sulfuric. Drainage areas such as this are extremely difficult to protect from corrosion. However, when carefully and properly applied, the epoxy surfacers do an excellent job.

Figure 11.19 shows an epoxy surfacer being applied by trowel to a concrete wall. Trowel application is usually, but not always, preceeded by spray application of the heavy surfacer. The troweling then brings the surfacer to a smooth, even, dense surface. This procedure, when followed by one or more coats of epoxy topcoats, makes a smooth, dense, chemical-resistant surface for any concrete structure subject to corrosion and abrasion.

Concrete surfacers such as this are used extensively as a coating for concrete floors that are subject to abrasion and corrosive chemicals. The finely graded aggregate in the surfacer is tightly held in the epoxy matrix and makes a highly abrasion-resistant surface. The combination of strong adhesion to concrete, abrasion resistance, chemical resistance, and density makes it well suited for difficult floor conditions. These same properties make it applicable for immersion in many chemical solutions (except strong acids).

Coal Tar Epoxies

Coal tar epoxies might be classed as a fourth type of epoxy coating that is uniquely applicable to concrete. These materials combine the useful properties of both the coal tar and the epoxy into a particularly effective coating for concrete surfaces. They require application over a properly prepared concrete surface, as they can be classed as a comparatively thin coating: two coats at 15 to 20 mils thickness. Thicker applications of 100% solids versions can be made for special situations. The coal tar epoxy coatings have good adhesion to concrete, are chemical-resistant, abrasion-resistant, and relatively easy to apply by roller or conventional or airless spray. They can be used wherever a black coating is acceptable.

An amine-cured coal tar epoxy coating is one of the few coatings that will effectively withstand the action of sewer corrosion, bacteria, hydrogen sulfide (H_2S), and acid condensate. Therefore, they have been used extensively as coatings for concrete structures in this field.

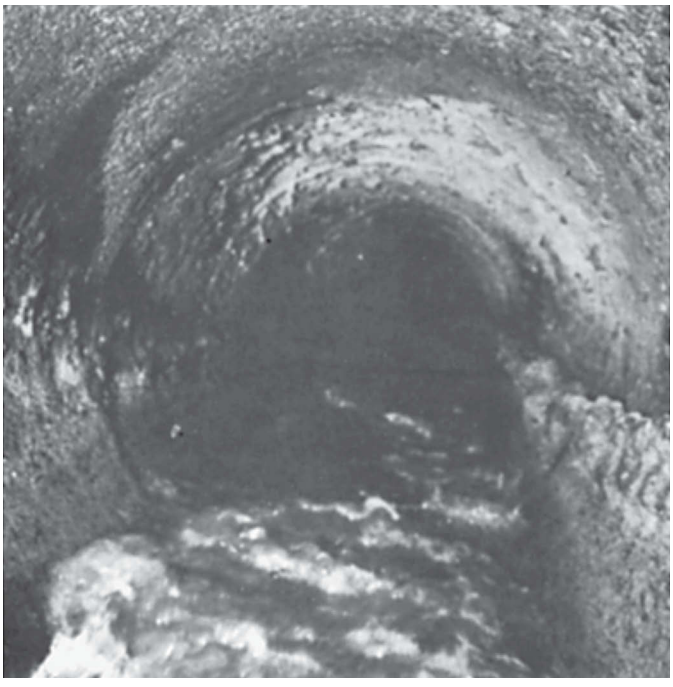


FIGURE 11.20: The interior of an unlined concrete sewer showing exposed aggregate above the water line.



Polyurethanes

Moisture-cured polyurethanes have been used very effectively on concrete hanger floors and warehouse areas where resistance to abrasion and color and gloss retention are very important. These materials are highly sensitive to atmospheric conditions during application, but when properly applied, provide excellent service.

Special Materials

There are some concrete structures that are subject to sufficiently strong corrosion conditions that require specially designed lining materials. One of these areas is that of a septic sewer where corrosive sewer gases develop. Several conditions combine to create the corrosion problem in sewers. These are a relatively warm atmospheric condition, high-sulfate water, and a relatively long retention time or life of the effluent. These conditions were most common in the more southern areas of the country, the west coast, the middle south, and the southern east coast until the ban on disposal of heavy metals took place in the 1980s. The more northern area now may have the same problems, depending on the sewage effluent, despite the lower average temperature of the sewage. The reason is that some of the heavy metals are a natural inhibitor to the conversion reaction by which bacteria converts sulfates and sulfides into H_2S, which is then oxidized into H_2SO_4.

While the subject of sewer corrosion has been discussed previously, it is worth reiterating due to the increasing need for efficient waste water systems and treatment plants throughout the United States and the world. These plants, and the concrete pipe and structures that go along with them, represent large areas of concrete. Wherever there is a serious septic sewage problem, corrosion of concrete surfaces occurs. The problem is the chemical reactivity of the concrete, which creates a need for a strong, impervious coating or lining. There have been literally hundreds of coating materials tested under sewage conditions, and very few, if any, have been effective where sewer corrosion has been severe. There is no known solvent borne, sprayed-on coating that has been effective on concrete under severe weather conditions for any economical length of time.

The cause of the reactions, as discussed in previous chapters, is a biologic one. The bacteria and the liquid sewage react with the sulfate and sulfide products that are in the sewage, creating H_2S. The H_2S reacts with the bacteria that are in the crown of the sewer or in the area of the treatment plant exposed to air. These bacteria form a slime on the concrete surface and absorb the H_2S, oxidizing it to H_2SO_4. The H_2SO_4 content on the exposed areas has been measured to as high as 10%.

The corrosion to concrete is thus quite severe, with a constant source of such an acid on the surface. Not only is the acid constantly being renewed, it is freshly formed on the surface, making it extremely penetrating. It will penetrate even the most minute imperfection in a coating. The newly formed acid penetrates and attacks the calcium products in the concrete, creating $CaSO_4$. $CaSO_4$ occupies several times the volume of the original calcium compounds. This creates a physical problem in addition to the chemical one. Figure 11.20 shows the interior of a flowing sewer that is unprotected. Note the exposed aggregate above the water line in the concrete sewer.

In many areas where there are such serious corrosion problems, concrete will disintegrate at rates as high as an inch or two a year, rapidly exposing the reinforcing steel to H_2SO_4 attack. Figure 11.21 shows the interior of a sewer structure. In this case, the structure was previously coated. However, note the complete coating failure, with the heavy attack on the concrete surface. The pile of CaSO4 debris on the shelf above the pipe shows the extent of the reaction.

Many coatings have been applied to such concrete sewer structures and piping. Almost all have resulted in a complete failure similar to that shown in Figure 11.21. The serious nature of this type of corrosion has not been understood, and it was generally believed that any coating that would withstand H_2SO_4 would solve the problem. Unfortunately, because of the nature of the concrete, such coatings are subject to imperfections, and even a minute imperfection will cause the concrete to disintegrate under the coating, pushing it from that particular area. Even 100% solids epoxies with excellent acid resistance, often fail due to lack of holiday detection of the applied film prior to placing the sewer in service. Any pinhole will provide a pathway for H_2SO_4 attack.

Most of these structures are also buried and are thus subject to earth movement. This is particularly true in piping. Where movement occurs, some cracking, particularly at the pipe joints, may also occur, which opens the concrete to immediate attack. Many early

concrete sewers were tile lined. However, under such conditions, they were completely spalled from the concrete surface within a few years due to the penetration of the acid into the joints between the tiles.

Because of the harsh corrosive conditions in sewers, a different approach was developed for the protection of formed concrete. A cast-in-place molded or extruded plastic lining, which could be heat welded to itself, was formed with "T" extensions on the back of the sheet to hold the sheet in physical contact with the concrete. The principle of this lining has been described and shown previously in Figure 11.7.



FIGURE 11.22: Plastic waterproofing sheet held in place prior to casting concrete against it. Knob-like extensions are visible on the concrete side of the sheet.

The sheet lining is formed into sheets of the size required by heat welding the sheets together. The sheets are then placed on the form and the concrete poured in a normal fashion. Many millions of square feet of surface have been coated this way in sewer applications. However, the same principle has also been extended to chemical areas such as the H_2SO_4 leaching of copper ores. Joints between the plastic sheets can be heat welded by hand fusing the two plastic surfaces together, forming a complete and impervious plastic lining for the entire surface. These sheets can now be applied to existing concrete structures through the use of a special mastic epoxy grout into which the molded knobs on the back of the sheet are pushed into the mastic epoxy grout that then cures and permanently embeds the knobs.

Coatings such as this for concrete structures have been in use since the late 1940s and, under sewage conditions, have been in continuous use since that time. The key to the success of such a coating has been: (1) its ability to bridge the structural cracks that may occur, and (2) its appreciable thickness that can withstand the tensile loads that may be found should some damage occur. Because the lining is either molded or extruded, it can be made completely impervious. While there is the possibility of human error in the welding, this can be overcome with proper training. A continuously plastic-lined tank or structure can be obtained in this manner. One of the newer sheet lining materials uses a specially formulated vinyl/urethane adhesive, which is applied to overlapping joints to achieve a waterproof joint.

The waterproofing of large structures, where waterproofing is a very critical item, also has followed the same plastic lining procedure as just described. The extensions on the back of the plastic sheet are small knobs, but the principle of their use is the same. Cracks can be bridged without replacement of the sheet. In this case, the plastic lining is either cast on the exterior of the structure or is cast as a lining between two sections of concrete to prevent water or moisture vapor from reaching the interior of the structure.

Figure 11.22 shows a large plastic waterproofing membrane or liner being held in place prior to casting a heavy structure against it. In this particular case, it was a large, heavy concrete mass in a nuclear power plant. By heat welding the joints, complete waterproofing of the structure is possible.

The coating and lining of concrete is a more complicated and difficult procedure than providing the same type of protection to steel. Steel is a smooth, impervious, uniform, dense surface, while concrete is soft, brittle, subject to cracking, filled with air and water pockets, porous, water permeable, and chemically active. It is not surprising then that special surface preparation, product design, and application methods are required to coat and protect concrete effectively from the corrosive conditions in which it is used.

Surface Preparation of Concrete Prior to Coating

Concrete is very similar to ferrous metal substrates when it comes to preparing the surface properly for the specified coating system, particularly on bare concrete that has been in service for some time.

The engineer/specifier has a range of options to consider for each particular concrete surface according to the condition of that surface and the service conditions to which the new coating system will be exposed. Guideline No. 310.2-1997[6] from The International Concrete Repair Institute (ICRI) is highly recommended as source of guidance for all concrete coating surface preparation.

The Guide lists the following methods of surface preparation of concrete with specific recommendations of how to prepare and execute each method:

- Detergent Scrubbing
- Low Pressure Water Cleaning
- Acid Etching
- Grinding
- Abrasive Blasting
- Steel Shot Blasting
- Scarifying
- Needle Scaling
- High and Ultra-High Pressure Water Jetting
- Scabbling
- Flame Blasting
- Milling/Rotomilling

One of the most important tools in this ICRI Guideline is molded replicas of nine different Concrete Surface Profiles (CSPs) for concrete that provide clear, visual standards for purposes of specification, execution, and verification of the surface profile prior to application of any coating. These are:

- CSP1 (Acid Etched)
- CSP 2 (Grinding)
- CSP 3 (Light Shot blast)

- CSP 4 (Light Scarification)
- CSP 5 (Medium Shot blast)
- CSP 6 (Medium Scarification)
- CSP 7 (Heavy Abrasive Blast)
- CSP 8 (Scabbled)
- CSP 9 (Heavy Scarification)

Appendix B of this ICRI Guide classifies concrete coatings according to three thickness ranges:

1. Concrete Sealers – 0-3 mils (0-75 mm) dry
2. Thin-film Coatings – 4-10 mils (100-250 mm) dry
3. High-build coatings, self-leveling coatings, and polymer overlays—10 mils to 1/4 in (250 mm to 6 mm) dry

The Guide also has a Method Selector for surface profiles according to various types of coatings:

- Sealers—CSP1, CSP2, CSP3
- Thin-Film—CSP 1, CSP 2, CSP 3
- High Build—CSP 3, CSP 4, CSP 5
- Self-Leveling—CSP 4, CSP 5, CSP 6
- Polymer Overly—CSP 5, CSP 6, CSP 7, CSP 8, CSP 9

In Summary, if you are about to attempt a coating project over concrete, the ICRI guide is an excellent investment that can help ensure a successful completion of the job within the specification requirements.

References

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5. ACI 515.1R-79, "A Guide for the Use of Waterproofing, Dampproofing, Protective and Barrier Systems for Concrete" (Farmington Hills, MI: ACI).
6. IRCI Guideline No. 310.2-1997, "Selecting and Specifying Concrete Surface Preparation for Sealers, Coatings, and Polymer Overlays," (Rosemont, IL: IRCI, January 1997 [reapproved 2002]).

12 Coating Selection

Introduction

The selection of a proper coating for use on a structure, marine installation, or plant equipment is a difficult decision. In fact, it may well be the most important decision involved in the whole coating process. Not only must the coating resist the demands of the corrosive atmosphere, it determines the type and quality of surface preparation, as well as the method of application. As Sidney Levinson states in Selecting Paints:[1]

> To the architect, the cost of painting various parts of a structure he designs amounts to a very small part of the total cost. Yet this thin film of paint, rarely more than five or six thou-(some text is missing here; please check book) which must protect the substrate underneath from injury or even destruction by man or by the elements; by moisture, sunlight, rapid temperature changes, dirt, chemical fumes or abrasion. And it must retain its appearance for many years even when exposed to these sources of destruction.[1]

Robert Baldwin, in Selecting Coatings for Plant Painting Projects,[2] also states:

> Picking the right coating for plant painting projects might better be described as a process of elimination, rather than selection....The plant engineering approach begins by eliminating coatings that require more surface preparation than is feasible. For example, a coating that must be applied over a surface sandblasted to white metal should not be considered unless such surface preparation can be provided. Likewise, slow drying or slow curing coatings cannot be considered when the project must be completed over the weekend. The coating would be subjected to severe service conditions before it was cured, inviting premature failure.
>
> Regardless of the process used, selecting the right coating is very difficult when the full range of proprietary products—dozens from each of hundreds of manufacturers—must be considered.[2]

Coating selection is recognized, then, as a difficult yet important process. It is important in that the coating must withstand the specific conditions under which it will be used. It is difficult because of the many variables involved, ranging from the substrate to surface preparation, from rural atmospheres to a complex industrial condition, from immersion to air exposure, or from wall paint to an inorganic coating. Also, there are literally thousands of different coatings manufactured and sold, from which one must be selected to overcome the specific conditions where it is to be used. This adds up to hundreds of variables, all of which affect the life or effectiveness of the coating selected. Actually, the number of variables and conditions that affect coating selection is the reason that so many coatings exist.

Since there are many variable coating properties, as well as many individual coatings from which to select, some method of reducing the number of selections is needed. One procedure is to list the generic coatings and their advantages and limitations (Table 12.1). While a coating cannot be selected simply by looking at such a chart, it does provide a guide for the selection of one, two, or three generic coatings, which may satisfy the coating requirements. With this information, further, more specific data can be obtained from literature, laboratory, or field tests, which provide a basis for a more definitive selection.

There are two key points to remember in the selection of a coating:

1. There is no such thing as a universal coating that can be used for all conditions. If there were, the corrosion engineer's life would be much easier. A few decades ago, linseed oil paints came as close as any coating to being the universal answer to all coating problems. They could be applied to wooden surfaces, as well as to metal surfaces, and provided reasonable protection to each. As a matter of fact, prior to the 1930s, most of the industrial, railroad, and so-called corrosion-resistant coatings were made from a linseed oil base.
2. All coating selections represent compromises made to satisfy all of the variables involved. The properties of coating ingredients are balanced to produce the best results for specific requirements at a reasonable cost and for an estimated service life. Again, using linseed oil-based paints as an example, most of the industrial and corrosion-resistant paints were based on red lead pigmentation for the prime coat. Some coatings contained as many as 26 lb of red lead to the gallon. However, because of the heavy pigmentation and the fact that red lead offered no advantage to coatings for wood, red lead was replaced by zinc oxides, iron oxide, or other pigments to satisfy the requirements of wood applications.

Because of the much more complex corrosion problems present today, many more compromises must be made in order to satisfy specific conditions. The same coating formulation ordinarily used for marine immersion is not the best choice for a marine topside application. Compromises or changes to meet the specific conditions are both necessary and advisable in order for the coating to meet the specific conditions to which it is being exposed.

TABLE 12.1: Evaluation of Coating Systems

High Chemical Resistance (Immersion or Splash & Spillage)	Outstanding Advantages	Chief Limitations	Typical Applications
Converted Epoxy	1. Alkali Resistance	1. Two Package	1. Chemical Plants
	2. Abrasion Resistance	2. Pot Life	2. Oil Refineries
	3. Recoatability	3. Yellowing	3. Tank Lining
	4. Surface Moisture Tolerance	4. Exterior Chalking	4. Floor Finish
	5. Adhesion	5. Exterior Fading	5. Marine Applications
	6. Solvent Resistance	6. Apply over 50 F	6. Machinery
	7. Water Resistance		7. Paper Mills
			8. Water & Sewage Plants
Epoxy Polyester	1. Abrasion Resistance	1. Two Package	1. Wall Finish
	2. Stain Resistance	2. Pot Life	2. Machinery Finish
	3. Acid Resistance	3. Alkali Resistance	3. Kitchens & Bakeries
	4. Ext. Gloss Retention	4. Apply over 50 °F	
	5. Water Resistance	5. Limited Flexibility	
	6. High Film Build		
	7. Ext. Color Retention		
Moisture-Cured Polyurethane	1. Acid Resistance	1. Package Stability after Opening	1. Floor Finish
	2. Abrasion Resistance	2. Yellowing	2. Tank Lining
	3. Single-Package Converted Coating	3. Exterior Chalking	3. Machinery
	4. Water Resistance	4. Exterior Fading	4. Textile Mills
		5. Recoatability	
		6. Adhesion to Metal	
Vinyl	1. Acid Resistance	1. Spray Application Only	1. Tank Linings
	2. Recoatability	2. Low Solids	2. Chemical Plants
	3. Exterior Color Retention	3. Low Flash Point	3. Oil Refineries
	4. Exterior Gloss Retention	4. Careful Surface Preparation	4. Marine Applications
	5. Water Resistance	5. Heat Resistance	5. Machinery
			6. Potable Water Tanks
Intermediate Chemical Resistance (Chiefly Splash & Spillage)			
Chemical Resistance Latex	1. Chemical Resistance	1. Abrasion Resistance	1. Storage Tanks
	2. Exterior Color Retention	2. Application Temperature	2. Chemical Plant Equipment
	3. Exterior Gloss Retention	3. Heat Resistance	3. Oil Refineries
	4. Ease of Application		4. Marine Superstructure
	5. Water Clean-up		
	6. Nonflammable		
	7. Surface Preparation		
Chlorinated Rubber	1. Chemical Resistance	1. Solvent Resistance	1. Chemical Plants
	2. Water Resistance (immersion)	2. Heat Resistance	2. Water Immersion
	3. Abrasion Resistance		3. Machinery
			4. Floor Finish
Epoxy Ester	1. Chemical Resistance	1. Exterior Gloss Retention	1. General Interior Plant Use
	2. Abrasion Resistance	2. Exterior Color Retention	2. Floor Finish
	3. Surface Preparation	3. Film Build	3. Primers
	4. Ease of Application		
	5. Water Resistance		
Phenolics (Oil Modified)	1. Water Resistance	1. Yellowing	1. Marine Applications
	2. Acid Resistance	2. Recoatability (Intercoat Adhesion)	2. Floor Finishes
	3. Abrasion Resistance	3. Exterior Fading	3. Water & Sewage Plants
	4. Hardness	4. Exterior Chalking	4. Machinery
	5. Ease of Application		

TABLE 12.1: Evaluation of Coating Systems (continued)

Intermediate Chemical Resistance (Chiefly Splash & Spillage)	Outstanding Advantages	Chief Limitations	Typical Applications
Tar Epoxy	1. Water Resistance	1. Bleeding	1. Crude Oil Tank Lining
	2. Chemical Resistance	2. Ext. Color Retention	2. Sewage Disposal Plants
	3. High Film Build	3. Ext. Gloss Retention	3. Pipe Lining or Exterior Coating
		4. Two Package	
		5. Pot Life	
		6. Dark Colors	
Low Chemical Resistance (General Purpose Products)			
Oil, Linseed	1. Ease of Application	1. Slow Dry	1. Wooden (Exterior) Buildings
	2. Minimum Surface Preparation	2. Soft Film	2. Metal Surfaces (Exterior)
	3. Flexibility	3. Low ChemicalResistance	
	4. Excellent Adhesion	4. Poor Solvent Resistance	
		5. Water Resistance	
		6. Abrasion Resistance	
Alkyd	1. Ease of Application	1. Chemical Resistance	1. Tank Exteriors
	2. Surface Preparation	2. Water Resistance	2. Structural Metal
	3. Low Cost		3. Machinery
	4. Good One Coat Hiding		4. Plant Equipment
	5. Durability		5. Interior or Exterior, Wood or Metal
	6. Gloss Retention		
Exterior Latex Products	1. Water Reducible	1. Freeze-Thaw Limitations	1. Exterior Wood
	2. Nonflammable	2. Heat Resistance	2. Exterior Concrete, Stucco, and Masonry
	3. Ease of Application		3. Exterior Metal
	4. Blister Resistance		
Silicone (Masonry Water Repellent)	1. Colorless	1. Not for Use on Limestone	1. New Brisk, Mortar, Sandstone, and Poured Concrete
	2. Invisible	2. Use Only on New Masonry	
	3. Effective for 10 Years		
	4. Prevents Staining		
High-Temperature Coatings			
Silicones	1. Air-Dry Tack-Free (Some Formulations)	1. High Cost	1. High-Temperature Stacks
	2. Service Temperature up to 1000 °F	2. Low Film Build	2. Boilers and Boiler Breeches
	3. Interior or Exterior Service	3. Limited Solvent Resistance	3. Exhaust Lines, Manifolds, and Mufflers
		4. Limited Chemical Resistance	
Special Products			
Zinc-Rich Coatings (Organic)	1. Tolerant of Surface Preparation	1. Solvent Resistance	1. Rust Inhibitive Primer
	2. High Cost	2. High-Temperature Tolerance	2. Exterior Equipment in Petroleum and Chemical Plants
	3. High Film Build	3. Poor Acid or Alkali Resistance	3. High-Temperature Stacks
	4. Abrasion Resistance		
	5. Primer and Finish Coat		
Zinc-Rich Coatings (Inorganic)	1. Solvent Resistance	1. Critical of Surface Preparation	1. Solvent Tank Lining
	2. High-Temperature Tolerance	2. High Coat	2. Exterior Equipment in Petroleum and Chemical Plants
	3. High Film Build	3. Poor Acid and Alkali Resistance	3. High-Temperature Stacks
	4. Abrasion Resistance		
	5. Primer and Finish Coat		

Source: NACE Course # 5, Corrosion Prevention by Coatings (Houston, TX: NACE).

Just as there is no universal coating that fits all conditions, there also is no specific set of conditions for which a particular coating can be entirely satisfactory. Each coating job is unique, even if it is for an identical process in a different plant. This is because environmental conditions can make a substantial difference. For example, a coating for refinery tanks in Galveston, Texas could require an inorganic zinc (IOZ) base coat and weather-resistant topcoats to ensure protection against the Galveston marine environment. On the other hand, crude oil storage tanks in Oklahoma could be adequately protected by a top-grade alkyd primer and topcoats. Therefore, each coating job must be individually considered, and specific conditions surrounding the job must be thoroughly evaluated in order to ensure proper protection by the selected coating.

TABLE 12.2: Considerations in Coating Selection

A. Coating Properties
1. Abrasion resistance
2. Flexibility
3. Color and gloss retention
4. Temperature range
5. Drying time
6. Mildew resistance
7. Appearance
8. Water or fuel resistance
9. Wettability
B. Nature of Substrate (wood, masonry, steel, old coating, etc.)
C. Basic Function of Coating on Substrate
1. Deterioration control (corrosion, weathering, fire, etc.)
2. Waterproofing
3. Temperature control
4. Marking
5. Appearance (color, texture, gloss, etc.)
D. Accessibility (time or space) and Equipment Available for satisfactory Surface Preparation and Application
E. Environmental Factors
1. Temperature (extremes and variations)
2. Humidity (dry, damp, immersed, marine, etc.)
3. Chemical contact (fumes, acids, alkalies, solvents, etc.)
4. Solar radiation
5. Biological problems (fouling, mildew, etc.)
F. Life Cycle Costs

Source: R.W. Drisko, "Chemistry and Technology of Coatings" (Port Hueneme, CA: Civil Engineering Laboratory).

Considerations in Coating Selection

There are so many factors to be considered when selecting a coating that all of them cannot be listed in relation to the specific nature of coating use. Table 12.2, however, provides a general list of considerations for coating selection, including most of the essential information needed to determine the proper coating material. Some of these points are discussed in more detail in the following sections.

One of the most important questions, and the first that must be asked, concerns the purpose or the reason for coating application. Why is the coating going to be used? Is the coating for corrosion resistance? Is it for resistance to atmospheric conditions? Are the atmospheric conditions rural, marine, or otherwise? Is the coating's purpose to be decorative? Is it to be applied on new construction or is it a maintenance coating? Once the reason for coating has been determined, the specific requirements for the coating can be more accurately outlined.

One of the first points to be considered is whether the coating will be used on new surfaces or whether it will be applied over previously coated surfaces. If the surfaces are new, such as new plant facilities that have not been previously exposed to serious corrosion conditions, an unequaled opportunity for coating selection is present. Every effort should be made to take advantage of this prime opportunity in starting with new, clean, uncontaminated surfaces that can be properly prepared. Essentially, there is only one time in the life of a plant or structure that a coating job can be done both properly and economically. This is during plant construction. If a poor material selection is made at this point, because of cost cutting or ignorance of operating conditions, the cost of in-plant maintenance can be both high and continuous during the life of the plant.

Another often-made mistake is to begin startup operations before the entire coating system has been applied. This could be particularly serious where corrosive conditions exist. There are several things that affect early coating failure when such a procedure is used.

1. The primer may not be sufficiently resistant to existing conditions to prevent corrosion from starting prior to the time the topcoats are applied.
2. Once the decision is made to apply the topcoats, even though the primer may be in good condition, there still may be enough surface contamination to require an excessive amount of work for its proper removal. In many cases, this means re-blasting the steel and starting over.
3. With some contamination present, particularly in the difficult-to-coat areas of a steel structure, blistering of topcoats is highly likely, ultimately resulting in coating break down and severe corrosion.

The best opportunity to coat a structure properly where corrosive conditions will be involved, is when the structure is new, uncontaminated, and the coating work can be scheduled under proper conditions so that maximum benefit from the coating can be obtained.

When the structure is already in place and maintenance becomes the main concern, coating selection becomes somewhat more difficult. This is primarily because the substrate in this instance is not the base material (e.g., concrete or steel); rather, a previous coating now forms the paintable substrate. Many times the kind of coating previously applied is unknown, which makes the selection of the new maintenance product even more difficult. Any maintenance procedure must take into consideration the type of coating that presently exists on the surface. If this is not done, the new coating may be completely incompatible with the old, resulting in an unsatisfactory coating system that leads to early failure. Without some record of the original coating application, it is often extremely difficult to de-

termine the type of the previous coating.

Table 12.3 indicates the common coating types and their areas of use. However, this can only serve as a guide, since there are a number of different coatings that may be used under the same conditions.

TABLE 12.3: Common Coating Types and Areas of Use

Area of Use	Coating Type	Environment
Exterior Iron and Steel	Oil	Rural-Mild
	Alkyd	Industrial
	Urethane	
	Oil-Based Phenolic	High Humidity-Mild Industrial
	Inorganic Zinc	Corrosive
	Vinyl	Industrial Marine
	Epoxy	Severe Weather
Interior Iron and Steel-Metal	Alkyd	
	Urethane	Mild Industrial
	Epoxy Ester	
	Vinyl	Acid or Other Corrosive Fumes or Dust Fallout
	Epoxy	
	Chlorinated Rubber	
Interior Storage Tank. Vinyl	Salt Solutions	
Chemical Solutions Acid	Epoxy Phenolic	Dilute Acid
	Epoxy	Alkalies
Interior Water Tanks	Vinyl	
	Epoxy	
	Chlorinated Rubber	Water Immersion, High Humidity
	Coal Tar Epoxy	
	Coal Tar	
	Asphalt	
Interior Concrete	Vinyl	Water Immersion, High Humidity
Tanks/Reservoirs	Epoxy	High Humidity
	Chlorinated Rubber	
Interior Solvent	Inorganic Zinc	Solvent Immersion
Storage Tanks	Epoxy Phenolic	Fumes—Condensation
	Epoxy	
Exterior Concrete, Plaster—Masonry	Cement	Mild—Industrial
	Acrylic	
	Vinyl Acetate	
	Vinyl	Corrosive
	Epoxy	Humidity
	Chlorinated Rubber	
Exterior Wood	Oil	Rural—Mild Industrial
	Alkyd	
Interior Plaster or Wall Board	Acrylic	Mild Industrial
	Alkyd	
	Chlorinated Rubber	
Wooden Floors	Alkyd	Mild Industrial Polyurethane
Concrete Floors	Epoxy Ester	Mild Industrial
	Polyurethane	
	Chlorinated Rubber	Spillage Water—Dilute Chemicals
	Vinyl	
	Epoxy	

SOURCE: C.G. Munger, "Repairing Protective Coatings—Effect of Coating Type," *Plant Engineering* (Feb. 17, 1977).

Evaluating Operating Conditions

Probably the most important step in coating selection is to evaluate the conditions under which the coating must operate. This cannot be a superficial evaluation, but must take into consideration all of the conditions that may exist. Even small and seemingly irrelevant factors should be taken into consideration.

For example, a tank was to be lined for the purpose of holding slightly acidic wastewater. All other conditions were reasonably innocuous, including ambient temperature. The overall water solid content was low, and a vinyl coating was selected for the tank lining. However, one factor had been overlooked during the evaluation. A small amount of high-boiling aromatic organic liquid contaminated the water. This contaminant was not soluble in the water, but floated on the surface. Although it was insignificant in volume, it accumulated on the coating surface as the liquid level changed, causing the coating to swell, lose adhesion, and blister. This action allowed the acidic water to attack the steel substrate, causing severe corrosion. Since the small amount of contamination was overlooked during the selection of the coating, a costly repair job was required.

Compatibility

If the existing coating is unknown, a practical determination can be made by cleaning a small area (usually several square feet) of the surface to be coated. Prepare the surface as dictated by the coating and the type and degree of failure. Then apply the selected coating to the test surface. When this is done, it is possible to determine (1) if the new coating is going to lift the previous one (i.e., swelling the previous coating and causing it to lose adhesion), (2) whether or not the new coating strikes into the old one (i.e., the immediate absorption of the new coating by the old coating, which often causes a loss of adhesion that may only become apparent at some later date), and (3) peeling, in which the new coating completely loses adhesion to the old coating. Generally, this can be determined within a reasonable period of time after all coats of the new coating have been applied (e.g., after an overnight dry). This simple application test will not necessarily indicate the exact type of the existing coating. However, it will indicate the general compatibility of the new coat with the old one.

A procedure for a more definitive identification of previous coatings has also been developed. It consists of a series of tests designed by the Naval Civil Engineering Laboratory at Port Hueneme, California, and is published in one of its technical data sheets.[3] A field

test kit was developed for the sole purpose of determining the type of coating over which a new maintenance coating was to be applied. Such a laboratory kit is available commercially.[4]

The Substrate

Where a new coating is to be applied over an old one, the substrate must also be taken into consideration. It is relatively unimportant if the previous coating is continuous and unbroken, retains strong adhesion, or requires coating only to add thickness for additional life. These conditions rarely exist so that for the most part, the substrate is exposed and corroded. In this case, the nature of the substrate is extremely important to the repair of the existing coating. The new coat must not only be compatible with the old coating, but it must be compatible with the substrate and substrate corrosion as well. The principal substrates encountered are steel, cast iron, galvanized metal, aluminum, and concrete. Each of these corrodes differently and each must be treated in a different manner in order to obtain the proper repair coating.

TABLE 12.4: Types of Coatings Commonly Used on Different Substrates

Substrate	Paint	Comments
Interior Wood	Oil	Generally slow drying and relatively soft.
	Alkyd	May be hard or soft.
	Latex (Vinyl or Acrylic)	Can be applied over oil, alkyd, or latex primer.
Exterior Wood	Oil	Good wetting of weathered wood and paint chalk; slow drying; soft.
	Alkyd	Good wetting; variations give variety of properties.
	Silicone Alkyd	Good wetting; good gloss.
	Latex (Vinyl or Acrylic)	Poor wetting on weathered wood and paint chalk; easily applied.
Interior Masonry, Plaster, and Wall Board	Acrylic Latex	Easily applied; brushing is good on coarse surfaces; must remove all loose chalk.
	Vinyl Latex	Same as Acrylic Latex.
	Chlorinated Rubber	Good for waterproofing.
	Acrylic	Fill coats of these materials will reduce water penetration. Same as Acrylic Latex.
Exterior Concrete and Masonry	Latex	Good for waterproofing.
	Vinyl Latex	For concrete in very corrosive environments.
	Alkyd	Never on continuously damp or immersed environments.
Interior Iron and Steel	Vinyl	Good resistance to water; poor resistance to strong solvents.
	Epoxy	Good durability and chemical resistance.
	Urethane	Good durability and chemical resistance.
	Oil	For mild environments only.
	Alkyd	For mild environments only.
	Silicone Alkyd	For mild environments only.
	Inorganic Zinc	Very abrasion resistant; limited life in seawater without topcoat.
Exterior Iron and Steel	Inorganic Zinc	For mild environments only; good gloss.
	Vinyl	Good durability; easily touched up.
	Epoxy	Good durability and chemical resistance, but chalks in sunlight.
	Urethane	Aliphatic type has good weathering over epoxy primer.

Source: R.W. Drisko, "Chemistry and Technology of Coatings" (Port Hueneme, CA: Civil Engineering Laboratory).

The substrate is equally important if the structure is new. However, the problem of selecting a coating for new surfaces is less complicated than for the old ones. A thorough discussion of the substrate and the problems involved is provided in Chapter 8. Nevertheless, the substrate is one of the conditions that must be given serious consideration during the selection of any coating for a corrosive environment. Table 12.4 lists some common substrates, together with the types of coatings that may be applied.

The Environment

The environment is an extremely important part of any coating selection. It makes a great deal of difference as to whether the environment is dry or moist; whether it is rural, industrial, heavy industrial, or marine; and whether the coating is to be used on the interior or exterior of a structure. The environment for a coating to be used in a rural area is much less severe than one that will be used in a marine area. On the other hand, there are differences in a rural atmosphere as well. The atmosphere of a plant in the southern part of the United States is generally much more corrosive than that in the northern area of the continent. This is because the temperature and solar radiation conditions differ significantly between the two locations. Coatings that will readily and quickly chalk in southern areas may last for a substantial period in northern areas.

Industrial atmospheres may have any number of different chemical components in addition to the normal atmospheric conditions in the same area. Marine corrosive conditions are generally the same the world over, with the exception of areas that are in the southern portion of the Northern Hemisphere, which are generally more corrosive because of the higher temperature and higher reactivity of the corrosion process due to temperature.

Soil Problems

There are many protective coatings that are used to coat pipe in underground and underwater conditions. The type of soil is extremely important in any underground installation. Soil in contact with pipe coating can severely damage the coating over a period of time because of earth movement caused by the swelling and shrinking of the soil, due to periodic wetting and drying. The damage to the coating can also include penetration by rock, improper backfill, and damage during handling and laying. Any coating selected for underground conditions must have properties that will withstand the physical problems involved in pipe installation as well as the corrosion problems encountered in soil conditions.

Internal Surfaces

There are a number of different factors that influence the selection of a coating for the interior of a plant, vessel, or tank. On the interior of a plant, the coating need not be developed or designed for exterior atmospheric exposure, since solar radiation has little effect on the interior. On the other hand, fumes, condensation, dampness, and spillage all create conditions that affect the coating to be selected.

For example, an epoxy ester might make an excellent coating for equipment inside a plant that is subject to mild chemical conditions. However, the same coating used outside of the plant and exposed to essentially the same chemical conditions would not be satisfactory due to its rapid degradation by solar radiation. In the early days of the epoxy esters, because of their relatively easy application and good appearance, many were applied to exterior areas subject to mild chemical conditions. Such coatings were not only a disappointment, but also a failure because of their rapid chalking and reaction to solar radiation conditions.

Coatings for plant interiors may also be formulated with different kinds of pigments than those used on the exterior. Interior pigments need not be particularly chalk resistant since they are not subject to weathering conditions, but should be pigmented for water, fume, and chemical resistance. Clear coatings that can be used for interior work would be completely unacceptable for exterior exposure.

Tank linings require a different kind of selection process. Generally, the coating must be selected for its specific properties with relation to specific chemicals or solutions where it must either protect the tank surface, or it must protect the contained material from the tank itself. Since tanks are generally single-purpose units, one of the prime considerations for the coatings is the contained liquid. In a closed tank, if the coating will satisfactorily resist the liquid and protect the tank surface, then other properties, such as resistance to solar radiation or weather resistance, are of little importance.

Corrosive Conditions

Since most of the coatings with which corrosion engineers are directly involved are high-performance coatings, one of the primary considerations for coating selection must be the principal corrosive condition that exists or against which the coating must protect. There are essentially three corrosive conditions that affect the coating: (1) fumes, (2) splash and spillage, and (3) total immersion in the corrosive material. The selection of a coating may be quite different for any one of these three conditions.

Fumes and Splash or Spillage

For fumes, such as those in a galvanizing plant or a sulfuric acid (H_2SO_4) leaching facility undercover, the coating would need to have strong resistance to acidic conditions, condensation, or precipitation of the acidic fumes on the coating surface. High humidity would be a considerable influence on the general corrosive condition, and one might expect high-humidity conditions under the examples given.

Nevertheless, the conditions in the fume area might be considerably less of a problem than those in the area where there was splash, spillage, or leakage from piping and pumps. In the case of fumes, the coating required would not need to have any abnormal thickness, but would need to form a continuous film over the surface. Where there was spillage, dripping, and similar liquid conditions, the coating would need to have greater physical properties and general thickness than for fumes alone.

Immersion

A coating for immersion service is unique in that, generally, it must have outstanding adhesion, as well as an excellent specific resistance to the product in which it is immersed. In this case, the concentration of the product in solution is essential, as is the temperature of the liquid. A 10% caustic solution in some ways can be more difficult than a 50% caustic solution at 150 °F. In this example, the 10% solution could allow some moisture vapor to pass into the coating and cause blistering, while the 50% solution is sufficiently hydroscopic so that it would tend to remove any moisture that might be in the coating and thus reduce any blistering tendency. This has been proven under actual service conditions.

The reverse situation can also be true. In the case of a volatile acid such as hydrochloric acid (HCl), the higher the concentration, the greater the tendency to penetrate the coating. In tank coatings, some minor side effects also must be considered. For example, a ship's tank was coated with an epoxy coating, and plans were made for it to transport molasses from Hawaii to Los Angeles. The tank was a dedicated tank, so that it returned from Los Angeles to Hawaii essentially empty. The coating effectively withstood the immersion in molasses, both in laboratory tests and on the first trip from Hawaii to Los Angeles.

On the second trip, however, it was noticed that the coating was blistered, and on the third trip, it was blistered to an even greater extent. What was not taken into consideration in the initial coating selection was that once the molasses was removed from the tank, there was sufficient water and condensation in the tank to cause the remaining molasses on the surface to ferment. While the coating was thoroughly resistant to molasses, it was not resistant to acetic acid, alcohol, and the other fermentation products, which developed on the return trip. Thus, it is often a minor element in an evaluation or coating selection that creates a problem, and not the principal conditions under which the coating must stand up.

Product Contamination

In tankage, contamination of the contained product must also be one of the considerations in coating selection. In many cases, the prime reason for the coating is to prevent contamination of the contained liquid. The coating therefore should be evaluated from this standpoint, as well as its resistance to the liquid itself.

TABLE 12.5: Coating Surface Preparation Comparison Guide

Coatings Formulated as Primers for Steel	Minimum Surface Preparation
Acrylic Lacquer	Normally used as topcoat
Alkyd Varnish	Tolerant of hand and power tool cleaning. (Better coatings normally used with blast cleaning.)
Bituminous Cutback	Commercial Blast
Bituminous Emulsion	Commercial Blast
Chlorinated Rubber	Commercial blast. (Tolerant of hand and power tool cleaning.) White metal blast for immersion service.
Epoxy Ester Varnish	Commercial blast. (Tolerant of hand and power tool cleaning.)
Epoxy Amine (2-part)	Commercial blast. Near white blast for immersion service.
Epoxy Polyamide (2-part)	Commercial blast. Near white blast for immersion service.
Epoxy Coal Tar (2-part)	Commercial blast. Near white blast for immersion service.
Latex–(Water Base)	Commercial blast (acrylic latex) Normally used as topcoat.
Oil-Base	Hand or power tool cleaning. (Better coatings normally used with blast cleaning.)
Phenolic Varnish	Commercial Blast. (Tolerant of power tool cleaning.)
Polyester Epoxy	Normally used as a topcoat
Polyurethane oil-modified	Normally used as a topcoat
Urethane -moisture cured	Normally used as a topcoat
Urethane (2-part)	Normally used as a topcoat
Vinyl Lacquer	White metal blast. Normally used as a topcoat.
Zinc-Inorganic	Near White blast. White metal blast for immersion service.
Zinc-Organic	Commercial blast. White metal blast for immersion service.

Source: R. Baldwin, "Selecting Coating for Plant Painting Projects," *Plant Engineering* (Feb. 6, 1975).

A coating for a liquid sugar tank is an example. If the liquid sugar is crude sugar and will be further refined, then the lining in the tank merely requires resistance to the sugar solution in order to protect the tank. On the other hand, if it is a refined sugar solution or glucose, which then may be used in sensitive food products, any taste transfer or other contamination to the sugar solution will cause serious problems in the end product. If the lining in the tank contributed an improper odor or taste and was not thoroughly cured or thoroughly free of solvent, serious sugar contamination could occur.

Coating Curing

The curing of a coating used as a tank lining is also an important consideration in the selection of lining materials. If high-temperature cured linings are to be used, the tank must be designed so that the proper temperature can be obtained over the entire coated area. There have been many failures experienced where tanks were designed in such a way that there were cold sections in the tank. These are areas where the tank could not be properly insulated or where supports or reinforced areas acted as a heat sink and could never be brought up to the proper curing temperature. The poorly cured lining in such spots soon failed in service. Where such conditions exist, and there are many of them, a coating with a longer curing time at lower temperature should be selected in order to develop equal resistance over the whole tank area. A secondary, but just as vital consideration, is the proper ventilation of the lining during application and curing. Air movement must be directed over the surface of all the lining, particularly the constricted areas between supports and stiffeners.

Surface Preparation

Another factor in the selection of a coating is the degree of possible surface preparation. In many instances, particularly on new construction, the best surface preparation possible is available for the coating. On the other hand, on the interior of a plant that is operating and yet where a coating is required, abrasive blasting may be a total impossibility. Many times blasting can be done during a shutdown period; however, with sensitive equipment, products, or reagents involved, blasting may still be impossible. This means that a coating that will tolerate less surface preparation must be applied. Under these conditions, a coating that will provide reasonable resistance as well as adhesion over a hand cleaned or alternative power cleaned surface would have to be selected. It must be realized, however, that in this case, the coating would have a shorter life and would require continued maintenance in order to provide the necessary corrosion protection.

Table 12.5 shows the minimum surface preparation recommended for a number of different generic types of coatings. In the example used above, the chlorinated rubber or epoxy ester varnish might have been the coating selected because of its toleration of less than the best surface preparation.

Timing

One other factor involved in the selection of a coating is the length of time available for coating application. This is not so much of a problem on new work, since it is usually scheduled along with the construction job. However, the application of a coating in an existing plant can be a problem, where application must be scheduled during a shutdown period, sandwiched in between plant operations, or completed over a weekend.

If it is an exterior application, the weather during the application is also an extremely important factor. If it has to be done during a hot, dry time of the year, one type of coating might be selected, while if it is done in the cold, damp time of the year, another would be preferable. Usually, any selected coating would have to dry and cure rapidly. Some coating application properties, including approximate drying times of various generic type coatings, are shown in Table 12.6.

There are also other application problems that are dictated by time. These would be such things as wind and dust, high temperatures, fallout from adjacent plants, moisture condensation, and similar difficulties. For example, a solvent-based IOZ coating was applied to the wind girder of a large oil storage tank. The application took place in the fall of the year and in the relatively late afternoon after the blasting of the wind ring had been completed. The tank was located in a marine area. During the time that the coating was being applied, the humidity changed sufficiently so that the wind girder condensed moisture shortly after the coating had been applied. This resulted in rapid curing of the coating because of the moisture present on the surface. The coating checked and cracked

over nearly the entire surface. This problem would not have occurred had the coating been applied during the middle of the day or during a somewhat warmer and less humid time of the year.

TABLE 12.6: Coating Comparison

						Drying Time		
Coating	Film Forming Solids, % by Volume	Recommended Dry Film Thickness, mils/ coat	Number of Topcoats Over Primer (if required)	Minimum Aplication Temperature °F	Flash Point (Open Cup)	To Touch, Hours	To Recoat, hours	Final Cure, Days
Acrylic Lacquer	25–37	1.5–2.5	1–2	40	53–85	1/4–3/4	12	1–7
Alkyd Varnish	43–56	1–2	2	40	50–100	2–12	3–48	4 days—several weeks
Bituminous Cutback	32–74	12–15	1–3	40	80	4–12	24–72	3–14
Bituminous Emulsion	10	12–15	1–3	40	–	1–2	12–24	10–15
Chlorinated Rubber	29–46	1.2–4	1–3	40	50–100	1/4–4	1/4–24	7
Epoxy Ester Varnish	34–44	1.5–2.5	2	50	85–100	2	6–72	4–14
Epoxy Amine (2-part)	37–60	2–8	1–3	50	60–90	2	12–18	3–10
Epoxy-Polyamide (2-part)	45–60	2–5	1–3	50	60–90	1–3	3–40	5–7
Epoxy-Coal Tar (2-part)	60–86	8–10	1–2	60	60–96	1/2–2	4–96	1–7
Latex (water-base)	35–50	1.5–4.5	1–2	40	–	1/4–2	1–12	5–30
Oil-Base	70–90	3	1–2	40	60–105	8	8–48	several weeks
Phenolic Varnish	32–43	1.5–4	1–3	50	60–105	1/2	8–48	7–12
Polyester-Epoxy	51–61	2.5–3.5	1–2	60	90–100	2–6	8–48	10–14
Polyurethane (oil-modified)	30–50	1–3	1–2	40	60–100	1/2–6	4–16	2–14
Urethane (moisture-cured)	30–50	1–4	1–3	40	60–90	1/2–12	3–48	2–7
Urethane (2-part)	30–100	2–40	1–3	40	60–90	1/2–12	3–48	2–14
Vinyl Lacquer	4–28	1–5	1–3	35	28–95	1/4–1	1/2–8	3–7
Zinc-Inorganic	4–71	1.5–5	1–2	40	50–70	1/4–1/2	1/4–1/2	1–7
Zinc-Organic	4–40	2–3	1–2	35	28–100	1/4–1/2	2–24	7

Source: R. Baldwin, "Selecting Coatings for Plant Painting Projects," *Plant Engineering* (Feb. 6, 1975).

Safety

Another consideration in coating selection is the safety problems that may be encountered. These vary from coating to coating and from one type of application to another. For instance, solvents in a coating create possible hazardous conditions, such as (1) explosion, (2) fire, and (3) personal contact with the solvent or a fume. Toxic pigments such as red lead in old coatings creates a need for personal protective equipment.

While safety during coating application will be discussed in more detail in a later chapter, there is one rule of thumb concerning the use of solvents that is worth remembering: keep the volume of solvent vapor in air below a concentration of 1%. Actually, it should be kept far below 1% to maintain the best safety conditions. This can be accomplished by proper ventilation, which eliminates the hazard of an explosion since the explosive limit of most solvents is well above 1%. Personal contact with solvents can be avoided through use of proper clothing and air masks. Catastrophic problems such as fire or explosion can be greatly reduced by the rule of thumb mentioned above.

Previous Experience

Previous coating experience is an excellent criterion for coating selection. If the experience has been good and the conditions are reasonably similar, then this experience lends confidence in making the coating selection. If the coating has not performed satisfactorily, then it is certainly a reason for eliminating the coating from consideration.

In order for previous experience with a coating to be valid for coating selection, the experience should be personal and not based on hearsay from someone else in the field or from coating salespeople. Personal observation of the application of a coating, followed by evaluation of the performance of the coating under actual operating conditions, makes for first-hand knowledge that cannot be

TABLE 12.7: Comparison of Resistant Coating Uses

	LACQUER COATINGS				COREACTING COATINGS		
Uses of Resistant Coatings	Vinyl Choloride-Acetate Copolymer	Vinyl-Acrylate Copolymer	Chlorinated Rubber	Coal Tar Pitch (Hot Melt)	Epoxy-Amine	Epoxy Polyamide	Coal Tar Epoxy
Broad Spectrum							
Abrasive Resistance	Good	Good	Good	Fair	Good	Good	Good
Bacteria & Fungus Resistance	Excellent	Good	Good	Good	Good	NR	Good
Chemical Resistance	Broad Spectrum	Good	Broad Spectrum	Good	Good	Good	Good
Acid-Oxidizing	Spray or Fumes	Fumes	Spray or Fumes	NR	NR	NR	NR
Nonoxidizing	Spray or Fumes	Fumes	Spray or Fumes	Fumes	Spray or Fumes	Fumes	Fumes
Organic	Immersion Fatty Acids	Fumes	Dissolves in Fatty Acids	NR	Spillage-Fumes	Fumes	NR
Acids							
Alkali	Good	Dusts	Good	Good	Good	Good	Good
Salts: Oxidizing	Splash-Spray	Fumes or Dusts	Fumes or Dusts	NR	Fumes	Fumes	Fumes
Salts: Nonoxidizing	Immersion OK	Fumes or Dusts	Immersion OK	Seawater OK	Immersion OK	Immersion OK	Immersion OK
Solvent: Aliphatic	Excellent	Fair	Good	NR	Excellent	Good	Good
Solvent: Aromatic	Swells	Dissolves	Dissolves	NR	Good	NR	NR
Solvent: Oxygenated	Dissolves	Dissolves	Dissolves	NR	NR	NR	NR
Water	Very Good Immersion	Good	Very Good Immersion	Excellent	Very Good	Very Good	Very Good
Moisture Permability	Low	—	Low	Low	Immersion	Immersion	Immersion
Contamination of Contacting Materials							
Food	OK-Odorless, Tasteless	—	Water OK	Water OK	Good	Good	NR
Nontoxic Chemical	Very Good	—	Good	—	Good	Good	Fair
Decontamination	Very Good	—	—	—	Very Good	Very Good	NR
Other Resistance							
Friction Resistance	—	—	—	—	—	—	— (Faying Surfaces)
Heat Resistance							
Wet	48 °C (120 °F)	38 °C (100 °F)	38 °C (100 °F)	48 °C (120 °F)	48 °C (120 °F)	48 °C (120 °F)	48 °C (120 °F)
Dry	65 °C (150 °F)	65 °C (150 °F)	60 °C (140 °F)	65 °C (150 °F)	95 °C (200 °F)	95 °C (200 °F)	95 °C (200 °F)
Radiation Resistance	10^8R	—	1×10^8R	—	1×10^9R	1×10^{10}R	5×10^8R
Soil Resistance	—	—	—	Excellent	—	—	Good
Weather & Light Resistance	Good—Properly Pigmented	Excellent	Good—Properly Pigmented	NR	Heavy Chalking	Fair-Good	Chalking
Principal Hazard							
Application	Solvent Fumes	Solvent Fumes	Solvent Fumes	Coal Tar Fumes[1]	Dermatitis	Solvent Fumes	Dermatitis

[1]Critical for immersion. NR = Not Recommended.

Source: C.G. Munger, "Coatings—Resistant," Kirk-Othmer: *Encyclopedia of Chemical Technology,* 3rd Ed., Vol. 6 (New York, NY: John Wiley & Sons).

TABLE 12.7: Comparison of Resistant Coating Uses (continued)

COREACTING COATINGS			CONDENSING COATINGS				INORGANIC COATINGS		
Uses of Resistant Coatings	Urethane Two-Package	Urethane Moisture Cure	Urethane-Aliphatic Isocyanate Cure	Baked Phenolic	Epoxy Phenolic	Epoxy Powder	Water-Base	Solvent-Base	Fused Ceramic
Abrasion, Bacteria/Fungus, & Chemical Resistance									
Abrasion Resistance	Outstanding	Outstanding	Outstanding	Good-Brittle	Good	Good	Very Good, Metallic	Very Good, Metallic	Very Good, Brittle
Bacteria & Fungus Resistance	—	—	—	Excellent	Excellent	Good	—	—	Excellent
Chemical Resistance	Good	Good	Good	Very Good	Very Good	Good	NR	NR	Very Good
Acid									
Oxidizing	Spray or Fumes	Fumes	Spray or Fumes	NR	Splash-Fumes	NR	NR	NR	Immersion OK
Nonoxidizing	Spray or Fumes	Fumes	Spray or Fumes	OK, Ambient Temperature	Splash-Fumes	Splash-Fumes	NR	NR	Immersion OK
Organic	Spray or Fumes	Fumes	Spray or Fumes	OK, Ambient Temperature	Splash-Fumes	Splash-Fumes	NR	NR	Immersion OK
Alkali	Spray or Dust	Dust	Spray or Dust	NR	Excellent	Good	NR	NR	NR
Salts									
Oxidizing	NR	NR	NR	NR	Fumes	Fumes	NR	NR	Immersion OK
NonOxidizing	Immersion OK	Spray	Spray	Immersion OK	Immersion OK & Spray	Splash-Fumes & Spray	OK Marine Splash	OK Marine Splash	Immersion OK
Solvent									
Aliphatic	Excellent	Very Good	Excellent	Excellent	Excellent	Excellent	Excellent	Excellent	Excellent
Aromatic	Excellent	Very Good	Excellent	Excellent	Excellent	Excellent	Excellent	Excellent	Excellent
Oxygenated	NR	NR	NR	Excellent	Alcohols, OK NR-Ketones	NR	Excellent	Excellent	Excellent
Water	Good—Primer Required		Good—Primer Required	Excellent	Excellent	OK Immersion	Good	Good	Excellent
Moisture Permeability	Medium-Low	Medium-Low	Medium-Low	Low	Low	Low	—	—	Low
Contamination of Contacting Materials									
Food	—	—	—	OK-Odorless, Tasteless, Nontoxic	OK-Nontoxic	—	—	—	
Chemical	—	—	—	Nontoxic	Good	—	—	—	Ok, Odorless
Decontamination	Very Good	Good	Very Good	Very Good	—	—	—	—	Tasteless, Nontoxic
Resistance									
Friction	—	—	—	—	—	—	Excellent	Excellent	Good (Faying Surfaces)
????									
Radiation	5×10^8R	5×10^8R	5×10^8R	—	1×10^{10}R	—	1×10^{10}R	1×10^{10}R	1×10^{10}R
Soil	—	—	—	—	—	Thin Film-Care Required for Backfill	NR	NR	NR
Weather & Light	Good, Yellows	Good	Excellent, Color & Glass Retention	NR	—	Good-Chalks	Excellent 20+ Years	Excellent 20+ Years	Excellent 20+ Years
Principal Hazard									
Application	Solvent Fumes	Solvent Fumes	Solvent Fumes	Phenol & Solvent	None	None-Water Base	Solvent Fumes	None	Fumes

[A]Critical for immersion. NR = Not Recommended.

Source: C.G. Munger, "Coatings—Resistant," Kirk-Othmer: *Encyclopedia of Chemical Technology,* 3rd Ed., Vol. 6 (New York, NY: John Wiley & Sons).

equaled by any second- or third-hand comments. Outside sources cannot evaluate the coating or coating potential with the same objectivity as someone who has made first-hand observations. However, this is not always possible, and outside reports and third-party evaluations may be the best information available. Nevertheless, wherever possible, personal inspections of existing coating installations are suggested whenever a critical coating selection is being made.

As previously stated in this chapter, no two applications are identical, and, therefore, a coating application in one plant can be considerably different from the coating in another. Nevertheless, the experience of vendors in the application and use of their coatings supplies important information and should also be taken into consideration during coating selection. Well-documented information on the life of a coating under similar conditions should be given serious consideration in the selection of any coating. Robert Baldwin, in his article, "Selecting Coatings for Plant Painting Projects," suggests:

Once the requirements and properties of various generic coatings have been compared to circumstances existing in the plant, the choices should be sufficiently narrowed so that specific formulations can be investigated. If it has not already been done, now is the time to involve the technical representatives of paint companies manufacturing all the generic types under consideration. They are intimately familiar with application and performance characteristics of their lines.

The following information should be obtained for each proprietary product:

- Resistance to corrosive chemicals
- Estimated life or recoating cycles
- Solids content by volume
- Mil feet per gallon
- Film thickness per coat
- Theoretical coverage per gallon
- Total applied cost of coating system
- Cost per square foot per year of service
- Names and addresses of users with exposure conditions similar to proposed plant project
- Ease of repairing damaged areas
- Recommended surface preparation
- Dry time and curing time
- Ease of application.

Each of the coatings under consideration should be compared item by item under these categories.[2]

Coating Cost

The cost of a coating is always given serious consideration in coating selection. There is no question that cost is a serious factor in coating selection. In fact, under some circumstances, it may be the only factor. Coating cost, however, in most circumstances should be less important than the coating properties that provide the basis for longtime, effective coating protection.

Cost should really only come into consideration once the coating or coatings have been selected that will satisfactorily overcome the corrosion problem for which they will be used. During the selection process, perhaps two or three coatings may all have the necessary qualifications. Cost, then, can enter the picture to determine which of the coatings that entirely satisfy the conditions involved will be the most economical choice.

It has been stated that the proper corrosion control system is the lowest cost system that will retain the qualities of the structure needed to fulfill the objectives of esthetics, safety, and performance throughout the service life of that structure. Retaining the structure qualities needed to fulfill the objectives is the key to this statement, and if a coating does not do this, for any reason whatsoever, cost becomes secondary.

Frequently coatings are selected by persons who are not entirely knowledgeable in the field, and lack the basic facts to make a sound decision. Statements like, "We can't afford to abrasive blast or to use exotic protective coatings like epoxy," are often made. However, a second-rate coating system used over less than the best surface preparation causes the company considerable losses because continual, costly maintenance is required to keep the structure from corroding to the point of becoming a safety hazard.

There have been numerous articles written on cost and how it should be related. Cost per square foot per year is a common way of comparing coatings and, generally, a good one. Cost studies can go from this point to discounted cash flow and the time value of money, all of which can become fairly complicated, even though they may present an accurate cost comparison.

It is not intended to include the details of this kind of cost comparison in this chapter. The NACE standard, "Direct Calculation of Economic Appraisals of Corrosion Control Measures,"[5] is an excellent reference if a detailed cost study is to be made. Another excellent cost comparison reference is a paper entitled, "The Simplified Cost Calculations and Comparisons of Paint and Protection Coating Systems, Expected Life and Economic Justification."[6] The information given in these two references should provide the details needed to begin an effective cost study.

Coating Properties

The properties of the coating itself are some of the most important considerations in coating selection. Many of the properties of various high-performance coatings are summarized in Table 12.7. This table provides a comparison of the generic types of coatings and their properties. However, this information alone should not be used to make the final decision as to what coating to select for any specific job. Once it is determined which generic type of coating needs to be used, then there is a direct comparison of the various coatings within that generic type. Without this further comparison, it is difficult to make a proper coating selection.

Generic Comparisons

It may be somewhat difficult to understand why it is necessary to test individual coatings in a generic type, even though they supposedly have been manufactured for similar exposures. Actually, there are hundreds of different formulations for any specific generic type of coating. Some manufacturers will take a standard formulation published either in a governmental specification or by a supplier, and manufacture the

coating according to that standard. Other manufacturers will use those standards as a starting point, and then spend considerable research time determining the best combination of ingredients within that generic type of material that will do the best job.

For instance, they may make a formulation that is easier to apply or that has less of a tendency toward problems like pinholing, they may add reinforcing pigments to the coating to make it tougher, they may add plate-type pigments such as mica to reduce the moisture vapor transformation rate, and they may add specific pigments to improve both the workability and the resistance of the coating. Since there can be such substantial differences between generic types of coatings, comparative testing is the only way to select the best material.

Comparative Tests

The best way to select a coating for a specific purpose, after determining the characteristics necessary, is to make comparative tests, both in the laboratory and under actual working conditions. While such a procedure is somewhat costly and requires the time of some technical personnel, where a large application job is involved, it can easily save many times the original coating cost before the job is completed or during the life of the coating.

The material cost of a coating is the smallest part of the cost of the total applied material. Thus, there is very little applied cost difference between a cheaper, less effective coating and the best coating that can be obtained. The difference, which amounts to a small percentage of the total job, is merely good insurance of adequate protection of the structure being coated.

Laboratory coating tests are, of course, the quickest and easiest to run. They can, however, be less than definitive. The testing of coatings under actual operating conditions is the most effective way of comparing the value of one coating over another. Figure 12.1 is an example of this. While the five inorganic systems tested were supposedly comparable, a field test in a marine atmosphere demonstrated the benefit of using this type of test for coating selection.

Figure 12.2 is an example of the actual field-testing of various types of coating systems under actual operating conditions. In this case, a petroleum production tank in an area of high hydrogen sulfide (H_2S) fumes required a better than average coating system to provide reasonable protection to the metal surface. The coatings involved in this test were IOZ (top), IOZ and polyamide epoxy topcoats (center), IOZ and an inorganic white topcoat (bottom), and an epoxy polyamide primer and epoxy polyamide topcoats (left side of tank).

The testing of coatings under marine conditions is a common practice. Panels may be exposed to a marine atmosphere, such as is illustrated in Figure 12.3, marine immersion conditions where panels are placed in tidal zones, or actual full immersion conditions. Such a marine test installation is shown in Figure 12.4.

A comparison of a series of antifouling coatings is shown in Figure 12.5. There are a number of commercial testing laboratories that have marine testing facilities. One of the best known is the LaQue Center for Corrosion Technology, Inc. (LCCT, Inc.) at Wrightsville Beach, North Carolina. Another is Ocean City Research at Ocean City, New Jersey. Many thousands of tests have been conducted at these stations, comparing materials, different coatings, different coating systems, and for many different companies throughout the United States, as well as for the United States Navy. These locations have become recognized standard marine test areas.

Many individual companies also maintain private panel testing stations in their plants at particularly corrosive areas. Such testing areas make for an easy comparison of coatings at relative-

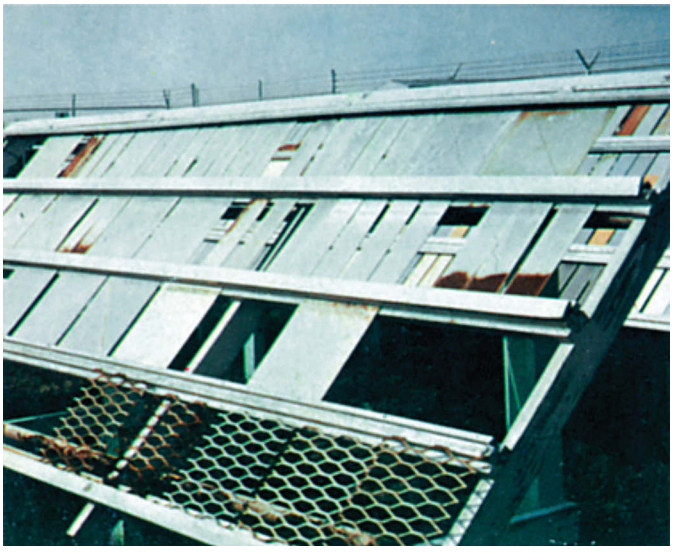


FIGURE 12.1: Comparative test of five IOZ coatings on expanded metal in a marine exposure. Best protection was provided by the center coating (no obvious corrosion), although originally all five were considered equivalent coatings.

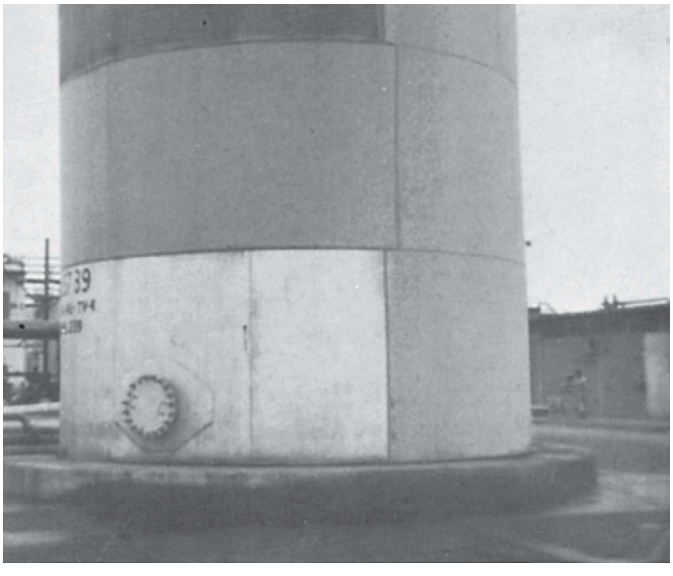


FIGURE 12.2: Field testing of various coatings exposed to actual operating conditions, which serves as an excellent method of coating comparison when time permits.



FIGURE 12.3: Test fence at the International Nickel Atmospheric Marine Test in Kure Beach, North Carolina.



FIGURE 12.4: Test panels, either fully immersed or subject to tidal variation, at the Battelle Memorial Institute's Tidal Marine Test Station in Daytona Beach, Florida.

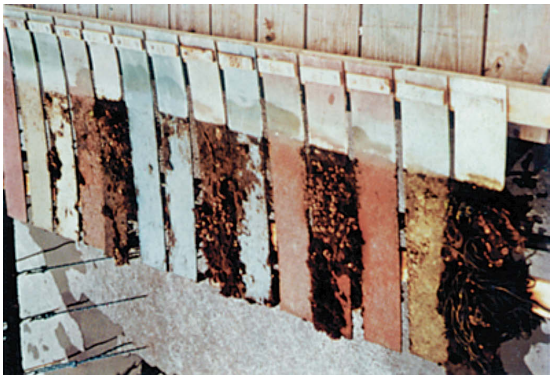


FIGURE 12.5: Series of antifouling test panels comparing the effectiveness of various coatings.

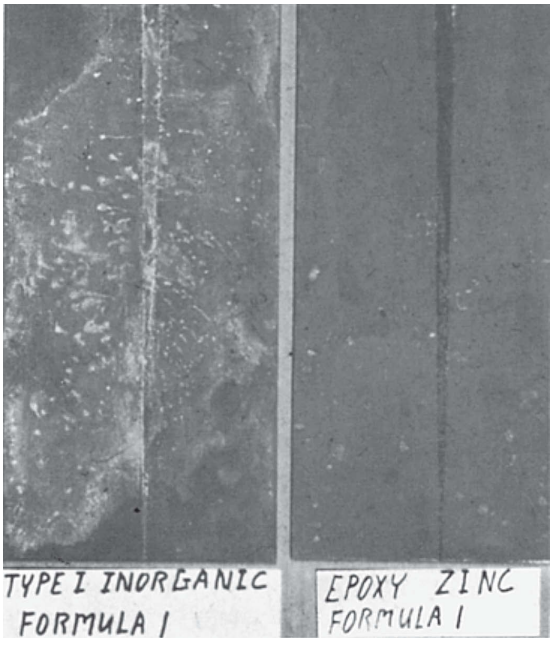


FIGURE 12.6: Comparison of two zinc-rich formulations after exposure to plant environmental conditions.

ly low cost. Once the panel preparation, which represents the greatest cost, has been completed, actual testing is merely a matter of time. Selection of a coating on the basis of such tests can be quite definitive with reasonably predictable results for large-scale applications.

Figure 12.6 shows the comparative testing of two zinc-rich coatings under plant operating conditions. Both were scribed down the center of the panel in equivalent manners. This test was of relatively short duration (a few weeks), and yet there was a decided difference between the protection provided by the two coatings.

Laboratory Tests

Laboratory coating tests can also provide some interesting comparative results. There are a number of laboratory tests that can be used essentially for screening purposes to indicate which coating can be most effective for a particular purpose. Laboratory tests can be quite valuable in determining a proper coating for an area where there is a single factor of corrosion or contamination involved. For example, a laboratory test can be definitive when comparing various coatings for exposure to 50% sodium hydroxide (NaOH) at 180 °F. This type of exposure can be easily duplicated in the laboratory. There are many similar types of exposures where laboratory tests would be equally effective.

There are, however, a great many exposures that include a number of variables (e.g., atmospheric corrosion in a plant). In cases such as these, laboratory tests can, at best, only be comparative between the materials or coatings being tested, and are only indicative of the resistance of the various materials to the actual plant exposure. Where there are many variables involved, it is preferable to test coatings under the actual exposure conditions. Small plant test racks holding only a few panels can be set up quite inexpensively.

Several organizations have established standards and methods for the laboratory testing of coatings. NACE Standard TM0174-2002, "Laboratory Methods for the Evaluation of Protective Coatings Used as Lining Materials in Immersion Service,"[7] outlines several comparative test methods for differentiating between coating materials. ASTM also has a number of standard tests to compare coating materials for various purposes. Table 12.8 lists some of the testing methods and standards established for coating comparison.

Salt Spray Tests

Laboratory comparison tests are used throughout industry to evaluate various coating materials. The salt spray test is one of the common laboratory tests that has been used by both government and industry for many years to compare the resistance of coatings. It consists of a fine mist of salt solution, which precipitates on the coating and keeps it continually wet with the dilute salt solution. The spray chamber is also highly aerated so that adequate oxygen is present for active corrosion.

It can be used as a test to compare coating adhesion, and as a test to compare resistance to the transfer of ions (e.g., sodium and chloride) through the coating. When a panel is scribed, it can be used as a test to determine the corrosion resistance of the coating and its resistance to undercutting. ASTM, in a description of the test, states:

The test has been used to a considerable extent for the purpose of comparing different materials or finishes. It should be noted that there is seldom a direct relation between salt spray (fog) resistance and resistance to corrosion in other media because the chemistry of the reactions, including the formation of films and their protective value, frequency varies greatly with the precise conditions encountered....Method B 117 is considered to be most useful in estimating the relative behavior of closely related materials in marine atmospheres, since it simulates the basic conditions with some acceleration due to either wetness or temperature or both.[8]

Figure 12.7 shows a typical salt spray cabinet, together with the pertinent working parts. This is taken from ASTM Standard B117-11, which fully describes the conditions, requirements, and workings of salt spray (fog) testing equipment.8 If a salt spray test is considered for evaluating coatings, it is recommended that the ASTM standard be followed.

Again, it should be reiterated that the salt spray test, as well as the other tests that will be described later, should be used only for comparison be-

tween coatings and should not be used as a tool to establish the life of a coating under actual operating conditions. Many years ago, Frank LaQue said, "The salt spray test only determines the life of a coating in the salt spray cabinet." The salt spray test, in particular, has been used to try to make such life comparisons, with people claiming that each hundred hours in a salt spray is equal to a year of life under actual conditions. Such life forecasts have never been accurately correlated between the laboratory test and actual life under service conditions. Any correlation that has been attempted has worked out poorly.

The most that can be said is that a coating that withstands salt spray for 1,000 to 2,000 hours without corrosion to the panel or damage to the coating itself should have good resistance to moist salt air conditions in the field, while those with good resistance up to 4,000 hours are likely to provide longer service lives in the same environment. Because of the many variables in field conditions, no measure of life can be accurately inferred from such a test.

Humidity Test

There are several types of humidity tests. The ASTM standard for testing Coated Metal Specimens at 100% Relative Humidity is ASTM D2247-11.[9] There are essentially two methods shown. The first is for a humidity cabinet similar to a salt spray cabinet in which panels are exposed to 100% humidity. The entire panel is exposed to condensing moisture.

The second is an apparatus where only one side of the panel is subject to humidity and condensation.9 This is the preferable procedure since it creates a temperature differential across the panel that makes a more severe test. This unit was developed by the Cleveland Society of the Federation of Societies of Paint Technology and is referred to as The Cleveland Test. The apparatus used is the Cleveland Condensing Type Humidity Cabinet. Details of the cabinet are shown in Figure 12.8.

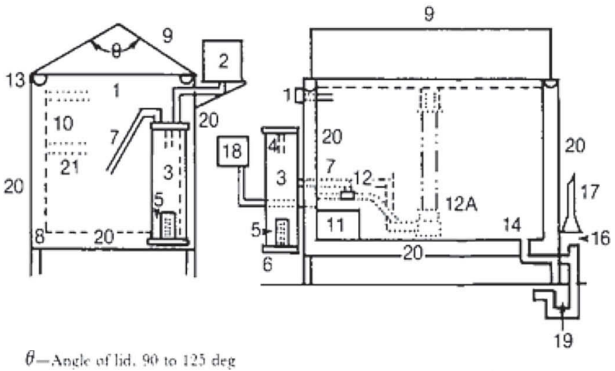
The Cleveland Test is one where coatings are compared for resistance to moisture condensation on the surface. The test mechanism has a storage area for water, which is kept warm and at a constant temperature by electric heaters. The panels are suspended on an angle above the water in such a manner that the moisture will constantly condense on the underside of the panel. The panels are held at a slight angle so that the condensed water runs off and is replaced by new condensation on a continual basis. If a coating has questionable adhesion, it will show up quickly in this test by the formation of blistering. Any coating that tends to release its adhesion under moist conditions will do so in this test.

As under most condensation conditions, the interior of the coating, or the coating that is exposed to the interior of this unit, is at a higher temperature than the surface of the panel on the exterior. Thus, there is a temperature gradient across the coating from the warm, moist interior to the cooler interface between the panel and the coating. Such conditions are much more severe than where a coating is merely immersed in a liquid with the temperature remaining the same over the entire panel.

This testing device can also be set up with an alternate wetting and drying condition, as well as with ultraviolet radiation. It is believed, however, that the primary value of this test is its ability to compare the water resistance and adhesion of various coatings.

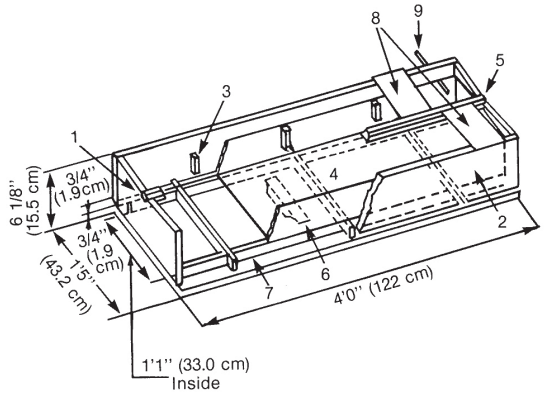
The Weatherometer Test

The weatherometer is a mechanical piece of test equipment in which there is an attempt to simulate weather conditions on an accelerated basis. The coating in most weatherometers is subject to cycles of warm water spray for a period of time. This is followed by a drying period, during which time high-intensity ultraviolet radiation is directed against the coating. These cycles of heating, cooling, wetting, drying, and radiation are accurately controlled. The panels are rotated around the light source to obtain even exposure, and the resistance of



θ—Angle of lid, 90 to 125 deg
1—Thermometer and thermostat for controlling heater (Item 8) in base
2—Automatic water levelling device
3—Humidifying tower
4—Automatic temperature regulator for controlling heater (Item 5)
5—Immersion heater, non-rusting
6—Air inlet, multiple openings
7—Air tube to spray nozzle
8—Strip heater in base
9—Hinged top, hydraulically operated or counterbalanced
10—Brackets for rods supporting specimens or test table
11—Internal reservoir
12—Spray nozzle above reservoir, suitably designed, located, and baffled
12A—Spray nozzle housed in dispersion tower located preferably in center of cabinet
13—Water seal
14—Combination drain and exhaust. Exhaust at opposite side of test space from spray nozzle (Item 12), but preferably in combination with drain, waste trap, and forced draft waste pipe (Items 16, 17, and 19).
16—Complete separation between forced draft waste pipe (Item 17) and combination drain and exhaust (Items 14 and 19) to avoid undesirable suction or back pressure.
17—Forced draft waste pipe
18—Automatic levelling device for reservoir
19—Waste trap
20—Air space or water jacket
21—Test table or rack, well below roof area

FIGURE 12.7: Typical salt spray (fog) cabinet. Source: ASTM, Salt Spray (Fog) Testing, Standard B117-11.



1—End supports, 3/4 by 6 1/8 in. by 1 ft 3 1/2 in. (1.9 by 15.5 by 39.4 cm) (slanted 1/4 in./8 in. (0.64 cm/20.3 cm) toward center).
2—Raised side supports, 3/4 by 4 7/8 in. by 4.0 ft. (1.9 by 12.4 by 122 cm).
3—Tank spacers, 1/2 by 3/8 by 2 1/2 in. (1.3 by 0.95 by 6.4 cm).
4—Water tank, 14 1/2 by 46 1/2 by 3 in. (36.8 by 118 by 7.6 cm) (distilled water and stainless steel preferred).
5—Depressed central panel support (rigid insulating type, for example, methylmethacrylate resin).
6—Six strip heaters (attached to bottom of tank) spaced equally for uniform heat, rheostat-controlled (115-V, 150-W steel sheath strip heaters and 7 1/2-A capacity rheostat).
7—Tank support and heat barrier, 3/4 by 1 3/8 in. (1.9 by 3.5-cm) stock.
8—Typical 8-in. (20.3-cm) long test panels or blanks (all positions on cabinet must be occupied) (blanks may be glass).
9—Thermometer (bulb 1 in. (2.5 cm) below test surface).

NOTE 1—Arrangement of 2 and 3 permits access of fresh air.
NOTE 2—A satisfactory construction material is 3/4-in. (1.9-cm) exterior grade plywood coated with a polyamide crosslinked epoxy.

FIGURE 12.8: Cleveland condensing humidity cabinet. Source: ASTM, Coated Metal Specimen at 100% Relative Humidity, Standard D2247-11, Philadephia, PA.

TABLE 12.8: Standard Methods of Testing Coatings and Linings	
ASTM B117-11	Standard Practice for Operating Salt Spray (Fog) Apparatus
ASTM B287-74	Acetic Acid-Salt Spray (Fog) Testing (Withdrawn 1987.)
ASTM B368-09	Standard Test Method for Copper Accelerated Acetic Acid Salt Spray (Fog) Testing (CASS test).
ASTM D610-08 (2012)	Standard Practice for Evaluating Degree of Rusting on Painted Steel Surfaces
ASTM D659-86	Method of Evaluating Degree of Chalking of Exterior Paints (Withdrawn 1989)
ASTM D660-93 (2011)	Standard Test Method for Evaluating Degree of Checking of Exterior Paints
ASTM D661-93 (2011)	Standard Test Method for Evaluating Degree of Cracking of Exterior Paints
ASTM D662-93 (2011	Standard Test Method for Evaluating Degree of Erosion of Exterior Paints
ASTM D714-02 (2009)	Standard Test Method for Evaluating Degree of Blistering of Exterior Paints
ASTM D772-86 (2011)	Standard Test Method for Evaluating Degree of Flaking (Scaling) of Exterior Paints
ASTM D822-01 (2006)	Standard Practice for Filtered Open Flame Carbon Arc Exposures for Paint and Related Coatings
ASTM D823-95 (2012) e1	Standard Practice for Producing Films of Uniform Thickness of Paint, Varnish, Lacquer, and Related Products on Test Panels
ASTM D870-09	Standard Practice for Testing Water Resistance of Coatings Using Water
ASTM D968-05 (2010)	Standard Test for Abrasion Resistance of Organic Coatings by Falling Abrasive Varnish, Lacquer, and Related Products by the Falling Sand Method
ASTM D1005-95 (2007)	Standard Test Method of Measuring Dry Film Thickness of Organic Coatings using Micrometers
ASTM D1014-09	Standard Test Method for Conducting Exterior Exposure Tests for Paints and Coatings on Metal Substrates.
ASTM D1186-93	Standard Test Method for Non-Destructive Measurement of Dry Film Thickness of Non-Magnetic Coatings Applied to a Ferrous Base.
ASTM D1212-01 (2007)e1	Standard Test Method for Measurement of Wet Film Thickness of Organic Coatings
ASTM D1400-94	Standard Test Method for Measurement of Dry Film Thickness of Nonmetallic Coatings applied to a Nonferrous Base
ASTM D-1653-03 (2008)	Standard Test Method for Water Vapor Transmission of Organic Coating Films
ASTM D1654-08	Standard Test Method for Evaluation of Painted or Coated Specimens Subject to Corrosive Environments
ASTM D1735-08	Standard Practice for Testing Water Resistance of Coatings using Water Fog Apparatus.
ASTM D2197-10	Standard Test Method for Adhesion of Organic Coatings by Scrape Adhesion
ASTM D2247-11	Standard Practice for Testing Water Resistance of coatings at 100% Relative Humidity
ASTM D3258-04 (2010) e1	Standard Test Method for White or Near White Paint Films by Staining
ASTM D3276-07	Standard Guide for Paint Inspection (Metal Substrates)
ASTM D3359-09e2	Standard Test Methods for Measuring Adhesion by Tape Test
ASTM D3361-02 (2006)	Standard Test Method for Unfiltered Open Flame Carbon Arc Exposures of Paint and Related Coatings.
ASTM D3363-05 (2011) e2	Standard Test Method for Film Hardness by Pencil Test
ASTM E376-11	Standard Practice for Measuring Coating Thickness by Magnetic Field or Eddy Current (Electromagnetic) Test Methods)
ASTM G8-96 (2010)	Standard Test Methods for Cathodic Disbondment of Pipeline Coatings.
ASTM G12-07	Standard Test Method for Nondestructive Measurement of Film Thickness of Pipe Line Coatings on Steel

the coating is measured in weatherometer hours. While this is a good comparative test, it should not be used as a definitive measure of the coating life under actual operating conditions.

ASTM has several standards related to the Weatherometer:

1. Recommended practice G23-93 for operating light and water-exposure apparatus (carbon arc type) for exposure of nonmetallic materials.
2. Recommended practice D822-01 (2006) for operating light and water-exposure apparatus for testing paint, var- nish, lacquer, and related products.
3. Recommended practice D3361-02 (2006) for operating light-and water-exposure apparatus (unfiltered carbon arc type) for testing paint, varnish, lacquer, and related products using the sea cycle.[10]

The weatherometer test compares the coatings for resistance to ultraviolet and simulated solar radiation, and can measure the comparative resistance of the coating to chalking, checking, cracking, rusting, blistering, and similar breakdown. It also can be used to measure gloss retention and color change. The wetting and drying cycle also has some merit in testing the adhesion of a coating, since such treatment causes accelerated stress within the coating similar to what it might receive in ordinary weather conditions. This type of testing can cause rapid failure in the coating film, and good control panels are required to obtain a proper comparison.

The above three tests, the salt spray, humidity tester, and weatherometer, make a good series of screening tests for coatings to withstand atmospheric exposure; either rural, mild industrial, or marine. A coating that stands up well under all three should also stand up well under actual exposure. However, no interpolation of actual life should be made from these tests.

J.A. Burgbacher, in a paper, "Laboratory Evaluation of Protective Coatings for Marine Environments,"[11] outlines a series of tests that were developed to determine the marine resistance of coatings for use on offshore platforms. He used a series of three tests: continuous immersion, salt spray, and intermittent immersion in seawater. A summary of the findings of these tests on comparing a large number of different types of coatings is interesting and might apply as well to the salt spray, humidity, and Weatherometer tests.

In summary, a series of tests has been devised to screen protective coatings for marine applications. These tests are so severe, poorer

TABLE 12.8: Standard Methods of Testing Coatings and Linings (continued)	
ASTM G23-93	Standard Practice for Operating Light Exposure Apparatus (Carbon Arc Type) With and Without Water for Exposure of Non-Metallic Materials
ISO 1513:2010	Examination and preparation of test samples.
ISO 1514:2004	Standard panels for testing
ISO 1518-1:2011	Determination of scratch resistance—Part 1: Constant Loading Method
ISO 1518-2:2011	Determination of scratch resistance—Part 2: Variable Loading Method
ISO 2409:2013	Cross-cut test
ISO 2810:2004	Natural weathering of coatings—Exposure and Assessment
ISO 2812-1:2007	Determination of resistance to liquids—Part 1: Immersion in Liquids other than water.
ISO 2812-2:2007	Determination of resistance—Part 2, Immersion in water.
ISO 4624	Pull Off Test for Adhesion using Portable Adhesion Testers.
ISO 4628-2:2003	Evaluation of degradation of coatings—Part 2: Assessment of degree of blistering.
ISO 4628-3:2003	Evaluation of degradation of coatings—Part 3: Assessment of degree of rusting.
ISO 4628-4:2003	Evaluation of degradation of coatings—Part 3: Assessment of degree of cracking.
ISO 4628-5:2003	Evaluation of degradation of coatings—Part 3: Assessment of degree of flaking
ISO 4628-6:2003	Evaluation of degradation of coatings—Part 3: Assessment of degree of chalking by the tape method.
ISO 4628-8:2004	Evaluation of degradation of coatings—Part 8: Assessment of degree of delamination and corrosion around a scribe or other artificial defect.
ISO 6270-1:1998	Determination Resistance to Humidity—Part 1: Continuous Condensation.
ISO 6270-2:2005	Determination Resistance to Humidity—Part 2: Procedure for exposing test specimens in condensation water atmosphores.
ISO 6272	Resistance to a Falling Weight
ISO 7253	Resistance to Neutral Salt Spray @ 350C
ISO 11341:2004	Artificial Weathering and exposure to artificial radiation—Exposure to filtered xenon arc radiation
ISO 12944-6:1998	Corrosion Protection of steel structures by protective paint systems—Part 6 Laboratory Performance Test Methods.
ISO 16276-1:2007	Assessment of and Acceptance Criteria for the adhesion/cohesion (fracture strength) of a coating—Part 1:Pull-off Testing.
ISO 16276-2:2007	Assessment of and Acceptance Criteria for the adhesion/cohesion (fracture strength) of a coating—Part 2: Cross-cut and X-cut Testing.
ISO/DIS 17463	Determination of corrosion protection properties of organic coatings by the accelerated cycle electrochemical technique (ACET)
ISO 20340:2009	Performance requirements for protective paint systems for offshore and related structures.
ISO 29601:2011	Corrosion protection by protective paint systems—Assessment of porosity in a dry film.
NACE TM0112-2002	Test to Determine the Potential Corrosion Effects of Ballast Water Treatment Systems on Ballast Tanks.
NACE TM0174-2002	Laboratory Methods for the Evaluation of Protective Coatings Used as Lining Materials in Immersion Service
NACE TM0304-2004	Offshore Platform and Splash Zone Maintenance Coating System Evaluation.
NACE TM0404-2004	Offshore Platform Atmospheric and Splash Zone New Construction Coating System Evaluation.
Source: A Web-based search of international Standards most commonly applicable to selection of coating systems. Louis D. Vincent PhD (March 2013).	

formulations fail in two weeks. Variations in performance of coating systems of any given generic type suggest that a testing program can be extremely profitable.

Coatings that perform poorly in the test will, in all probability, give substandard performance offshore. Conversely, outstanding performance should be expected from the system that showed least deterioration on tests. Somewhere between these extremes the corrosion engineer will have to establish the cutoff as to which coatings merit consideration and this decision will have to be based largely on practical experience.[11]

Cyclic Torture Tests

Proprietary cyclic tests have been developed that are combinations of the above with the additional ingredient being a method of creating a severe drop in temperature over a short time span followed by reheating in an humid atmosphere. While the equipment and cycles vary between proprietary systems, the basic procedure involves several days of exposure to Cleveland Humidity or Weather-ometer testing, followed by 12 hours in freezing conditions then several days exposure to heated salt fog. The cycles are repeated for a pre-set number or cycles or continued to failure of the best coating system in the test. Besides providing freeze-thaw exposure, these tests are also a measure of the coating systems' absorption and desorption properties.

Control Panels

Control panels, or specimens, are extremely important in all laboratory testing. It is only by controls that the tests can be compared with a standard. For example, if a series of coatings is tested in a humidity test and there is no control, the only knowledge gained is the resistance of the coatings in comparison with each other. If a control is included (e.g., a coating which is known to have good humidity resistance), the information obtained is not only comparative within the coatings tested, but also provides a comparison with a proven coating. This provides a standard of comparison by which to make the coating selection.

Exposure test racks, both for weathering and for marine exposures, are a valuable way of comparing coatings. However, because the



FIGURE 12.9: Typical coated KTA panels exposed under plant conditions.

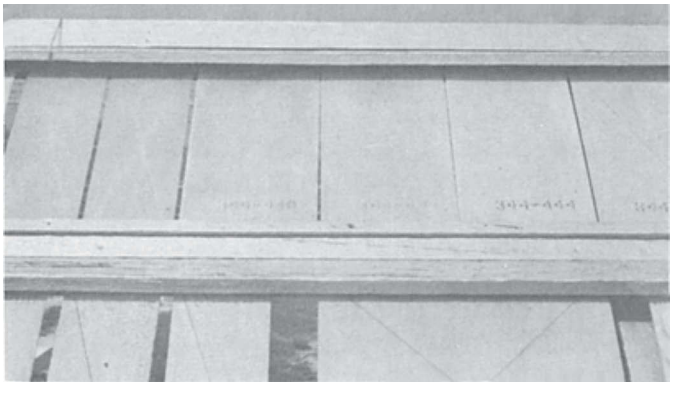


FIGURE 12.10: Typical atmospheric exposure rack showing three different sized panels, most of which are scribed.

TABLE 12.9: Screening Test Reagents for Coatings and Linings

Simple Immersion	
Water	
Neutral Salt	Sodium Chloride
Acid Salt	Ferric Chloride
Alkaline Salt	Sodium Carbonate
Oxidizing Salt	Sodium Hypochlorite
Acid	10% Sulfuric Acid
Volatile Acid	10% Hydrochloric Acid
Oxidizing Acid	10% Nitric Acid
Organic Acid	Acetic Acid
Alkali	10% Sodium Hydroxide
Aliphatic Hydrocarbon	Gasoline—VM&P Naphtha
Aromatic Hydrocarbon	Toluol
Vegetable Oil	Corn Oil
Alcohol	Ethyl Alcohol
Chlorinated Hydrocarbon	Trichlorethylene
Ester	Butyl Acetate
Ketone	Methyl Isobutyl Ketones

coatings are usually exposed to an extremely severe weather or marine atmosphere, actual applications may not follow the same pattern as indicated in the test.

Actual operating condition tests are also valuable. This is the exposure of test panels directly on a structure where the coating is to be used. Where the structure is large and the atmosphere is relatively constant around the structure, this is a good comparison procedure and should determine which coating would be most satisfactory in that exposure. However, there are some problems involved as well. If panels are applied directly to the structure, problems may result from that direct contact. It is always recommended that panels be insulated from both the structure and each other so that there is no outside influence on any particular test.

An example of this was the installation of a series of IOZ panels on the interior of a tanker. The test was to determine whether the IOZs would stand such an exposure. The panels were welded directly to the steel in the tanker tank, and since the IOZ is anodic to steel, the panels attempted to protect the entire tank and thus failed rather rapidly. On the other hand, when this was discovered and the panels were insulated from the tank, a good comparison of the various IOZ coatings resulted.

Test Panels

There have been many different types of panels recommended for testing in various corrosive atmospheres. These are specially constructed in an attempt to illustrate all of the variables found in a steel structure, including angles, corners, crevices, welds, and so forth. However, because of the panel complexity, variation in application may cause a variation in the results obtained. Whenever such panels are used, the application variable should be taken into consideration.

Figure 12.9 shows two coated panels that had been exposed in an acidic atmosphere on a rack attached to the plant structure. The comparison of the two coating systems involved is very good.

Flat, rectangular panels are generally preferred for the comparative testing of coatings. These can vary in size, depending on the desires of the person testing, and can range from 2×6-in panels to 12×12 in or larger. A preferred size is 4 × 8 in. Such a panel provides sufficient area to reduce the edge effects (corrosion and undercutting on the panel edges), is small enough so that a number of panels can be placed on one rack, and is large enough that a uniform coating can be applied. The coatings also can be scribed to test the corrosion resistance of the coating.

The flat panel has the advantage that most of the application variable is eliminated when the samples are carefully prepared, making for a more consistent comparison of the coatings being tested. Figure 12.10 shows three different size exposure panels: 4 × 12 in, 6 × 12 in, and 12 × 12 in.

Immersion Tests

The selection of coatings or linings for immersion service is often somewhat easier than one for general atmospheric service. This is because most immersion service is rather specific and therefore a laboratory test can be set up that can reasonably duplicate the conditions under which the coating must operate. For example, in testing for marine immersion, coatings can be immersed in 3% salt solution that provides many of the conditions that exist in marine immersion. The one thing that it does not include is the high oxygen content of the water, particularly just below the splash zone. This can be accomplished by adding air to the static immersion test. In this case, the air is merely bubbled through the salt solution, saturating it with oxygen. This makes a simple and yet effective immersion test for many coatings. Again, while the test itself is not entirely definitive, the comparison of coatings in this test does indicate those that will perform better in actual service. An even better method is to use actual seawater in this immersion test, also bubbling air through the liquid. However, this is not necessarily an accelerated test. Nevertheless, it is one that can be done

in the laboratory without the necessity of traveling back and forth to a marine test station.

There are many other simple immersion tests used to determine the resistance of a coating. Some specific ones could be sugar syrup at 82 °C (180 °F), 50% caustic soda at 65 °C (150 °F), or crude petroleum at 70 °C (158 °F). Each of the above could be the condition on the interior of a storage tank, so that duplication of the conditions in a laboratory is relatively easy, and the results of the test can be quite definitive.

A recommended series of screening tests is shown in Table 12.9. There are few coatings that will withstand all of these reagents. On the other hand, when determining the general resistance of a series of coatings, it does indicate the resistance area of the various coatings being tested. All of these are simple immersion tests and require only a closed container of sufficient size that a sample can be placed within the liquid. Usually, it is good to have the sample half in and half out of the liquid, since many times the adhesion of the coating will change at the water line. When the coating is tested for adhesion across that area, the line can easily be detected. This is an important part of the test, since some of the reagents may very well cause the coating to lose adhesion without any other obvious reaction.

Other simple tests that may be made on these immersion samples would be hardness (before and after immersion), swelling and softness of the coating as compared with its original state, and possibly, an increase or decrease in weight of the sample. There are also many other obvious results, such as blistering, discoloration, and actual dissolution, all of which can provide some valuable information regarding the resistance of the coating. Even where some specific requirements are necessary for a coating, this series of tests can give a good indication of a coating's overall resistance, even though the coating composition may be unknown prior to the test.

There is another, more specific yet valuable test for the evaluation of coatings and linings. This is the so-called one-side test, or tests using Atlas cells. This test consists of applying a coating to one side of a plate and fastening it into the test apparatus with the coating on the inside and the bare steel on the outside. This not only tests the coating for specific resistance to the liquid contained in the test container, but where there is a temperature differential from the test liquid to the outside ambient air, it also tests the ability of the coating to withstand the temperature differential between the internal and the external surfaces of the coating. This is the normal condition of a coating on the interior of an uninsulated tank. This is a practical test and is an excellent way to determine the adhesion of a lining to a container. Most internal coatings and linings are subject to this differential temperature.

In this apparatus, there are generally two plates, one for each side of the container. This is illustrated in Figure 12.11, which shows the various parts of the test apparatus. Figure 12.12 indicates the apparatus in use, with all of the electrical connections, condensers, monitors, and other equipment that can be used, particularly when the cells are at elevated temperatures. Variations of this test include the use of three zones of exposure inside the Atlas cell such as unleaded gasoline, water, and vapor space. The intent is to duplicate the conditions inside a tank where vapor space exists above the cargo and a water pad can accumulate on the tank bottom as a result of condensation.

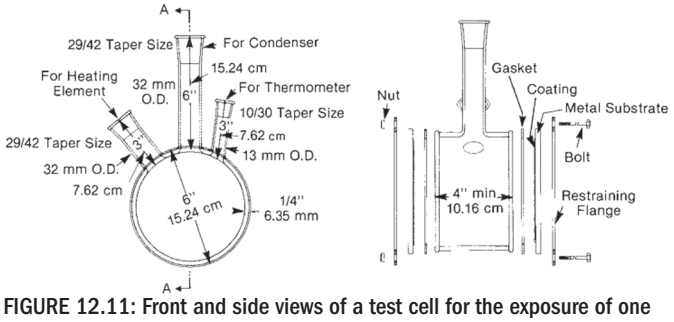


FIGURE 12.11: Front and side views of a test cell for the exposure of one side of two separate panels that are mounted on the cell. This glass cell has openings for a thermometer, a condenser, and a heating element. Source: NACE TM0174, "Laboratory Methods for the Evaluation of Protective Coatings Used as Lining Materials in Immersion Service" (Houston, TX: NACE, 1974.).

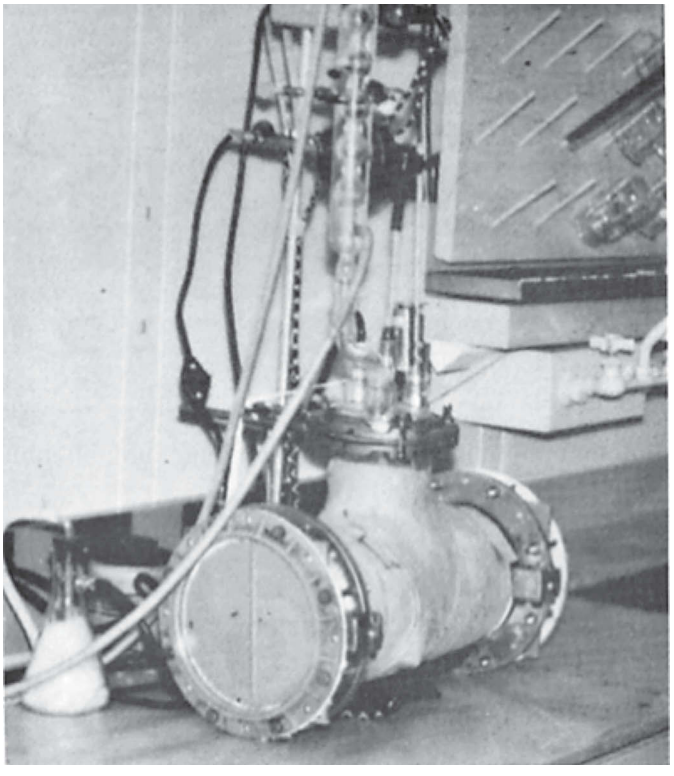


FIGURE 12.12: Illustration of a test cell for one-side testing designed to approximate the volume-to-surface ratio found in a standard 8000-gal (30.283-liter) tank car. Source: NACE TM0174, "Laboratory Methods for the Evaluation of Protective Coatings Used as Lining Materials in Immersion Service" (Houston, TX: NACE, 1974).

These last two series of tests, the simple immersion test and the one-side test, are well described in a NACE Standard entitled, "Laboratory Methods for the Evaluation of Protec-tive Coatings Used as Lining Materials in Immersion Service."[7] Selection of a lining is greatly simplified if the lining material performs satisfactorily in these one-side and simple immersion tests.

Electrochemical Impedance Spectroscopy

In recent years, Electrical Impedance Spectroscopy (EIS) has been used extensively in both manufacturer and independent laboratory testing to provide a guide to expected performance of a coating or coating system in an intended service—most commonly immersion in either water or hydrocarbon liquids. The impedance of a coating, determined by EIS, is the electrical resistance of the coating, as measured by alternating current electricity. Coating impedance can be regarded as a measure of barrier properties or, con-

versely, a measure of permeability to water, gases, and small-molecule corrosive species. Impedance measurements are most applicable for coatings system used in water immersion or in environments with high humidity. High-performance coatings with excellent barrier properties have high impedance (i.e., low permeability to water). Poor performance coatings with high permeability to water have low impedance. Whereas this is a very useful tool in the hands of an experience analytical chemist, it is a very complicated process that has to be carefully set up in an attempt to replicate the expected service conditions. As a result, correlation to years of service cannot be accurately determined.

Summary

As discussed, there are many methods of selecting coatings for a particular use. Some of the most common ones are:

1. Select a coating based on cost. This is not recommended.
2. Select coatings from general charts of generic coatings. This provides information on the general properties of coatings.
3. Compare literature on coatings from various manufacturers. This gives information on what coatings are available
4. Request coatings information from various vendors. This provides information on the coatings that are available.
5. Make laboratory comparison tests of coatings from several manufacturers. This provides specific information on the resistance of various coatings.
6. Obtain a recommendation for a coating from the supplier with the best reputation in the field. This provides an outside source of information based on experience.
7. Make a selection of a coating from field tests. This indicates a coating that is the best one tested.
8. Select a coating based on personal experience. This may be the best criteria if the experience is similar to the proposed coating exposure.

The above methods of coating selection are generally in order of increasing value. Actually, the best procedure is to use all of the methods, combining the information developed. The question of coating material cost should only be considered after all other selection methods have been explored. If the above procedure is followed, a good coating selection can be made for almost any exposure.

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13 Coatings and Cathodic Protection

Introduction

Coatings and cathodic protection (CP) have often stood on opposite sides of the fence as mutually exclusive and opposing approaches to corrosion protection. Proponents of coatings are often on one side discounting the advantages of CP and claiming that a good, well-applied coating is the only necessary protection for steel. On the other side are proponents of CP, who often claim that any immersed or buried metal structure can best be protected by a well-engineered CP installation. In some conditions, both sides may be correct in their assertions. However, under many more commonly occurring conditions, the ideal corrosion protection is actually a combination of both protection concepts.

CP and coatings are both engineering disciplines with the primary purpose of mitigating and preventing corrosion.[1] Each process is different. CP prevents corrosion by introducing electrical currents from external sources to counteract the normal electrochemical corrosion reactions. Coatings form a barrier to prevent the flow of corrosion current between the naturally occurring anodes and cathodes or within galvanic couples. Each of these processes has been successful in its own right. Coatings by far represent the most widespread method of general corrosion prevention. CP, however, has protected hundreds of thousands of miles of pipe and acres of steel surface subject to buried or immersion conditions.

As corrosion protection has become more critical, and all types of metal structures more valuable, a marriage of the two corrosion prevention systems has naturally occurred. Experience has shown that damage to organically coated structures is almost unavoidable during construction and service. Breaks or holidays in coatings expose metal surfaces to corrosion, particularly in underground or immersion service. Attempts to eliminate all coating holidays drastically increases costs and are usually unwarranted. Thus, under many conditions, the combination of both systems actually provides better, more reliable, and, in many cases, less costly corrosion protection.

The concept of corrosion protection by coatings has been well described in earlier chapters. In the case of coatings for use with CP, it is necessary to use those coatings that are based on the impervious coating concept. This is because wherever coatings are used in connection with CP, they generally must be either immersed or in moist underground conditions. Without immersion or moisture, the CP mechanism will not operate properly.

As discussed in a previous chapter, the impervious coating concept requires the coating to be relatively impervious to the transfer of moisture, oxygen, air, and the various ions that may be in contact with the coating. Also, it must be resistant to the passage of electrons or electric current so that it forms an impervious film over the surface to be protected. As previously noted, the coating is not fully impervious to moisture vapor. Each coating material has a moisture vapor transfer rate characteristic of that particular material. Nevertheless, the coatings used in connection with CP are much more impervious than those types of coatings used in atmospheric exposures. Figure 13.1 is an example of a coating that should be satisfactory with CP.

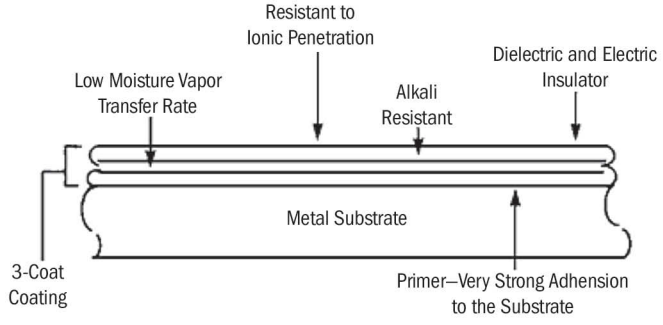


FIGURE 13.1: An example of a coating that is compatible with CP.

Cathodic Protection

Cathodic protection is a technique used to reduce the corrosion of a metal surface by providing it with enough cathodic current to make its anodic dissolution rate become negligible. The CP concept operates by extinguishing the potential difference between the local anodic and cathodic surfaces through the application of sufficient current to polarize the cathodes to the potential of the anodes. In other words, the effect of applying cathodic currents is to reduce the area that continues to act as an anode, rather than reduce the rate of corrosion of such remaining anodes. Complete protection is achieved when all of the anodes have been extinguished.

From an electrochemical standpoint, this indicates that sufficient electrons have been supplied to the metal to be protected, so that any tendency for the metal to ionize or go into solution has been neutralized. Frank LaQue summarized this when he said:

> The most probable mechanism of cathodic protection of steel in seawater is a sufficient number of electrons from a preferred external source to accommodate a cathodic reaction, such as oxygen reduction or hydrogen evolution, over the whole surface of the metal being protected. Without cathodic protection, the electrons reacting with oxygen at the cathodic surfaces must be supplied by corrosion at the anodic areas. As additional electrons are supplied from an external source, the oxygen reduction reaction is accommodated by these additional

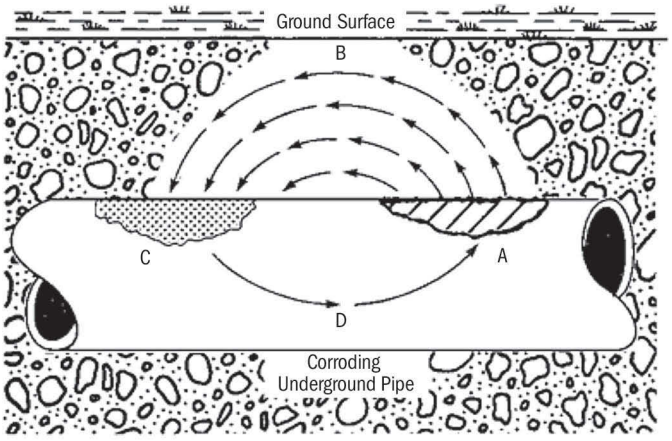


FIGURE 13.2: DC flow on a typical corroding structure: (A) anodic area, where current leaves the steel to enter the surrounding earth—steel is being corroded here; (B) current flow through earth from anodic area to cathodic area; (C) cathodic area, no corrosion at pipe surface; and (D) current flows through the pipe steel from cathodic area back to anodic area to complete the circuit. Source: *Corrosion Basics—An Introduction*, Chapter 5, "Cathodic Protection," L.S. Van Delinder, ed. (Houston, TX: NACE, 1984), p. 179.

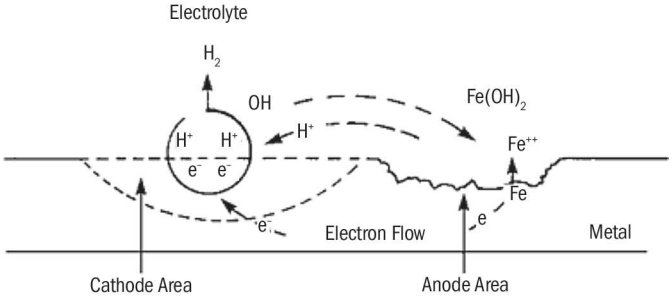


FIGURE 13.3: Electron flow concept of a corrosion cell.

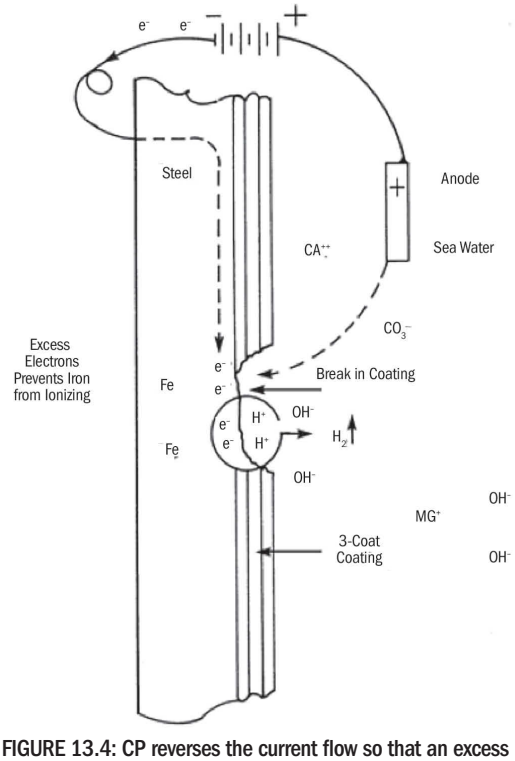


FIGURE 13.4: CP reverses the current flow so that an excess of electrons is present on the metal to be protected. Source: C.G. Munger, R.C. Robinson, "Coatings and Cathodic Protection," *MP* 7 (1981).

electrons; and fewer are required from the original anodes, some of which are converted to cathodes. The current reaching the cathodic surfaces from the remaining anodes decreases as the external current increases so that the total cathodic current density (CD) does not change substantially until all of the anodes are extinguished and the CD increases on the whole of the metal surfaces.[2]

An understanding of CP can be complicated by the existence of two different concepts concerning the direction of current flow in a corrosion cell. The engineering approach, which is used by most CP engineers, shows the current flow from the area of corroding metal through the electrolyte to the cathode (Figure 13.2). As indicated, the circuit is completed by the current returning from the cathode to the anode through the metal.

The scientific concept of the corrosion cell is that the iron changes from metallic to ionic iron at the area of corrosion, while simultaneously releasing electrons. These electrons pass through the metal to the cathode area where the cathodic reactions, such as oxygen reduction and formation of hydrogen gas, occur. The circuit is completed through the electrolyte by the transfer of positive charges, derived from the positive ions coming from the anode (i.e., corroding area), in the general direction of the cathode. It is this neutralization of the electrons that is the controlling factor in the corrosion that exists at the anode.

The reason for the existence of two different concepts is that theory on the direction of electric current flow was presented before the electron theory had been fully developed. The electron flow concept (Figure 13.3) is easier to understand than the electric current flow concept, although the latter is the one most commonly used in electrical engineering.

The purpose of CP is to reverse the current flow or electron flow so that an excess of electrons is present on the metal to be protected. With an excess of electrons, corrosion is reduced to nil. In other words, when there is an excess of electrons on a steel surface, any tendency for the iron to go into solution as a positive ion is reduced to zero. As long as there are negative electrons present in excess, all of the positive iron ions are held in the metal surface (Figure 13.4).

Coatings

The current or electron flow is the key to any corrosion that takes place at the anode. The total amount of corrosion that will occur on the anode is directly proportional to the total value of current flow in the circuit, while the penetration rate is a function of the CD per unit area and is directly related to the anode/cathode area ratios.3 This area relationship is extremely important. As previously discussed, if there is, for instance, a large anode with an area of 100 coupled to a small cathode with an area of 1, the corrosion on the anode will be only slight. On the other hand, if the area ratios are reversed so that the cathode area is 100 and the anode area is 1, the corrosion at the anode will be severe. This is why coatings become important in reducing the size of any cathodic area to a minimum and reducing the current flow to a small quantity. This is indicated in Table 13.1, which shows the approximate current requirements for protection of steel in various environments.

As can be seen from Table 13.1, the CP required varies over a wide range, depending on the area involved. The table also shows that a poorly coated area of steel in water requires substantially less CP than bare steel under the same conditions. A well-coated area of steel under the same conditions requires less than 1/1,000 of the current required for even a poorly coated area steel. Reducing the area where CP is required and providing a dam or impervious coating over the surface clearly reduces the CP requirements of the substrate while still providing full protection.

The coating mechanism of providing a dam that prevents any current flow to or from the surface of the metal is quite complex. This is due to the many variables that exist in a coating, many of which can be directly affected by reactions at the anode or cathode or by the mechanism of CP.[1]

Coating Characteristics

Where coatings are used with CP, they must have several essential physical and chemical properties in order to be effective. Most of these are illustrated in Figure 13.1.

TABLE 13.1: Approximate Current Requirements for Cathodic Protection of Steel

Environment	mA/ft^2	mA/m^2
Sulfuric Acid Pickle (Hot)	35,000	380,000
Seawater		
Cook Inlet	35–40	350–430
North Sea	8–15	90–160
Arabian Gulf	7–10	80–110
U.S. Coast	7–8	80–90
Gulf of Mexico	5–6	50–60
Indonesia	5–6	50–60
Soil	1–3	10–30
Poorly Coated Steel in Soil or Water	0.1	1.0
Well-Coated Steel in Soil or Water	0.003	0.03
Well-Coating Steel in Soil or Water	0.0003 or less	0.0023 or less

Source: R.S. Treseder, ed., *NACE Engineers Reference Book* (Houston, TX: NACE, 1980).

Dielectric Strength

A coating used with CP must have good dielectric strength. Its dielectric characteristics must be sufficient so that both CP potentials and current flows would not affect its ability to act as a corrosion prevention membrane. When a CP potential is applied to a steel surface, the coating over that surface must have sufficient dielectric strength to resist the potential and to prevent any current flow through the coating. Coatings with a low dielectric strength, or those that will allow some current flow, often allow the buildup of cathodic deposits on the surface or under the coating, causing coating breakdown. This is a common occurrence where coatings contain metallic pigments.

Adhesion

Any coating, in order to be effective under immersion conditions, and particularly when combined with CP, must have strong adhesion to the surface over which it is applied. Marginal basic adhesion, or marginal adhesion caused by the application of the coating over less than properly prepared surfaces, will cause early coating breakdown when subject to CP potentials. If there is marginal adhesion and if there are breaks in the coating, which CP is designed to protect, delamination of the coating from the surface, blistering, or both, may occur.

Electroendosmosis

Adhesion is also important where electroendosmosis may be encountered. Electroendosmosis is defined as the forcing of water through a semipermeable membrane by an electrical potential in the direction of the pole that has the same charge as the coating membrane. Most coatings

are negatively charged, and under CP, the cathode has an excess of negative electrons, making it negatively charged. Thus, under CP, coatings with a high moisture vapor transfer rate and/or questionable adhesion would be more subject to damage and blistering by cathodic potentials.

This has often occurred under actual CP exposures where extensive blistering of pipeline coatings has occurred. The blisters were all filled with liquid, indicating the electroendosmotic reaction. Similar conditions have occurred in water tanks where adhesion was poor prior to the application of the cathodic current. While there is no corrosion to the steel underneath the coating, there is usually a substantial increase in current demand.

Alkali Resistance

It is essential that the coating be chemical-resistant, particularly toward alkalies. One of the key chemical reactions that take place at the cathode is the development of a strong concentration of hydroxyl ions. This is due to the removal of the hydrogen ions in the area by the excess of electrons that are present on the cathode. This is illustrated in the chemical diagrams for the formation of molecular hydrogen.

$$\underset{\text{Water}}{2H_2O} \rightarrow \underset{\text{Hydrogen Ion}}{2H^+} + \underset{\text{Water Ionization}}{2OH^-} \quad \underset{\text{Hydroxyl Ion}}{} \qquad (13.1)$$

$$\underset{\text{Hydrogen}}{2H^+} + \underset{\text{Electrons}}{2e^-} \rightarrow \underset{\text{Cathode Reaction}}{H^2} \quad \underset{\text{Molecular Hydrogen}}{} \qquad (13.2)$$

As shown, each molecule of hydrogen that is formed on the cathode leaves two free hydroxyl ions in the area that creates the strong alkaline condition. If the coating is not sufficiently alkali-resistant, it can be completely disintegrated by this strong alkaline reaction. Even the current flow between local anode and cathode areas on a piece of steel can develop sufficient alkali to disintegrate some coatings in the cathode area. Coatings that contain aluminum pigment and are subject to CP often fail because of the reaction of the alkali with the metallic aluminum.

Ionic Resistance

The coating also must be resistant to the passage of ions. While this may be considered a part of chemical resistance, there are many variations in the susceptibility of coatings to ionic transfer based on coating composition. When combined with CP, it can be readily understood that a coating that had some tendency to transmit either positive or negative ions might soon be forced from the surface by the action of the cathodic current. Its electrical resistance would be affected, as well as its resistance to the passage of moisture. Coatings have, in fact, been forced from the surface by the formation of calcareous salts underneath the coating due to CP currents.

Electron Resistance

Resistance to the passage of electrons is equally important for coatings that are used with CP. Apparently, some coatings readily transmit electrons, since large buildups of calcareous deposits have been seen on the surface of coatings exposed to cathodic currents. Inorganic coatings that are not dielectric can allow calcareous deposits to form. In fact, this reaction has occurred with some epoxy coatings.

Coating Thickness

Coating thickness is an extremely important characteristic, particularly where coatings are to be combined with CP. Several critical properties are directly affected by thickness. Electrical resistance is improved as coating thicknesses increase. The moisture vapor transfer rate is directly proportional to coating thickness. Ionic transfer is reduced as the coating becomes thicker, as is electron movement.

Therefore, to be practical when used with CP, the coating should have an optimum thickness for the coating type involved. Coating thickness may have a negative effect on adhesion under certain circumstances. For example, unreinforced epoxy coatings applied at too great a thickness may continue to cure, shrink, crack, and, in many cases, have been known to actually pull themselves off from the steel substrate. Therefore, the thickness of the coating should be as great as is practical based on its composition.

Moisture Vapor Transfer Rate

The coating, to be effective under immersion conditions while also subject to electric potentials, should have a low moisture vapor transfer rate, as well as low moisture absorption. Moisture absorption is the molecular moisture that is absorbed into and held within the molecular structure of the coating. This property is important to coating effectiveness only where the moisture absorption might be sufficiently high to lower the dielectric characteristics of the coating and therefore, offer less resistance to the passage of the current.

Moisture vapor transfer, on the other hand, is important, not only to a coating used for immersion service, but even more so to one exposed to an exterior source of current, such as CP potentials. Coatings with a high moisture vapor transfer rate are much more susceptible to electroendosmosis than are tightly adherent coatings with a low moisture vapor transfer rate. It is a general rule of thumb, all other properties being equal, that the lower the moisture vapor transfer, the more effective the coating.

Inorganic Zinc Coatings

The coating properties described in the previous section are generally for organic coatings, and the characteristics described are particularly important for organic coatings. The inorganic zinc (IOZ) coatings, which are also important for corrosion prevention, do not necessarily have these same characteristics. On the other hand, IOZ coatings, including galvanizing, can be used in connection with CP, and excellent results can be obtained.

As previously discussed in Chapter 6, on IOZ coatings, these materials are designed to provide CP and to produce a potential that is close to that of freely corroding zinc. In the case of galvanized steel, the potential would be the same as that of zinc. These coatings are also conductive in order to provide CP so that any impressed cathodic current can freely pass through the coating with little or no effect on it.

This has been proven in a number of areas, particularly in tidal zones where IOZ coatings alone have been applied to piling or offshore structures down to below the mean low tide level. The remainder of the area was protected by CP so that the tidal area of the IOZ coating received CP during the time when the surface was covered with water. In these instances, the CP applied to the structure merely augmented the protection offered by the IOZ without harm to the inorganic coating. As a matter of fact, the electrons impressed on the surface by the CP current prevented either the underlying steel or the zinc from going into solution during the time that the area was covered with water, while the IOZ coating protected the area during exposure to the atmosphere.

The IOZ coatings, because of their excellent adhesion, combining both mechanical and chemical adhesion to the steel, have made an excellent base over which to apply organic coatings and to reduce both the undercutting and blistering that might occur where the organic coating was applied to the steel surface alone. This same characteristic of providing an excellent base coat for organic coatings also applies to many organic coatings subject to CP. An IOZ base coat provides the strong adhesion needed by the organic materials to resist the CP current. IOZ coatings can, then, be used in connection with organic coatings to improve coating effectiveness when combined with CP. This has been proven through actual service, as well as by extensive laboratory tests.

Chemical Reactions

When considering the use of CP and coatings, the chemical reactions that take place at the anode and cathode areas are very important. Some of these reactions were briefly considered earlier in the chapter. However, due to their significance, a full description of the processes in the order they occur is warranted.

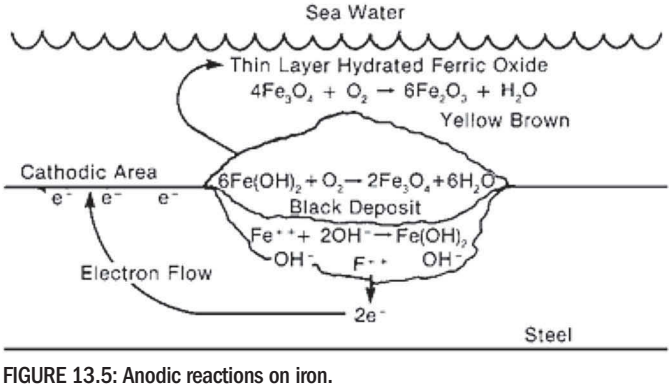


FIGURE 13.5: Anodic reactions on iron.

Anodic Reaction

The anodic reaction should be considered first. While this reaction is extremely important in the corrosion process, it is much less important where the CP process is involved. When metallic iron is placed in an electrolyte, an almost immediate solution of the iron takes place at specific areas on the surface. These areas are usually corners, edges, sharp protrusions, or any area where the metal has been damaged. The iron goes into solution as the ferrous ion, and in so doing, releases electrons into the metal substrate. Iron ions going into solution quickly react with the hydroxyl ions in the area, forming ferrous hydroxide. This can then continue to react with oxygen, forming the black oxide of iron, and continuing even further to the red oxide of iron. The insolubilization of the iron ion as soon as it goes into solution creates a continuing demand for the iron ion, so that as long as there is an outlet for the electrons that are released, the iron will continue to go into solution (Figure 13.5).

Cathodic Reactions

The most important reactions shown in Figure 13.5 are those of the iron going into solution as ions and the release of the elec-

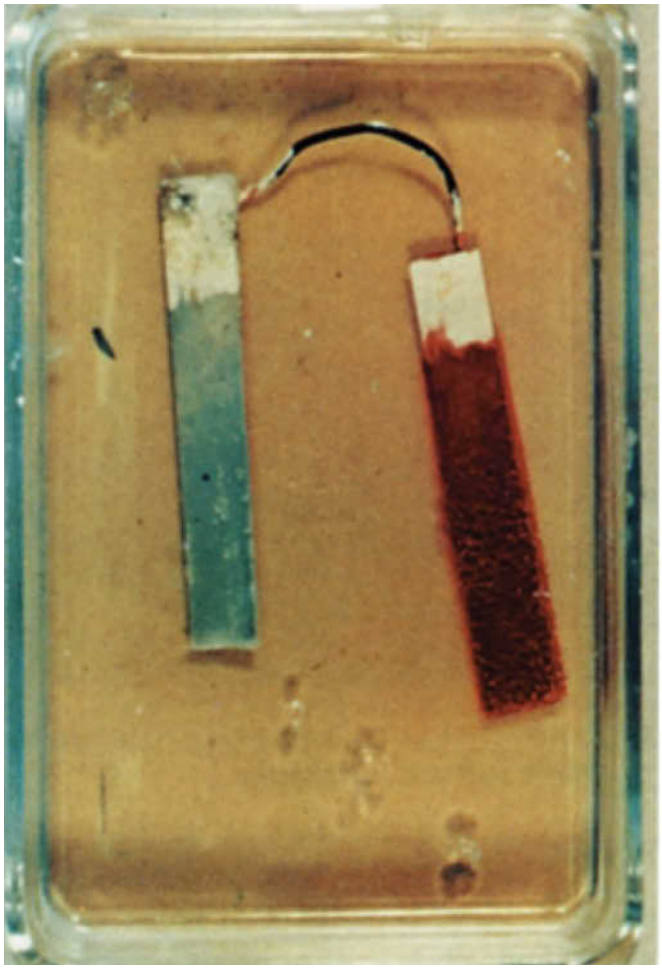


FIGURE 13.6: A zinc-iron couple in a phenolthalein indicator bath. The bright red iron panel has an excess of OH^- ions and is being cathodically protected by the zinc.

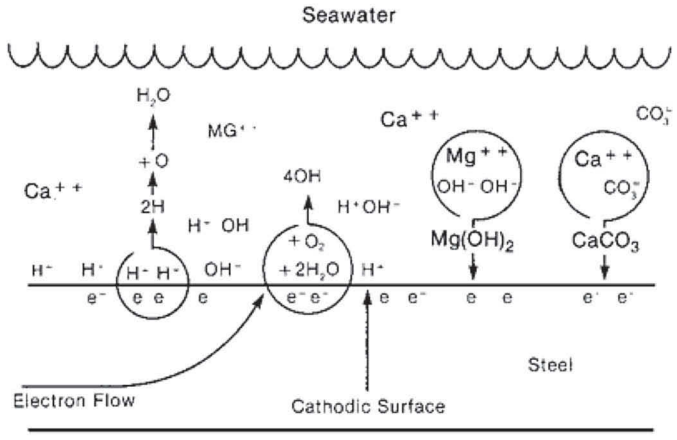


FIGURE 13.7: Chemical reactions at the cathode under CP. Source: C.G. Munger, R.C. Robinson, "Coatings and Cathodic Protection," *MP* 20, 7 (1981).

trons. The action of CP on this freely corroding iron anode is to reverse the process by creating an excess of the electrons on the iron surface. The excess of electrons, from whatever outside source, reduces the tendency or ability of the iron to form ions, so that no iron goes into the solution. It can be said that the solution potential of the iron has been completely neutralized by the excess electrons. When this occurs, the anodic area, or the pit, becomes cathodic and thus prevents the iron from going into solution.

The chemical reactions at the cathode are the most important since as they take over under CP; the entire surface becomes cathodic. Thus, any coating applied over such a surface is subject only to the cathodic chemical reactions. As the metal surface is saturated with electrons from whatever exterior source and the water adjacent to the surface is ionized, the hydrogen ions from the water react with the electrons on the surface forming atomic hydrogen, which can then react with the oxygen that is dissolved in the water to form additional water.

The second reaction that occurs is for water and oxygen to absorb electrons, thus forming hydroxyl ions. These two reactions absorb electrons from the surface, which need to be continually replaced in order for CP to be effective. They are continually replaced from an outside source of electrons, either an impressed current or current from a galvanic anode. With a coating over the surface, these two reactions occur only at a break in the coating, as was shown in Figure 13.4. The remainder of the surface is insulated from the liquid, and if the coating is impervious, as it should be, no reaction occurs underneath or on the coating.

There are two other reactions at the cathode, involving calcium and magnesium ions. Seawater, or even fresh water, it must be remembered, contains calcium and magnesium ions in solution. As the hydrogen ions are removed from the metal surface, hydroxyl ions are left in excess close to the metal surface. Hydroxyl ions are also generated by the reaction of the electrons with water and oxygen. This creates a heavy concentration of the negative hydroxyl ions, which is easily demonstrated with zinc and an iron panel connected by an exterior wire in a phenolthalein indicator solution. When there are hydroxyl ions present, the phenolthalein becomes bright red.

Figure 13.6 shows the iron-zinc couple. Note the bright red coloration of the iron panel that is being cathodically protected by the zinc panel. This concentration of hydroxyl ions is sufficient to disintegrate many alkali reactive coatings that might be used under CP conditions.

This excess of hydroxyl ions, which creates an unstable situation in the water layer adjacent to the steel, is demonstrated in Figure 13.7. This causes the calcium and magnesium ions to react with the hydroxyl ions and the carbon dioxide (CO_2) from the air, forming magnesium hydroxide [$Mg(OH)_2$] and calcium carbonate ($CaCO_3$). These materials precipitate on the steel surface and can build up a substantial calcium deposit. This reaction is verified by W. Fink in *The Corrosion of Metals in a Marine Environment*,[4] in which he says:

> The application of cathodic current promotes the formation of hydroxyl ions on the cathodic areas. Also, the concentration of calcium and magnesium ions tends to increase in the film of seawater over the cathodes. As a result of these changes, the solubility of calcium carbonate and magnesium hydroxide is exceeded and the calcareous coating is deposited.[4]

All of these reactions are shown in Figure 13.7. That these calcium deposits are built up is indicated in Figure 13.8, which shows a center pole of a coated domestic water tank with linear holidays in the coating. CP was also used on the tank, and the calcareous deposits build up wherever a coating holiday occurred.

Consequences of Poor Coating Selection

The cathodic reactions that occur when CP is applied to a steel surface have a definite bearing on the effectiveness of the coating



FIGURE 13.8: Calcareous deposits built up at holidays in the coating on the center pole of a domestic water tank. Deposits are due to impressed current CP.

applied over the steel surface. The coatings, which become a part of a coating and CP system, must be designed to overcome any of these chemical reactions. The following are some examples of the effects of CP on coatings when the coatings are not properly selected or formulated.

Hydrogen Blistering

A coating that has high water absorption or a high moisture vapor transfer rate will have moisture available at the steel coating interface and, as such, the electrons that are present there can react with the ionized hydrogen ions, forming hydrogen gas. If the adhesion of the coating is questionable, hydrogen blisters can form due to the hydrogen produced from the moisture. This is not an uncommon occurrence, even though the hydrogen has to develop at a sufficient rate to build up pressure underneath the coating.

In some cases, coatings are sufficiently porous to hydrogen so that any of the gas produced would pass through the coating rather than produce blisters. Of course, when this occurs, there are excess hydroxyl ions that develop and create a strongly alkaline condition underneath the coating, which can also act to release the coating adhesion and to react with any acidic pigments or other acidic materials that may exist within the coating itself.

Reactive Pigments

Often, metallic pigments, such as aluminum, are incorporated into a coating to help reduce the moisture vapor transfer and to make the coating more impervious to water. Aluminum pigments are very reactive with alkalies. Particularly under an excess of CP, coatings containing aluminum pigments may disintegrate because of the reaction of the aluminum and hydroxyl ions.

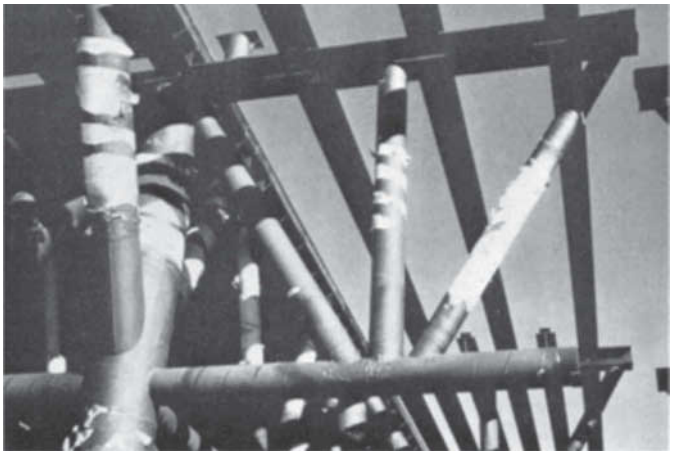


FIGURE 13.9: A coal tar wrap on an offshore platform where CP built calcareous deposits under the coating and stripped it from the surface.

Delamination

Coatings that allow some ionic penetration, or are sufficiently affected by the hydroxyl ion buildup at the coating-steel interface to allow ionic penetration, may actually be pushed off from the surface by the precipitation of the calcareous deposit underneath the coating. In this case, the coating is pushed off from the surface and usually breaks and spalls away, leaving a large area to be cathodically protected.

This has been shown to take place in tests of asphaltic-based coatings, which were softened by the reaction of the hydroxyl ions and were then pushed off from the surface. Figure 13.9 shows an offshore platform that was taken out of service. The coal tar wrap coating was damaged, and CP deposits had built up under the coating at the damaged area, pushing it off from the surface. In this instance, the white deposits are the calcium deposits from the cathodic reaction.

Calcareous Deposits

Some coatings seem to be permeable to electrons. In this case, the electrons pass through the organic coating and are neutralized on the surface of the coating. When this occurs, the calcareous deposit can build up on the exterior of the coating. In fact, with only a small amount of excess cathodic current, quite a heavy layer can build up. While this has been demonstrated in tests, it is not common in actual practice.

Special Problems

Inorganic Coatings

Inorganic coatings are, of course, porous to electrons. As a matter of fact, the IOZ coating concept is based on the solution of the zinc in the coating and the development of electrons to provide CP. When the CP current is at, or no more than, the potential developed by the iron-zinc couple, little or no reaction occurs within the coating. In this case, the zinc in the coating does not go into solution, and the coating acts as an effective film.

On the other hand, if an excess of electrons is forced onto the surface by an impressed current system with a higher potential than the zinc-iron potential, excess alkali can build up and possible breakdown of the IOZ coating can occur. Hydrogen can also be produced, and while the IOZ coating is porous, if sufficient hydrogen is produced within the coating, blistering can occur. It is also possible for the calcareous deposits to form on the outside of the zinc coating so that all of the cathodic reactions would have some effect, providing the cathodic current is applied in excess of that needed for corrosion protection.

Vinyl Coatings

Vinyl coatings generally have excellent alkali resistance and are resistant to the transfer of ions, as well as having a relatively low moisture vapor transfer rate. They generally perform well under CP, as long as the cathodic potential is not increased above the 1-V limit. Most vinyl coatings rely on acid groups built into the molecule for adhesion to metal surfaces. Many of the primers for vinyl resins are formed from a tripolymer that contains maleic acid ($C_4H_4O_4$). While this has a bond to the steel, it may still react with excess hydroxyl

ions that may be formed by absorbed moisture in the film. This reaction with the acid groups on the vinyl resin molecule tends to release the coating adhesion and create blistering.

All of these are examples of negative reactions of CP with the use of coatings, and are primarily demonstrations of what can happen if the wrong coating is selected or the CP system is improperly designed for the coating that has been selected. This is to emphasize the importance of considering the CP and the coating as parts of an overall protective system, which must be designed together in order to obtain proper effectiveness. There are actually millions of square feet of surface that are protected by both coatings and CP, and they are generally performing better than either one of the protective systems alone.

Testing

With the number of coating systems available today, there have been several tests established to determine the comparative resistance of various coatings combined with CP. The object of these tests is to determine which coating systems perform best under CP conditions.

Early Tests

There were some early tests run at the Harbor Island Test Station at Wrightsville Beach, North Carolina, as well as some tests established at the North Florida Test Station of the Battelle Memorial Institute at Daytona Beach, Florida. These tests were conducted in the early 1950s, and the principal coatings that appeared satisfactory for marine immersion at that time were the vinyl, epoxy, asphalt, and early IOZ coatings. Each of these coating types was tested, using a range of CP potentials varying from zero for the control and beginning with −0.8 V and increasing the potential in increments to −1.4 V to determine the effect of such potentials on the various coatings. Duplicate panels of each coating were used, one scribed and one unscribed. The tests were conducted in natural seawater, with the tide changes creating a flow of seawater across the panels at all times.

This series of tests was one of the first, if not the first, well-controlled tests to determine the effect of CP on coatings. In these tests, all of the coatings performed reasonably satisfactorily below a 1-V negative potential, and each of the coatings failed rather characteristically at negative potentials above 1 V. Tests were conducted over a one-year period, keeping the potentials as constant as possible.

Where the negative potential was above 1 V, each of the coatings reacted differently. For example, the vinyl coating tended to blister along the scribed area, with calcareous deposits forming in the scribe. The asphalt coating became generally soft and mushy, with the greatest effect occurring in the area of the scribe. This was attributed to the high concentration of alkaline hydroxyl ions reacting with the ingredients in the asphalt coating.

The epoxy coating that was used, an amine cured epoxy, reacted quite differently. In this case, there was a fine, general blistering of the coating overall, indicating the possible formation of hydrogen on the steel underneath the coating. In addition to this, under the higher potentials, calcareous deposits formed on the surface of the coating in a heavy, thick layer. This indicated that there must have been a transfer of electrons through the coating, causing the precipitation of the calcareous salts over the entire surface. In this case, the precipitation of calcium deposits was not at the scribe alone, but extended out over the entire panel. Thickness appeared to be a controlling factor, as well as the general coating resistance.

The vinyl coatings that were applied in thicknesses of only 2 mils showed some effect on the coating at all potentials, while the vinyl coatings that were applied at 8 mils showed little effect at potentials over 1 V in the one-year test period. The vinyl coatings were also overcoated with an antifouling paint and were unaffected, even at the direct iron-magnesium potential. The antifouling coating continued to be effective, even at these potentials.

The early IOZ coatings were also included in this test. Surprisingly, at voltages above 1 V, some blisters formed in the coating, indicating considerable hydrogen formation, and the formation of calcareous deposits over the surface as well.

The conclusions drawn from these early tests were:

1. Coatings, to be effective, must be dielectric so as to prevent the passage of cathodic current through the coating.
2. The coating must be resistant to moisture vapor transfer in order to prevent hydrogen blistering.
3. Coatings must be highly resistant to alkalies so that they are not disintegrated, or the adhesive bond affected by the high hydroxyl concentration.
4. Coatings must be of sufficient thickness to prevent the passage of current and to maintain a dielectric condition.
5. None of the coatings was appreciably affected at the negative potential of −0.9 V.

These early tests were among the first controlled tests of coatings and CP and they helped establish the −850 to −800 mV range of potentials for the effective use of coatings with CP.

Later Tests

There were later tests established to determine the effect of cathodic current on coatings. One test series was set up to determine the compatibility of impressed current CP (ICCP) in connection with IOZ coatings, both alone and overcoated.[5] The samples tested were bare steel; zinc anode material; steel with zinc primer only; steel with a complete paint system, including IOZ primer, 8 mils of epoxy coating, plus 3 mils of an antifouling; and the previous coating system without the zinc primer. The tests were designed to answer five basic questions.

1. At what polarization levels and CD will hydrogen gas begin to evolve from bare steel?
2. At what polarization level and CD will hydrogen gas begin to evolve from bare zinc anode material?
3. Will hydrogen gas evolution begin at the same level when IOZ primer is cathodically protected?
4. How will topcoats affect the activity of the zinc primer?
5. How does a system containing zinc primer compare with the same system without zinc primer?

The answers to these questions were:

1. A polarization level at which hydrogen gas evolution begins on bare steel is −996 mV and a CD of 35 mA per square foot.
2. A polarization at which hydrogen gas begins to evolve from the surface of the zinc anode material is −1.33 volts at a CD of 67 mA per square foot.

TABLE 13.2: Cathodic Disbonding Determinations for Coated Steel Pipe Specimen[1]

		Determination[2]		
		Unsealed[3]	Potential[4]	
Specimen Coating	Exposure Cathodic Time, Days	Areas sq. cm.	Volts to CSE	Current mA
Extruded Polyethylene	0	0.3	–1.18	1.00
Butyl Rubber Primer	699	0.3	–1.17	0.03
Avg. 45 Mils DFT				
Polyethylene Tape	0	0.3	–1.18	1.65
Double Wrapped	365	0.3	–1.18	
Avg. 40 Mils DFT	699	0.3	–1.15	0.40
Coal Tar Epoxy	0	0.3	–1.16	1.35
No primer	84	0.3	–1.15	0.72
Avg. 24 Mils DFT	334	5.4	–1.18	0.47
Powdered Epoxy	0	0.3	–1.19	1.53
Avg. 19 Mils DFT	299	25.8	–1.20	1.78
	365	67.9	–1.20	2.65

[1]Specimens were 4 in diameter X 24 in long pipe with one end plugged.

[2]Tests were conducted using ASTM G872 procedures.

[3]One ¾ in diameter holiday was drilled through coating prior to test.

[4]Pipe potential to copper sulfate electrode (CSE) determined after magnesium anode disconnected.

3. Polarization levels at which hydrogen evolution began on the IOZ primer were about –1.31 V, and a CD of 64 mA per square foot.
4. A polarization level of the zinc primer plus the topcoat was similar to the zinc primer only.
5. Without the zinc primer, the epoxy coating polarized and began hydrogen evolution at a slightly higher potential than that of bare steel.

The conclusions from this series of tests were:

1. The CD and the polarization levels at which hydrogen gas begins to evolve from the surface of the IOZ primer are higher than that for similar paint systems without the zinc primer.
2. Any potential and CD that is safe with the epoxy system without the zinc primer is also safe for the systems including the zinc primer.
3. In order to avoid damage to either coating system, the polarization level of 1 volt referenced to a silver chloride half-cell must not be exceeded.



FIGURE 13.10: Cathodic disbonding test for pipe coatings with the four magnesium anodes at the corners of the salt tank.

Cathodic Disbonding Tests

There are numerous underground coatings that are often combined with CP. There have also been a number of tests to determine the most effective combination. One of these is the cathodic disbonding test where coated pipe samples are subject to cathodic current to determine their adhesion retention and resistance to cathodic potentials and current flow. One such test was carried out with four different pipe coatings. This is conducted on 4-in (102-mm) pipe, 24 in (0.61 m) long, in accordance with ASTM G8726 procedures (Figure 13.10).

The results of these cathodic disbonding tests are shown in Table 13.2, with the pipe coatings tested listed in the order of increasing disbonding of the coating at the holiday. The two polyethylene coated pipes, extruded and double wrapped, were unaffected during the tests. This is due to the high dielectric strength, excellent adhesion, and coating thickness (40 mils). The coal tar epoxy showed only minor disbonding after approximately one year's exposure, while the powdered epoxy coating showed a disbonded area of more than 10 times that of the coal tar epoxy.

Three of the pipe sections are shown in Figure 13.11, with the polyethylene tape showing no disbonding, the coal tar epoxy showing a minor undercutting at the ¼ in (6.4 mm) drilled hole, while the powdered epoxy shows a relatively large area (the area marked out in black) of coating disruption. Basic adhesion, water resistance, and coating thickness can account for the different performances of the coal tar epoxy and the powdered epoxy. All coatings were subject to a direct couple to a magnesium anode with approximately 1.5 V potential.



FIGURE 13.11: Cathodic action at the small holiday in each pipe: Pipe 1—polyethylene tape, double wrapped (40 mils); Pipe 2—coal tar epoxy (24 mils); and Pipe 3—powdered epoxy (19 mils). Source: Ameron Corp., Monterey Park, California.

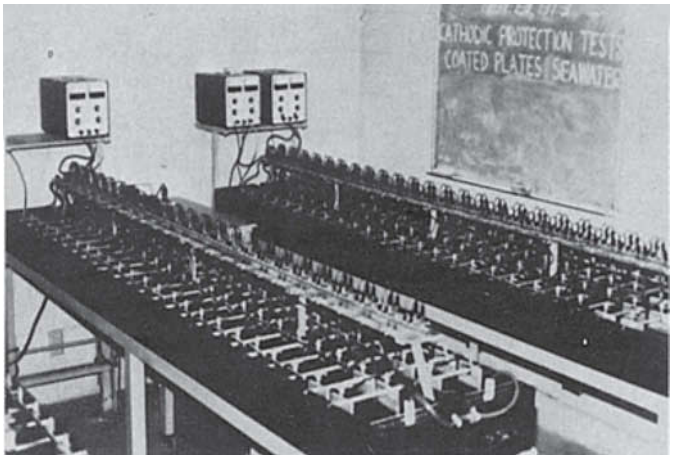


FIGURE 13.12: Apparatus for testing samples of four specimens of each coating system without and with CP at −850, −1100, and −1200 mV protection levels. Source: Ameron Corp., Monterey Park, CA.

General Testing

In 1975, Ameron, Inc. began an extensive series of tests to evaluate a number of coating combinations under CP, representing one of the most carefully controlled and extensive series known.7 There were 23 coating systems put into test subject to potentials of 0.0, –850, –1,100, and –1,200 mV, compared to a copper/copper sulfate ($Cu/CuSO_4$) reference cell. The coating systems are listed in Table 13.3. Actually, three different test series were initiated during the five-year period, since many of the coating systems failed quickly and were replaced by other systems.

The test specimens consisted of four 8 in x 7 in x 9 ft (203 mm x 179 mm x 2.7 m) wooden cells filled with synthetic seawater and equipped with water circulating and aeration devices, make-up and renewal systems, necessary electrodes, potentiostats, wiring, shunts, and monitoring instruments. To provide ICCP,

TABLE 13.3: Coating Systems Tested

#	Description	Total Avg. Dry Film Thickness (mils)
1	Inhibitive Epoxy Primer (2 mils) Epoxy Polyamide Topcoat (6 mils)	8.6
2	Inhibitive Epoxy Primer (2 mils) Epoxy Polyamide Topcoat (6 mils) (Panels Unscribed)	8.8
3	Epoxy Polyamide Topcoat (4 mils) Epoxy Polyamide Topcoat (4 mils)	7.6
4	Inhibitive Epoxy Primer (2 mils) Epoxy Polyamide Topcoat (6 mils) Epoxy Polyamide Topcoat (6 mils)	13.9
5	Salt-Contaminated Surface Inhibitive Epoxy Primer (2 mils) Epoxy Polyamide Topcoat (6 mils) Copper/Rosin Antifoulant (4 mils)	11.3
6	IOZ Primer (0.75 mil) Inhibitive Epoxy Primer (2 mils) Epoxy Polyamide Topcoat (6 mils)	9.4
7	IOZ Primer (0.75 mil) Inhibitive Epoxy Primer (2 mils) Epoxy Polyamide Topcoat (6 mils) Copper/Rosin Antifoulant (5 mils)	13.8
8	Salt-Contaminated Surface IOZ Primer (0.75 mil) Inhibitive Epoxy Primer (2 mils) Epoxy Polyamide Topcoat (6 mils) Copper/Rosin Antifoulant (5 mils)	14.7
9	Epoxy Amine Primer (5 mils) Epoxy Amine Topcoat (6 mils)	11.4
10	High Solids Epoxy Amine	10.3
11	100% Solids Epoxy Cladding	188.0
12	One Coat Coal Tar Epoxy Polyamide	18.2
13	Inhibitive Epoxy Primer (2 mils) Coal Tar Epoxy Polyamide (10 mils)	13.3
14	Inhibitive Epoxy Primer (2 mils) Coal Tar Epoxy Polyamide (18 mils)	21.6
15	IOZ Primer (3 mils) Inhibitive Epoxy Primer (2 mils) Coal Tar Epoxy Polyamide (16 mils)	22.7
16	Coal Tar Epoxy Amine (9 mils) Coal Tar Epoxy Amine (9 mils)	17.9
17	Inhibitive Epoxy Primer (2 mils) Coal Tar Epoxy Amine (9 mils)	11.6
18	Inhibitive Epoxy Primer (2 mils) Coal Tar Epoxy Amine (9 mils) Coal Tar Epoxy Amine (9 mils)	19.3
19	Aluminum Chlorinated Rubber Primer (9 mils) Chlorinated Rubber Topcoat (6 mils)	9.8
20	Aluminum Chlorinated Rubber Primer (3 mils) Aluminum Chlorinated Rubber Primer (3 mils) Chlorinated Rubber Topcoat (6 mils)	6.5
22	Chlorinated Rubber Primer (3 mils) Chlorinated Rubber Topcoat (3 mils) Chlorinated Rubber Topcoat (3 mils)	9.1
23	Aluminum Pigmented Hydrocarbon Coat (2.5mils) Aluminum Pigmented Hydrocarbon Coat (2.5mils) Aluminum Pigmented Hydrocarbon Coat 2.5mils)	7.0

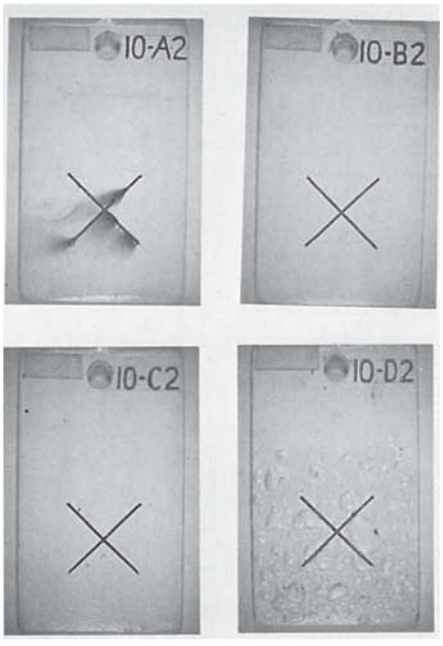


FIGURE 13.13: Coating system number 21 of a chlorinated rubber primer and topcoat (9.0 mils) after five months exposure testing. (a) No CP; (b) −850 mV; (c) −1100 mV; and (d) −1200 mV. Source: Ameron Corp., Monterey Park, CA.

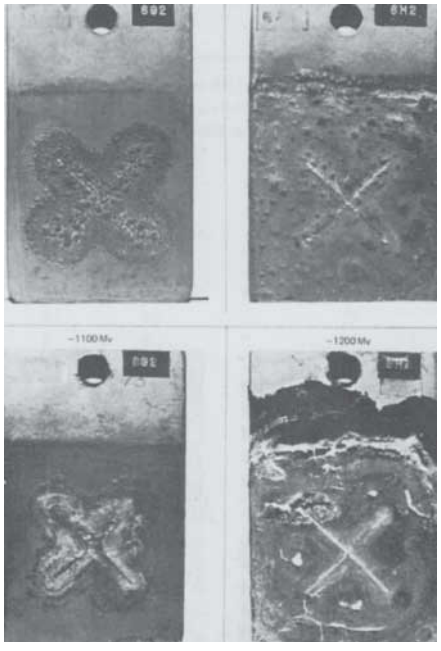


FIGURE 13.14: Coating system numbers 20 [(a) and (b)] of aluminum-pigmented chlorated rubber (6.5 mils): (a) –1100 mV; and (b) –1200 mV. Coating system number 23 [(c) and d)] of aluminum-pigmented hydrocarbon (7.0 mils): (c) –1100 mV; and (d) –1200 mV. Both systems are shown after 10 months exposure testing. Source: Ameron Corp., Monterey Park, CA.

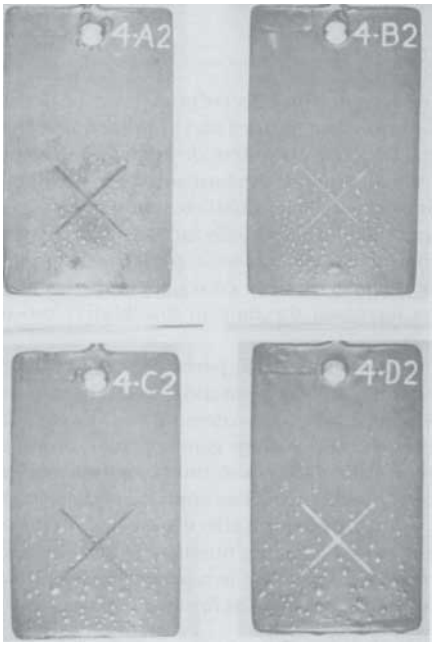


FIGURE 13.15: Coating system number 10 of a high-solids epoxy amine (10.3 mils) after five months exposure testing. (a) No cathodic protection; (b) –850 mV; (c) –1100 mV; and (d) –1200 mV. Source: Ameron Corp., Monterey Park, CA.

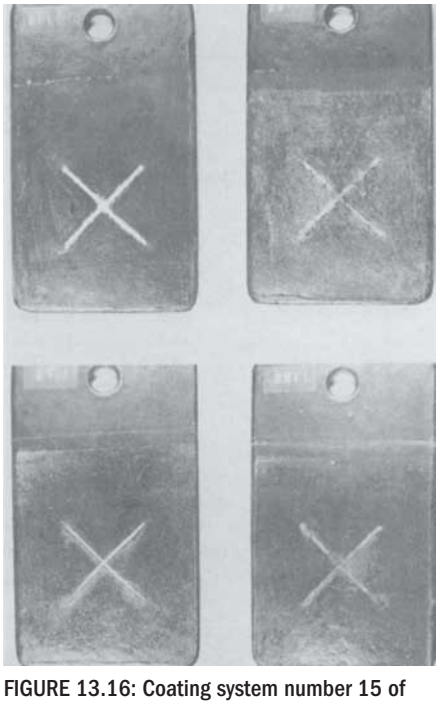


FIGURE 13.16: Coating system number 15 of inorganic zinc primary/epoxy primer and coal tar epoxy polyamide topcoat (22.7 mils) after four years exposure testing. (a) No cathodic protection; (b) –850 mV; (c) –1100 mV; and (d) –1200 mV. Source: Ameron Corp., Monterey Park, CA.

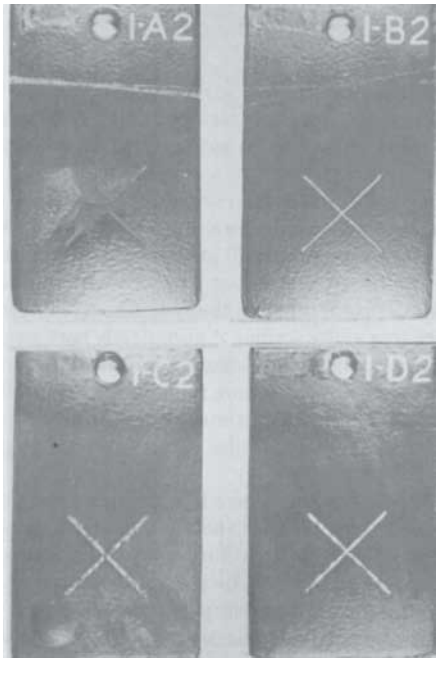


FIGURE 13.17: Coating system number 14 of an epoxy primer and coal tar epoxy polyamide topcoat (21.6 mils) after three years exposure. (a) No cathodic protection; (b) –850 mV; (c) –1100 mV; and (d) –1200 mV. Source: Ameron Corp., Monterey Park, CA.

a continuous platinized titanium electrode was installed along the longitudinal center axis of a cell and connected to a potentiostat. To control and monitor potential levels, two continuous silver/silver chloride (Ag/AgCl) electrodes were installed symmetrically, one on each side of the center electrode. Figure 13.12 shows some of the test cells during the testing program.

The performance of the 23 coating systems is shown in Table 13.4. Blistering was the most common type of failure because of the adhesion and undercutting related failures. The only coating systems with a significantly different failure were the aluminum-pigmented coating systems. Solution of the aluminum by the strong alkali buildup caused this failure.

First coating blisters developed at the most vulnerable locations, either adjacent to damaged coating at the scribes or at inadequately coated edges. Blistering at these locations is not truly representative of deterioration under normal service conditions and leads to increasing protective current requirements of the specimens and accelerated coating deterioration. For these reasons, blisters closer than about ½ in from the scribes were neglected and occurrence of first blisters on the plate surfaces was used to assess

TABLE 13.4: Test Performance of Coating Systems

		0.0 mV		–850 mV		–1100 mV		1200 mV	
		Days to First Blisters		Days to First Blisters		Days to First Blisters		Days to First Blisters	
		At	On	At	On	At	On	At	On
Coating #	Thickness/Mils	Scribe	Plate	Scribe	Plate	Scribe	Plate	Scribe	Plate
Epoxy Series									
1	8.6	20	20	20	20	20	27	20	20
2	8.8	–	>532	–	>532	–	532	–	>532
3	7.6	8	20	8	27	13	20	8	13
4	13.9	20	48	20	41	20	34	13	34
5	11.3	3	3	3	3	3	3	3	3
6	9.4	13	365	309	365	69	111	13	55
7	13.8	13	64	13	167	55	62	34	69
8	14.7	13	41	20	55	13	34	13	34
9	11.4	69	199	44	58	44	58	22	37
100	10.3	22	22	22	22	22	22	13	13
111	188.0	>1484	>1484	>1484	>1484	>1484	>1484	>1484	>1484
Coal Tar Epoxy Series									
12	18.2	60	60	60	152	60	60	41	60
13	13.3	174	667	199	667	120	260	293	293
14	21.6	667	>878	590	>878	174	321	351	351
15	22.7	>1484	>1484	>1484	>1484	>1484	>1484	>1184	>1184
16	17.9	321	667	260	667	293	293	120	260
17	11.6	260	260	146	146	120	120	91	91
18	19.3	293	>878	779	>878	351	392	321	321
Chlorinated Rubber Series									
9.8	9.8	524	>532	13	532	13	41	10	245
20	6.5	27	245	200	365	10	152	10	20
21	9.0	>156	>156	>156	>156	69	69	2	13
22	9.1	>156	>156	>156	>156	91	91	7	7
Hydrocarbon Coating									
23	7.0	27	152	20	110	20	41	20	2

coatings performance. Although there were some minor differences in blistering performance of a coating system without CP and with –850 mV protection, it became significant only with further increase in the protection level. In all cases, the worst blistering occurred at the highest protection level, and the scribed sides of the specimens deteriorated most.

With –1,100 and –1,200 mV protection, many of the coating systems had medium to dense blistering and few systems had none. Testing of chlorinated rubber systems 21 and 22 were terminated after 5 months exposure due to excessive blistering and deterioration. Aluminum based systems numbers 20 and 23 started to dissolve around the scribe in about 45 days. Photographs of specimens from these systems are shown in Figures 13.13 and 13.14.

Figure 13.15 shows system number 10, a high-solids epoxy amine coating. The blistering shown is typical of many of the amine epoxy formulations and is similar to the results obtained with the epoxy amine coatings in the early CP tests.

The best performing system, in terms of lack of blistering and lowest current demand, is system number 15. This is the polyamide coal tar epoxy used in conjunction with an IOZ-rich primer and epoxy inhibitive primer.

Figure 13.16 shows the excellent performance of this system after four years of continuous exposure. After a period of approximately 20 days, the current demand dropped to 10 μA per square foot. This is an extremely small value, considering that the system specimens had 1% bare steel area at the scribes. A completely bare steel specimen under similar circumstances would be expected to require about 5 mA per square foot after the initial 20 days polarization. Thus, the current needed to protect system number 15 is about 1/500 of the current needed to protect bare steel.

This same coating system has shown similar good results in other seawater tests and has been used extensively on large mobile offshore drilling equipment. Figure 13.17 shows the performance of the previously described epoxy system (inhibitive epoxy primer and coal tar epoxy polyamide topcoats) without the inorganic. Excellent adhesion and appreciable thickness, combined with the basic excellent water resistance of the coal tar epoxy are major contributors to its success.

To determine the effect of primers on the performance of a coating system, primed and unprimed specimens with the same topcoats were tested. In all cases, systems with primers had superior performance. For coating systems with zinc primers that inhibit corrosion at damaged areas, the service life is substantially increased over systems without primers. The differences in performance were greater

TABLE 13.5: Effect of Coating Thickness on Cathodic Disbonding

	Disbonded Area, In.^{2}	
Coating Thickness, Mils	Each Panel	Average
20	0.42	
20	0.58	0.500
26	0.12[A]	
46	0.07	
37	0.10	0.090
40	0.10	
71	0.04	
65	0.07	0.057
58	0.06	

[A]This value not used in calculating the average. It is less than one-half the value of the average of the other two values.

Source: S.H. Alexander, "Variables Which Influence Cathodic Disbonding Test Results," CORROSION/59, paper no. 13 (Houston, TX: NACE, 1959).

with polyamide coal tar epoxy topcoats, for which the primers increased the time to first blisters two to three times.

Thickness is of real importance where coatings are to be used with CP, as has been stressed before. This series of tests also demonstrates this in Table 13.4, where the thicker coatings generally have shown the best resistance. Other factors also enter into these results; nevertheless, thickness remains an important factor. It is no coincidence that the two most effective coatings in the test were also the thickest (coatings numbers 11 and 15). Alexander confirms this information in a paper: Variable Which Influence Cathodic Disbonding Test Result.[8] He states:

> Coating thickness was studied over a range of 20 to 70 mils. The effect of coating thickness is quite pronounced. Disbonding increased almost tenfold as the thickness decreased from the 65 mil range to the 20 mil range.[8]

Further data is given in Table 13.5.

Coating number 11 is a thick, tough, resistant epoxy coating designed for the splash zone and tidal area of offshore platforms. It is the one coating type tested which has been designed for this service where it is exposed to the most corrosive conditions as well as heavy abrasion and impact. As such, it should be combined with CP for the best overall corrosion protection.

Its thickness (188 mils) is a key factor in its effectiveness, combined with good adhesion and overall electrical and chemical resistance. This coating type is recognized as an effective answer to the tidal area problems on offshore structures. Its performance in this test confirms this. Figure 13.18 shows its excellent resistance to CP after four years in tests.

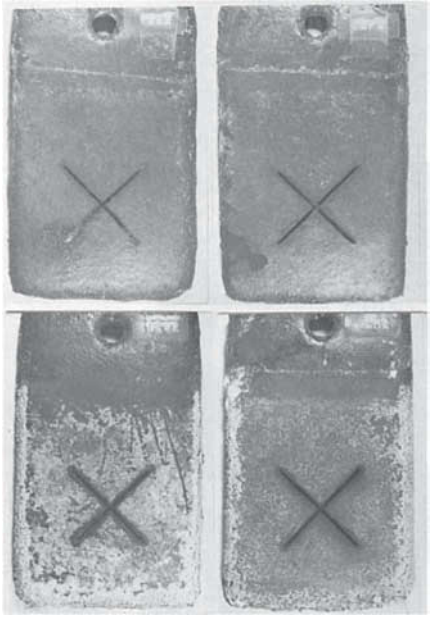


FIGURE 13.18: Coating system number 11 of 100 solids epoxy cladding (188 mils) after four years exposure testing with no undercutting at the scribes. (a) No CP; (b) −850 mV; (c) −100 mV; and (d) −1200 mV. Source: Ameron Corp., Monterey Park, CA.

The effect of the CP potential is shown in Table 13.4. Almost all of the coatings tested (compared to the controls) showed little effect at the preferred protection potential of −850 mV. Some even showed better performance (longer time to the first blister) at the −850 mV protection level than the control panels of the same coating without CP. At the −1,100 mV level, almost all of the thinner and more questionable coatings blistered in shorter intervals, while the time to first blister at the −1,200 mV level for most coatings reduced substantially over the controls at the −850 mV potential.

Only the thick, tidal-area epoxy and the coal tar epoxy polyamide coating over an inorganic base coat showed no blistering over the duration of the test. The latter coating was the best performing coating in terms of lack of blistering and lowest current demand; in fact, both of the latter systems (systems numbers 11 and 15) had the lowest current demand throughout the test period, and the current demand after polarization remained practically constant.

Each of the coating systems used in this series of tests performed in a different way—most failing by blistering in a reasonably short period of time. The coating type that performed best overall, with the exception of the heavy coating for tidal exposure, was the coal tar epoxy. When combined with an inorganic base coat, it was the most outstanding coating system tested.

The coal tar epoxy also performed well in the salt-box cathodic disbonding test and has proven superior in many actual CP installations on offshore structures, ship hulls, water tanks, and similar exposures. In fact, it is commonly used as a shield around ICCP anodes on ship hulls and other structures because of its resistance to cathodic disbonding. In this case, it is subject both to heavy current flow and maximum potential. Figure 13.19 shows a coal tar epoxy coating used for an anode shield on a large tanker. No blistering or other failure is in evidence, even after sweep blasting.

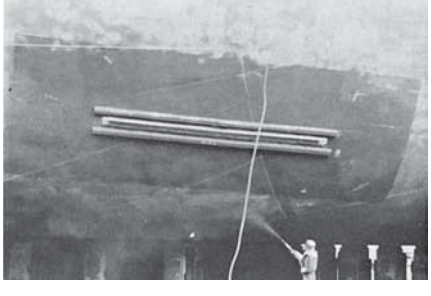


FIGURE 13.19: A coal tar epoxy coating used for an anode shield on a large tanker with no failure in evidence.

Coating Failure

Blistering is one of the most common forms of failure of coatings under CP. Blistering can be caused by a lack of one of the essential coating properties outlined earlier in this chapter. Any coating lacking resistance to alkali, electroendosmosis, or which has some basic adhesion problems, will eventually fail by blistering under CP. Figure 13.20 shows an organic, zinc-rich coating with typical blistering failure after exposure for 114 days in seawater and subject to an average current potential of −1,034 mV saturated calomel electrode (SCE) and an average current of 0.120 mA.

An even more dramatic example is the blistering on the bottom of a large tanker where the ICCP system went out of control and applied excessive potential to the hull. The coating was an epoxy system (IOZ preconstruction primer, epoxy primer, epoxy topcoat,

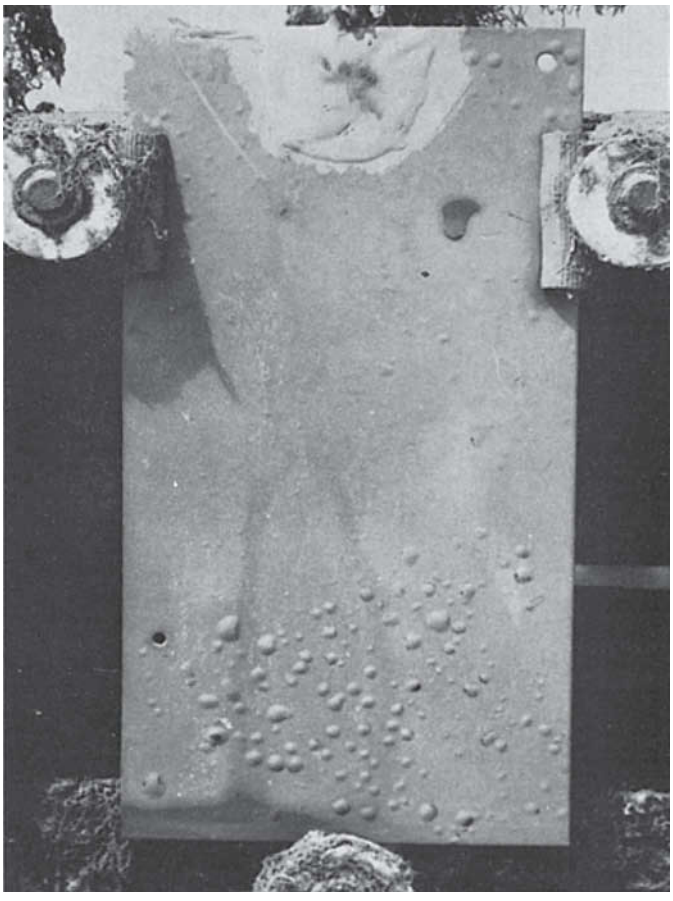


FIGURE 13.20: An organic zinc-rich coating with typical blistering failure after exposure for 114 days in seawater and subject to an average current of 0.120 mA.

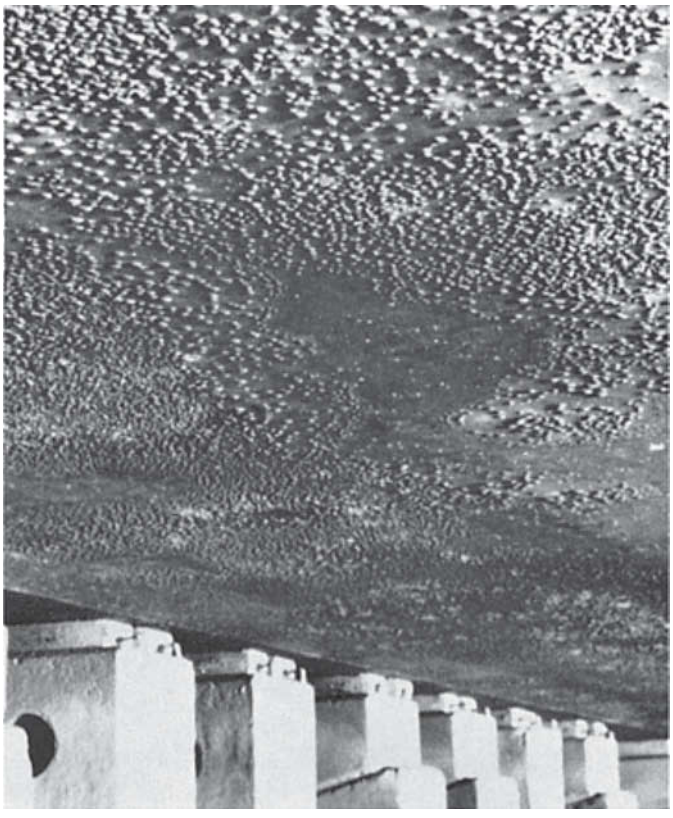


FIGURE 13.21: Blistering on the bottom of a large tanker due to overprotection by CP.

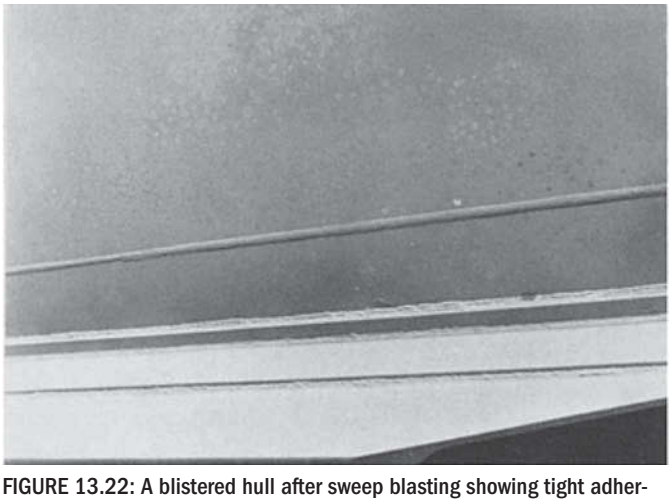


FIGURE 13.22: A blistered hull after sweep blasting showing tight adherent coating between blisters.

and antifouling) applied over a well-sandblasted surface. The blistering shown in Figure 13.21 was present after several months of service, and cathodic deposits can be seen where the blisters were broken.

In this case, the blisters were filled with a yellow-brown liquid having a pH of 11.3 and a chloride content of 12.4 g/L. The blistering was between the inorganic preconstruction primer and the epoxy. There was no corrosion under any of the unbroken blisters. This indicates that there was a basic adhesion deficiency between the IOZ and the epoxy aggravated by the cathodic current, with the water passing through the epoxy into the area of poor adhesion by electroendosmosis. The high pH of the liquid occurred because of the normal cathodic reaction on the surface of the zinc primer

$$4e + 2H_2O + O_2 \rightarrow 4OH- \qquad (13.3)$$

Liquid under blisters of this type is not uncommon, and generally the pH of the liquid is above that of the surrounding liquid. Once the hull coating was sweep blasted and the blisters removed, it appeared as shown in Figure 13.22. The inorganic base coat appeared unaffected. Normally, there is little corrosion under blisters of this type, even without the inorganic base coat. Where the coating is over a sandblasted surface, the original surface is usually bright and the blasting profile readily visible. Where no IOZ is present, corrosion begins as soon as the blister is broken.

Most Common Type of Coating

Popular coatings for use in connection with CP have been the hot-applied coal tar pitch or coal tar enamel coatings. These can be applied as the hot melted pitch alone or as a hot melt combined with fiberglass and other reinforcing material to form a built-up coal tar coating system. These coatings are usually of substantial thickness (i.e., 125 mils or greater). Under most conditions, the steel is blasted and a coat of coal tar primer is applied, followed by the application of the coal tar hot melt, either reinforced or unreinforced. Under most conditions, the coal tar coatings for pipe have been reinforced with glass fiber matte or cloth. While there have been difficulties with the coal tar hot melt systems, by far the great majority of the pipe coated in this manner has performed well with no great



FIGURE 13.23: Corrosion of piling on an offshore structure in a tidal zone.

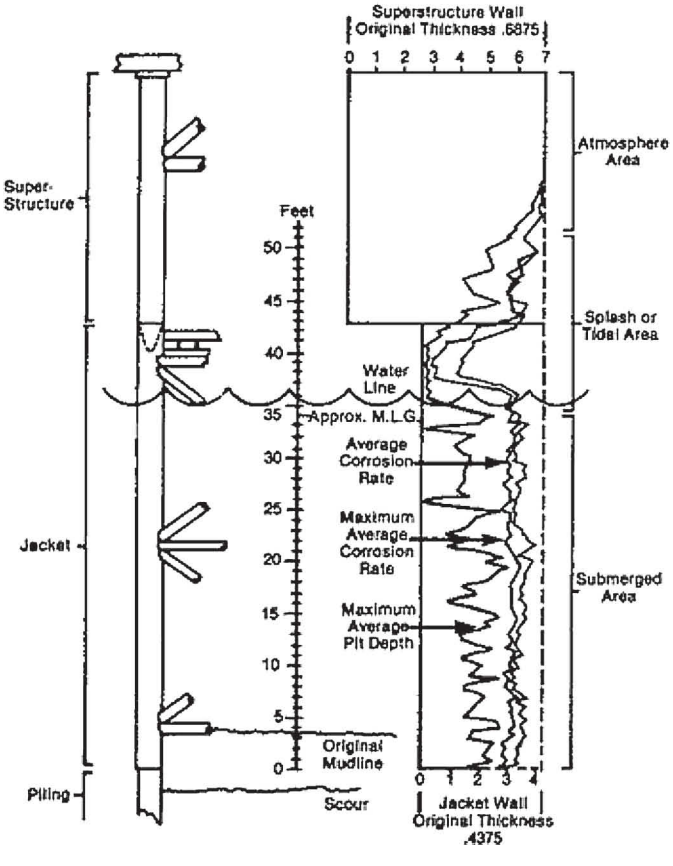


FIGURE 13.24: Corrosion on an offshore structure after eight years service in the Gulf of Mexico. Source: Grosz, O. L., *Important Methods of Corrosion Control in Offshore Operations*, Chevron USA, New Orleans, Louisiana. Reprinted from Offshore (June, July 1958).

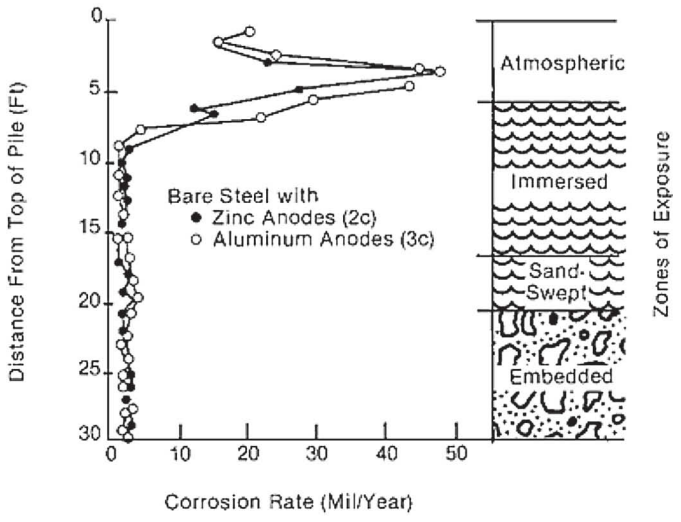


FIGURE 13.25: Corrosion profile of cathodically protected bare carbon steel. Source: A. Kusnar, D. Wittmer, "Coatings and Cathodic Protection of Pilings in Sea Water: Results of Five Years Exposure," *MP* 12 (1979).

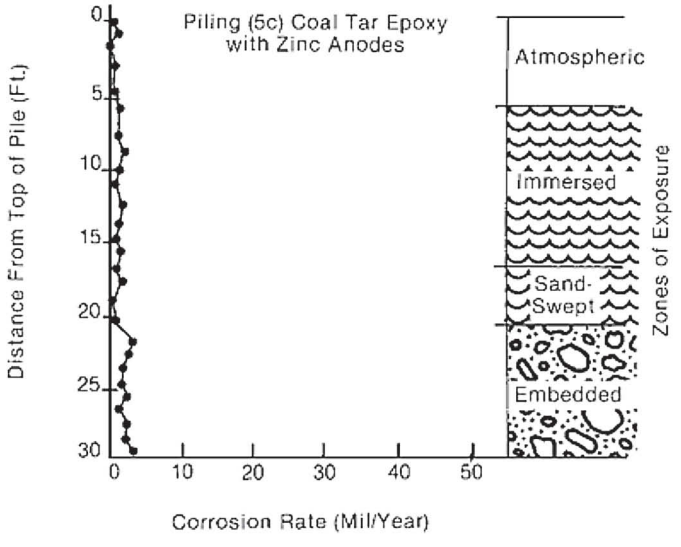


FIGURE 13.26: Corrosion profile of coal tar epoxy-coated, cathodically protected piling. Steel conversion factors: 1 foot = 0.3048 m; 1 mil = 0.0254 mm. Source: A. Kusnar, D. Wittmer, "Coatings and Cathodic Protection of Pilings in Sea Water: Results of Five Years Exposure," *MP* 12 (1979).

blistering, even under higher than normal potentials.

Where these coatings have failed in connection with CP, it has been primarily a problem of adhesion to the steel surface, and with some questionable adhesion, electroendosmotic blistering occurred, pushing the coating from the steel surface. All in all, many hundreds of millions of square feet have been coated in this manner and protected with CP as well. The properties that make this coating type successful are its generally good adhesion to steel surfaces, its resistance to water and moisture penetration, and its appreciable thickness, which is much greater than usual for spray-applied coatings such as epoxies or coal tar epoxies.

Most Common Areas of Use

There are numerous areas where coatings and CP are used; however, there are a few where the combination of the two systems makes a much more effective corrosion-resistant system than can be obtained by either one alone. These areas take the best properties of both systems and combine them to provide the best type of corrosion protection for such areas. Some of these are as follows.

Tidal Areas

Under tidal conditions, immersion, moisture, and even drying conditions exist. Tidal changes occur cyclically on approximately a 12-hour basis. There are the effects of temperature and humidity at the lower tide level, and the effects of immersion and an excess of

TABLE 13.6: Comparison of Coated Water Tank Performance With and Without Cathodic Protection

Description	Duration of Cathodic Protection	Tank Potential, Volts to CSE[C]	Interior Surface Observations
North Tank[A]	None for 10 Years	–0.67 to –0.71	Coating Deteriorated
			Inside Rusted/Pitted
			Tank Repairs Needed
Middle Tank [A]	None for 10 Years	–0.65 to –0.71	Coating Partly Deteriorated
			Some Rusting and Pitting
			Tank Repairs Needed
South Tank[1,2]	Continuous for Three Years	–1.10 to –1.18	Coating Sound
			No Steel Corrosion Noted
			Protection System Adjusted
[A]Steel Tank ¾ MG capacity with 50 mil enamel coating			
[B]Impressed current cathodic protection system rated 12 volt, 5 amp d.c.			
[C]Copper Sulfate Electrode (CSF) placed against immersed tank surface.			

oxygen in the water at high tide level and in the splash zone. All of these create serious corrosion conditions. When the tide is high, the area is fully immersed, and under these conditions, can be protected by cathodic current in a manner similar to protection of a structure that is constantly immersed. At low tide, the area is completely exposed to the atmosphere and usually remains somewhat damp with full oxygen exposure from the air. Under these conditions, severe corrosion takes place in the tidal area where CP is only partially effective.

On the other hand, this tidal area can be covered with a protective coating and the area protected from the atmosphere and from the corrosion that normally occurs. Such corrosion is shown in Figure 13.23, which is the area of an offshore structure shown at low tide. In this case, the original coating was not adequate, and after a short period of time, corrosion occurred.

The tidal area is one of the most corrosive conditions found in a marine environment. This type of corrosion is shown in Figure 13.24, which is the corrosion profile of an offshore structure after eight years of service in the Gulf area. In this case, the steel piling was nearly perforated in the tidal area.

The benefit of the combined system is shown in the following two figures. Figure 13.25 shows the corrosion profile of piling under seawater conditions when protected by either zinc or aluminum anodes. As can be seen, the tidal area still is an active area of corrosion, even though the corrosion rate for the fully immersed metal is quite low. Figure 13.26 shows the profile of a piling that was coated with coal tar epoxy and also protected with zinc anodes. Here, the atmospheric and tidal areas are fully protected, as well as the area that is fully immersed. The piling from which this data was derived was part of a test conducted by the United States Army Construction Engineering Research Laboratory. One of the conclusions from this five-year test was:

> Coal tar epoxy coating with zinc anodes for CP provides protection to the atmospheric zone and the immersed zone and has an added capability of protecting the steel in the immersed zone should damage to the coating occur.[9]

Water Storage Tanks

An area that produces many of the same conditions is the interior of water storage tanks. In this case, the underside of the roof of the tank along with the area a short distance down the shell is constantly exposed to a highly humid atmosphere. The shell of the tank, for most of the distance from the roof to the bottom, is periodically exposed to immersion and then to the highly humid atmosphere on the interior of the tank.

An added factor in the case of water storage tanks is the temperature that is created by the sun on the exterior of the tank. When the water level in the tank is low, the coating that was previously subject to immersion is heated quite rapidly from the exterior, creating a vapor pressure. If the coating has poor adhesion characteristics, the pressure between the coating and the steel will cause blistering. Unfortunately, many such tanks have been coated with coal tar coatings. Since the coal tar is thermoplastic, even to the point of flowing when heated, warm areas of the tank pose serious problems.

Thermoset coatings, such as a coal tar epoxy, have less of a problem in this way. However, they, too, are subject to the vapor pressure caused by the warm exterior of steel and the moisture that may be absorbed into the coating. While the coating protects this area and the above-water area in the tank, CP provides coverage for any damaged areas on the bottom of the tank or on the sidewalls where damage is most likely. On the sidewalls, should the coating blister and the blisters break, the part-time CP will materially reduce the corrosion caused by the break in the coating.

Table 13.6 shows a comparison of the coating performance of three steel water tanks. These 750,000-gal tanks contain Colorado River water that has a high conductivity, and is therefore more corrosive than most. Each of the three tanks was coated with 50-mil hot-applied coal tar enamel. In this case, the enamel was applied by the daubing process, which is the reason the coating appears so uneven. Also, this type of application, where brush marks are a factor, may show linear steaks of corrosion because of thinning in the brush-marked areas. Two tanks were not protected by CP for 10 years, while the third tank had corrosion protection installed after approximately seven years.

These types of hot-applied coal tar enamels and coal tar epoxies do not meet the requirements of the National Sanitation Foundation (NSF) testing and are no longer used in potable water tanks.



FIGURE 13.27: Corrosion on the interior of a coal tar enamel-coated water tank with no CP after 10 years service.



FIGURE 13.28: Corrosion in pinholes on a coal tar enameled tank with no CP after 10 years of service.



FIGURE 13.29: The boottopping of large tankers is an area where the combination of coatings and CP has proven advantageous.

Figures 13.27 and 13.28 show the interior of one of the unprotected tanks and some of the corrosion that had started over the 10-year period. The coating definitely had started to deteriorate over this period, with blistering occurring and rusting showing wherever there was a pinhole in the coating.

The third tank, which had a combination of the same coating and CP, showed no steel corrosion within the same period of time. The coating in this tank appeared sound. While there were some white calcareous deposits present on the inside surface, indicating some pinholes or imperfections in the original coating, there was no coating adhesion failure at these points, even though the system was operating at a high current level for most coatings. The good adhesion, water resistance, and thickness of the coating enabled it to satisfactorily withstand these conditions.

Often, where tanks of this type are overprotected, electroendosmosis can occur with blistering of the coating. In this case, the coating withstood the excess potential. However, if there had been an area of questionable adhesion, the water would have been driven through the coating to the metal-coating interface with resultant blistering.

Boottopping

The boottopping area on a ship has a similar combination of wetting and drying conditions, with the coating being fully immersed, possibly weeks at a time, followed by an equal period where the boottopping may be fully exposed to the atmosphere. This is particularly true on the large supertankers that often have a boottopping as wide as 30 to 50 ft. An example of such a tanker is shown in Figure 13.29.

While this ship is not completely empty, an extensive area of boottopping can be seen. Many of the large crude carriers and ships of this magnitude have installed ICCP systems. Where such systems have been properly maintained and controlled, the combination of coatings and CP have effectively prevented corrosion to this area of the ship, as well as to the bottom.

On the other hand, as previously seen, there have been a number of instances where excessive impressed current has caused extensive damage to the coating of the bottom and the lower boottopping area. Coating in the vicinity of the impressed current anodes is often exposed to excessive electroendosmotic blistering, as well as the breakdown of the coating. Calcareous deposits form underneath and around any coating break. This has been overcome by a combination of heavy polyester glass flake coatings surrounding the electrode or coal tar epoxy coatings applied in the same area. The combination of firmly adherent, corrosion-resistant coating and CP has provided excellent corrosion resistance to many of these large ships.

Undersea Storage Tanks

With the advent of offshore petroleum production throughout the world, there have been many undersea storage tanks installed for the crude petroleum produced by the offshore wells. These are often massive structures that use the flotation principle (i.e., the crude is floated on the surface of the seawater in the tanks, seawater is pumped out, the oil enters, and the seawater is pumped in to empty the tank of the oil). In almost all of these cases, a combination of galvanic anodes and coal tar epoxy coatings has been used for the protection of these massive structures, both on the interior and exterior.

Figure 13.30 shows such a large undersea storage tank being towed into position. Note the galvanic anodes attached at intervals to the exterior of the structure.

Offshore Platforms

Much was said previously regarding the corrosion of offshore platforms. Except for some of the early installations, most have used a combination of CP and coatings, although not for the complete structure. Most of the structures are coated down to a level slightly



FIGURE 13.30: Large undersea storage tank with galvanic anodes attached at intervals to the exterior of the structure. Source: Chicago Bridge & Iron, Oakbrook, Illinois.



FIGURE 13.31: Tidal area of an offshore drilling platform coated with IOZ to below the low tide area and cathodically protected with zinc anodes after two years service.

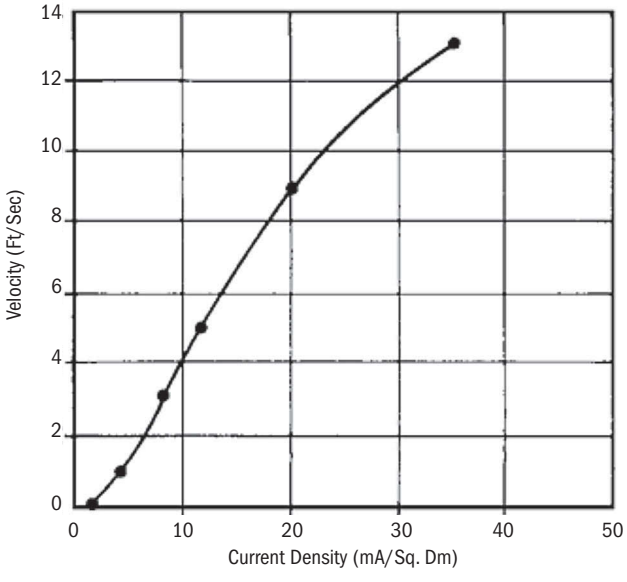


FIGURE 13.32: Effect of seawater velocity on current density requirements for protection of bare steel. Source: F.L. LaQue, *Marine Corrosion*, (New York, NY: John Wiley and Sons, 1975), p. 205.

below the mean low tide line, while the remainder of the underwater structure is often protected either by galvanic anodes or impressed current.

The tidal area has been previously discussed as the most corrosive area on an offshore platform. In addition to being subject to considerable physical damage, it is an area where maximum corrosion protection is needed. Thus, the area is best protected when the coating is augmented with CP.

Figure 13.31 illustrates an offshore structure that is protected in the tidal area by both a coating and CP. In this case, the coating was IOZ. In the center of the photograph, a vertical wire is shown, which is the wire lead to a zinc anode providing galvanic CP to this area. Even though exposed for several years, this area of the platform shows little or no corrosion.

As the offshore platforms have become more sophisticated and costly, they have been used in greater and greater depths of water. More of the new platforms are being entirely coated to augment the CP in the immersed area. Not only are these areas relatively inaccessible for the life of the platform, the weight and quantity of the anodes required for galvanic protection is significant. The massive uncoated steel area demands a high CD in order to be polarized to an effective protective potential. In addition, the protection range of the anodes is limited, often to a line of sight, and many anodes must be attached to provide complete protection to all crevices, corners, and shielded areas.

The galvanic anodes have a life, which is usually substantially less than the design life of the structure, and the complete replacement of the spent or damaged anodes is extremely costly. If the CP system fails for any particular reason, there is no backup system to protect the steel from attack by the seawater environment. The combination of coatings and CP reduces the number of anodes, increases anode life, and provides a dual system to protect the structure in case there is damage to either the CP system or the coating.

High Water Velocity

The combination of the two protective systems can be highly beneficial where relatively high seawater velocities are encountered. As shown in Figure 13.32, comparing the applied CD in milliamps per square decimeter with water velocity in feet per second, the cathodic current required at 10 ft/s is 4 to 5 times as great as that at 1 ft/s. This is illustrated by an example cited in Frank LaQue's book, Marine Corrosion.

Temperature, dissolved oxygen content, and especially the flow velocity in the seawater influence the current required for protection of uncoated submerged surfaces of offshore structures such as oil drilling rigs. The high velocity of ocean currents and the high oxygen content of water off the Alaskan coast have required much higher CD as in other locations such as the Gulf of Mexico.[2]

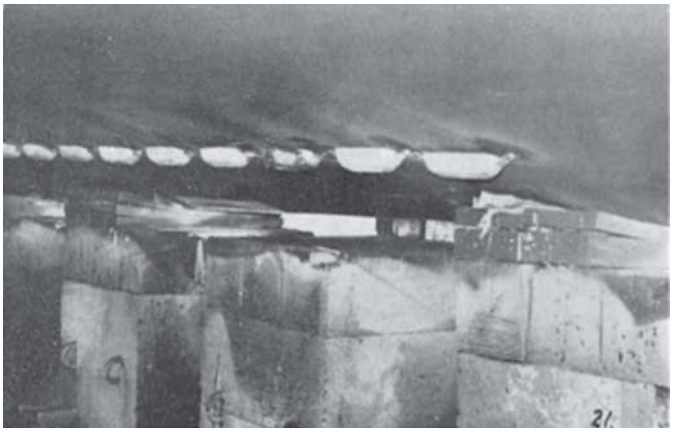


FIGURE 13.33: Zinc anodes on the bottom of a fishing vessel to provide hull protection.

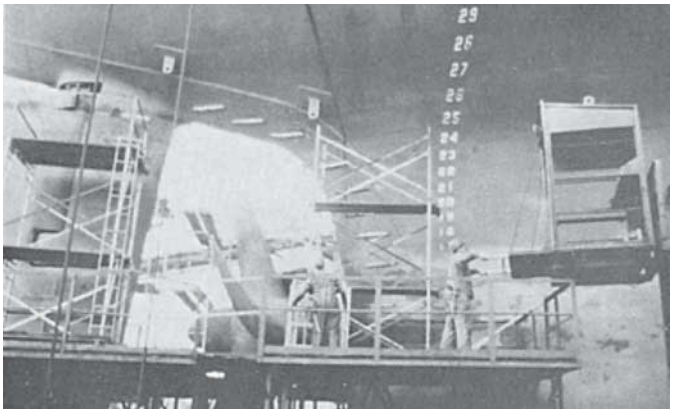


FIGURE 13.34: Zinc anodes installed on the stern area and rudder adjacent to the bronze propeller on a large ship.

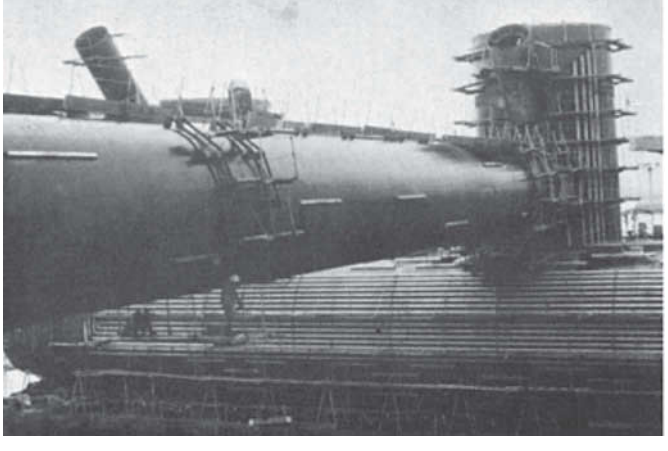


FIGURE 13.35: Portion of a pontoon of a large semi-submersible drilling platform protected by a coal tar epoxy coating and zinc anodes.

He also states:

> Practical experience with cathodic protection of ships has indicated that a ship at rest with a new intact paint system can be protected by a current density of about 1/10th milliamp per square foot. Underway, the current increases from one to three milliamps per square foot depending on the condition in the bottom paint.[2]

Where such conditions exist, the combination of both systems not only provides for a better current distribution, but also lowers the amount of cathodic current required over that for an uncoated structure.

Improved Current Distribution

Distribution of CP currents over large structures is important, and is made possible by the insulating characteristics or dielectric properties of protective coatings. In the case of a bare structure, because of the conductivity of the liquid or soil, considerable driving force is required to distribute the current evenly over the surface. On the other hand, with protective coatings on the surface, the current is distributed only to bare areas in the coating. It makes a much more even distribution, reduces the amount of current required, and provides full protection for any area which is uncoated, or where the coating is broken.

Ships such as fishing vessels, and even larger ships, use this principle to protect the underwater hull from corrosion. Figure 13.33 shows the location of zinc anodes on the bottom of a large tuna clipper. In this case, the keel is protected as well as the hull of the boat up to the heavy load line. Zinc anodes operate only if a break in the coating occurs, and the flow of electrons from the zinc anodes is distributed through the hull to the break.

Galvanic Corrosion

The barrier principle of the coating combined with CP team up to prevent galvanic corrosion. The best example of this is the use of large bronze propellers on ships, which create a serious galvanic couple between the steel hull and the bronze propeller. In this case, with the propeller being strongly cathodic to the hull, if there is any break in the coating (and there is considerable abrasion on the leading edge of the rudder), deep pitting can quickly occur.

On the other hand, with the combination of CP and a strong coating, such corrosion can be prevented. It is standard practice aboard ship to apply the best coatings possible in the best manner possible in the stern area of the ship, on the stern frame, and on the rudder. These areas are subject to excessive turbulence, as well as the galvanic cell established between the propeller and the steel hull. In order to provide both CP and the coating, zinc anodes are generally applied to the rudder and the stern area of the ship to offset the action of the galvanic cell. Installation of zinc anodes is shown in figure 13.34. Zinc anodes can be seen attached at intervals to the stern area of the ship and the rudder surrounding the propeller.

Semisubmersible Structures

Much has been said of offshore drilling platforms and the problems that exist there. The same problems exist, only in some cases to a greater extent, on the large semisubmersible drilling rigs that are presently being used. Most of these are extremely large, costly, and complicated structures. To ensure full protection of the entire critical structure, coatings as well as CP are the most standard procedure.

For example, one of the largest semisubmersible drilling platforms in the world was coated with the following coating system. An IOZ preconstruction primer was applied to the entire steel area prior to erection of the structure. When the structure was complete, a polyamide epoxy primer was applied over the preconstruction primer. Following the epoxy primer, a coat of heavy-bodied polyamide coal tar epoxy was applied, using a total dry film thickness of 20 to 25 mils.

The system was then augmented with zinc anodes attached at regular intervals over the complex structure. In this case, the structure measured approximately 100 yd^2. The underside of the drilling platform was over 150 ft above the top of the immersible pontoon area. In addition, the platform was able to be self-propelled for placement and for holding in place during the drilling operation. The struc-

ture, when complete, was so large that there were no dry docks in the world capable of repairing the structure. Thus, it was assumed that the coating and the CP system would have to maintain the structure corrosion-free for the life of the structure.

Figure 13.35 shows a section of the pontoon area following the application of the final coat of the coal tar epoxy as well as the zinc anodes. The zinc anodes can be seen at intervals on the structure. The structures, because of their complexity and sophistication, require the best corrosion protection available, and it is for this reason that the combination of both coatings and CP was selected.

Cargo Ballast Tanks

The protection of the interior of cargo ballast tanks aboard tankers has been a subject for discussion for a considerable period of time. There has been some success obtained by the use of anodes in dedicated seawater ballast tanks. The Zinc Institute published an article, Installation of Zinc Anodes in Cargo Ballast Tanks.2 on two ultra-large cruise carriers. The zinc anodes in this particular case were used as supplementary protection to selectively applied epoxy type coatings in these tanks. In the case of these two vessels, almost 1,000,000 lb of zinc anodes were required for the combined protection.

Ballast tanks have also been well protected by the use of zinc anodes alone. On the other hand, the combination of the coating and the zinc anodes reduces the number of anodes required and provides backup and much longer-term protection for these tanks, which seriously corrode without the best protection possible.

Many companies have attempted to protect the cargo ballast tanks with galvanic anodes as well. In many cases, this has resulted in less than the best protection to the tanks, particularly where the ships are crude carriers. In the cargo ballast tanks, progressive pitting has resulted with numerous cases of such pitting occurring within an inch of the anode position. Ships carrying sulfur crude with considerable hydrogen sulfide (H_2S) dissolved in the crude have been particularly troublesome where CP alone has been attempted. Figure 13.36 shows the pitting which resulted in a sulfur crude ballast tank. The photograph was taken on one of the horizontal stiffeners on the interior of the tank and the zinc anodes can be seen on the horizontal surface.



FIGURE 13.36: Zinc anodes on a horizontal stiffener in a cargo ballast tank. There is pitting adjacent to the anodes, and the light surface coloration is a white sulfur precipitate and not a calcareous CP deposit.



FIGURE 13.37: Zinc anodes on the edges of steel plate in an uncoated cargo ballast tank, showing corrosion under and close to the zinc anodes.

Figure 13.37 is a close-up of a zinc anode located on such a steel stiffener. Corrosion of the steel can be seen closely adjacent to the zinc anode. In this case, H_2S not only reacted with the zinc, but it reacted with the iron as well. It can do this regardless of any moisture being present. Therefore, the sulfide reaction can occur during the time that the crude petroleum covers both the iron and the zinc surface. Sulfide is strongly cathodic to steel and the zinc anode was deactivated by the zinc sulfide formed on its surface. Deep pitting of the steel surface was the result.

Generally, where chemical corrosion such as this is a problem, CP alone is not a complete answer. In several of the large crude carriers, the interior of the tanks were thoroughly cleaned by blasting, and a retrofit application of an epoxy primer and coal tar epoxy coating was made in addition to the zinc anodes in order to overcome the deep pitting problem.

Underground Structures

Underground structures are not unlike structures that are fully immersed. As a matter of fact, many underground structures are beneath the underground water level and, in essence, are under immersion conditions. In any case, the soil is usually damp at the level of the structures so that reasonable conductivity exists at most times. In underground pipelines running cross-country, there are many different areas of soil conductivity, and anodic and cathodic areas develop between these areas of differing activity. Most underground pipelines are therefore protected by both CP and coatings, with the combination providing good corrosion protection to the pipe.

There are several problems that necessitate the use of the combined corrosion protection systems (e.g., holidays in the coating). Damage to the coating on the exterior of the pipe due to backfill operations is another example. The weight of the pipeline over a long period also can cause penetration of the coating by rock or similar hard materials in the backfill. Such coating breaks and discontinuities are almost impossible to detect once the pipe is in the ditch and the backfilling started.

Most pipelines are under pressure as well. Pitting of the pipe can cause stress problems from either water or high-pressure gas. The pipeline is generally inaccessible once it is in place, so that a minimum of maintenance and repair is desirable without extreme cost.

Thus, the combination of both coatings and CP has provided the best answer to pipeline corrosion protection.

Also, many underground tanks, particularly in gas stations, were given a light coat of an asphalt coating and were placed in the ground without any other protection. Large quantities of gasoline and oil have been lost because of such poor protection, and at the present time, many municipalities have prohibited metal tanks from being used. Fiberglass-reinforced plastic tanks have replaced the metal tanks in many areas, although metal tanks are still used in some places. In these cases, coatings are applied and are usually combined with CP to eliminate the loss of fuel, as well as to prevent the contamination of groundwater. Newer regulations often require redundant systems such as double wall tanks, CP, and dynamic monitoring systems with underground fuel tanks.

Summary

To obtain maximum corrosion resistance from the combination of coatings and CP, a number of factors, which have a basic influence on their combined effectiveness, must be taken into consideration.

1. Application of coatings needs to be done in the best possible manner, with excellent surface preparation. Poor application and poor surface preparation can only lead to coating failure under the influence of cathodic current by either hydrogen or electro-endosmotic blistering.
2. For the coatings to be effective, they must be highly dielectric and must maintain such dielectric properties over their entire life.
3. Coatings must be highly chemical-resistant, particularly toward alkalies, because of the strong buildup of hydroxyl ions by the cathodic current. Any coatings that have even a small tendency to saponify, or which contain pigments that are alkali reactive, should not be used.
4. Coatings should have a low moisture absorption and a low moisture transfer rate, in addition to being di-electric, in order to prevent hydrogen blistering under the cathodic current.
5. Optimum coating thickness is essential in order to act as a longtime barrier and insulator for the cathodic current. Each coating has its own optimum thickness. However, in general, it can be stated that the thicker the coating (based on its own inherent properties), the better the results when used with CP.
6. It is indicated that antifouling coatings using alkali-resistant resins and pigments, applied over a proper dielectric coating, are not affected by the application of CP potentials.
7. From all evidence, indicated from actual tests as well as field installation, the cathodic potential, where used in connection with coatings, should be below –1 V, and the optimum potential is –0.85 V.

If these factors are taken into consideration, the results of both laboratory testing and actual use of the combined system indicate that maximum corrosion protection can be obtained through the use of coatings and CP.

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14 Coating Failures

Introduction

Coatings are much like human, animal, or plant life. Sooner or later failure occurs and "life" ceases. According to this concept, all coatings are doomed to failure. However, the coating failures described in this chapter are those that occur quickly in the life cycle and thus are not anticipated. As G. W. Seagren says,

> Paint is an expendable material that is used to protect or decorate another material more costly to replace; and the best paint for any given application is the one that will give optimum service during the longest period of service. Eventual failure of any paint is inevitable; but rapid deterioration of a coating is undesirable and can be prevented by careful observance of sound painting practice.
>
> Paint failure may be defined as deterioration of the paint system, or corrosion of the coated structure, more rapidly than would normally be expected, under the service conditions.[1]

Coating failure is also affected by the attitudes of those involved in coating application. During new construction, the application of coatings is usually the last job to be completed. By this time, the plant or equipment is ready to operate, at least for test runs; workers are anxious to finish the job; management is pushing to get into production; and the painters are pushed by all concerned (the owner, the general contractor, and their supervisors) to complete the work as rapidly as possible. The same is true for coating repair, only perhaps more so since repair time is always limited. The resulting attitude is "get the job done fast." This operating philosophy can only result in lack of proper care during application and thus eventual coating failures.

It has been estimated from past experience that 70% of all coating failures have resulted from poor or inadequate surface preparation.[2] This percentage (while admittedly imprecise) only increases when a lack of care in application of the coating is evidenced. Thus, care in surface preparation, application, and inspection is the best insurance against coating failure. While such close attention to the physical application of the coating may initially seem costly, it is much less costly than continuing repair over the life of the structure.

A coating is a complex material, made up of a whole series of interacting ingredients (e.g., resins, plasticizers, pigments, extenders, catalysts, fungicides, solvents, etc.). They are applied as a very thin film of a few microns or thousandths of an inch thick. Solvents must evaporate. The nonvolatile portion must deposit a continuous film over the surface, react with and adhere to the surface, react with internal curing agents or with oxygen from the air to become insoluble, and provide a good-looking finish as well. This thin film must then withstand wind, rain, sun, humidity, cold, heat, oxygen, physical abuse, chemicals, biodegradation, and other forces.[3] It is understandable, then, that as resistant as the modern protective coatings are to corrosive environments, they are still subject to many destructive variables and mechanisms. Obviously, with as complex and sophisticated materials as protective coatings, there can be many causes for coating failures, including the following:

1. Quite often a failure is caused by an inadequate or poorly written specification. Too often specifications from one job are simply edited and applied to another job without proper consideration for such items as site conditions where the structure will be fabricated and coated, environmental conditions at the final site where the structure will be placed into service, and several other factors that are "site specific" and must be carefully evaluated prior to writing the coating specification.
2. A number of types of failures can occur due to the basic formulation of a coating. Such failures can be chalking, checking, cracking, discoloration, and similar phenomena.
3. Many coating failures are due to improper coating selection. A coating that was designed for steel surfaces is often extended out over a concrete or wood surface, rapidly failing over these other surfaces. A coating that may be excellent for the exterior of a ship can be a complete failure on a chemical reaction vessel. Thus, careful selection according to the particular exposure is extremely important.
4. Many coating failures also result from the nature of the substrate (i.e., a coating can be the incompatible with the surface over which it is applied). In this case, a chemical reaction may occur between the surface and the coating. In addition, the density or smoothness of the surface may cause the coating to have poor adhesion. Thus, the substrate directly affects the performance of a coating.
5. As previously discussed, a large number of coating failures can be traced back to improper or poor surface preparation. In this case, lack of or poor surface profile, surface contamination, condensation, mill scale, or many other surface-oriented difficulties can influence the performance of a coating.

6. Application and surface preparation together form a substantial part of the difficulties that create coating failure. Inadequate thickness, pinholes, overspray, improper drying, improper curing—all are causes for rapid coating failure.
7. Adhesion is related to a number of the other causes for coating failure. In fact, adhesion-related failures are numerous and generally catastrophic. Such failures include blistering, flaking, peeling, and intercoat contamination.
8. As previously noted, the design of a structure itself is often the cause for severe failure. Sharp edges, crevices, skip welds, back-to-back angles—all are focal points for failure.
9. Exterior forces are forces such as chemical exposure, abrasion, reverse impact, severe weathering—all of which can cause rapid coating failure.

While all of the above are potential causes of failures, it is relatively rare that only one item causes a failure. More often it is several items in conjunction with each other that brings about the actual failure. The above are all relatively common, general causes for coating failure, each of which will be individually discussed.

Specification-Related Failures

While this subject is covered in depth in Chapter 17, it is worthwhile to consider the overall manner in which good specifications should be written for each and every project on its own merits. Therein lies the cause of most specification-related failures; a failure on the part of the specification writer to inform himself/herself of the overall nature of each specific project. Too often the specification writer falls prey to the "Xerox Syndrome," whereby they pull out a copy of a previous project specification, make a few editorial changes, and issue it to a new project without due consideration to the unique requirement of the new project. Included in these site-specific requirements are environmental conditions under which the fabrication and painting activities will have to be performed. This can easily lead to the selection of a good coating system that fails simply because it was not designed for that particular service environment.

Formulation-Related Failures

There are some coating failures over which the corrosion engineer has little or no control. Those that have to do with the formulation of the coating itself are one of these general types. If the coating is formulated poorly and the corrosion engineer selects that coating, the coating will fail in spite of any effort that is made to insure its proper application.

Failures do occur as a result of the basic ingredients used and their combination in the coating, the resins used, the pigment used, or even improper solvent formulation, but these are quite rare. Bodies of work on the statistical frequency of coating formulation-related failures by Louis Vincent and Mark Weston indicate that these are rarely in excessive of 1 to 3%.[4] The formulation-related types of coating failure are as follows.

Chalking

Chalking was probably one of the most difficult types of coating failure that the automotive industry has had to contend with over the years. The early natural cellulose lacquer coatings often failed rather rapidly by chalking, and it was not until the advent of some of alkyd, acrylic, and polyurethane-based materials that pastel colors, which are so popular today, became possible. Even then, over a period of time, the color on a car painted with alkyds would change from a light blue to a light gray. When this occurred, it was necessary to abrade the surface, using a body-cleaning compound, to remove the chalk and return the automobile to its original color. This same type of action takes place on all kinds of industrial structures; however, some coating materials are superior to others in this regard.

The mechanism of chalking is essentially one where the coating binder tends to gradually disintegrate, leaving the surface covered with the pigments that have been held on the surface by the binder. This process continues until the surface coating is worn through, at which time the primer is visible or corrosion begins to occur on the substrate. Action such as this is shown in Figure 14.1, which shows the deck of a ship where an epoxy coating chalked so rapidly that the entire topcoat eroded down to the primer.

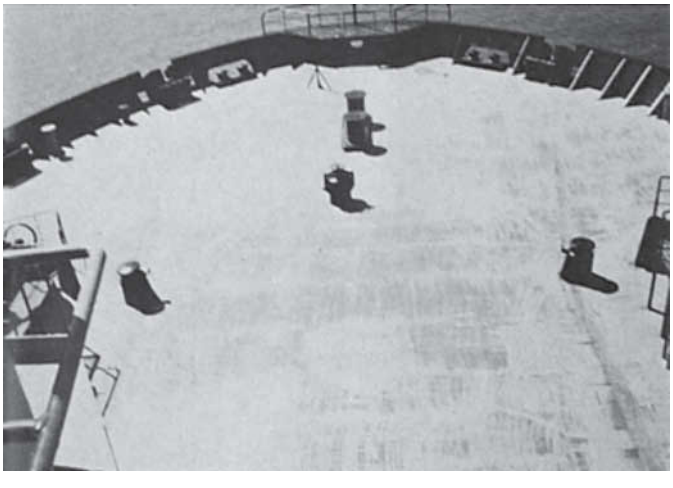


FIGURE 14.1: Rapid chalking of the coating on a ship's deck.

Chalking is strictly a surface phenomenon. While in many cases it takes a period of months or years to chalk down to the state shown in Figure 14.1, it can also be a rather rapid process, with an entire top coating several mils thick eroding within a year. At the time that the automotive coatings failed by chalking, it was common practice to polish the coating using a very fine abrasive, followed by a coat of wax to protect the binder from weather exposure. This, to a substantial degree, aided in reducing the chalking. On the other hand, it was a temporary solution, making it necessary to wax a car every few months. With the advent of ultraviolet-resistant polyurethanes, the automotive industry has largely shifted to combinations of body-coat, clear coat finishes that give much longer color and gloss retention properties than previous generic coating types. Even so, it is not unusual to see cars that serve almost exclusively in sunlight to have the ultraviolet resistant clear-coat polyurethane chalk and lose body after a few years, exposing the body-coat underneath the topcoat.

Powdering or chalking of a coating is due to the exposure of a coating to the actinic rays of the sun and the action of the radiation on the organic binder. Shaded areas seldom tend to chalk. All of the airborne reactants (e.g., humidity, oxygen, and air pollution) play a part in the chalking action. These react with the resins in the binder, causing it to disintegrate, thus leaving the pigments free on the surface.

One example is amine epoxy coatings or epoxy ester coatings, which chalk very rapidly. Epoxy ester coatings are generally used only

for interior work because of their rapid chalking tendency. Other resins, such as the acrylic or acrylic-modified resins blended with other resins (such as vinyls, epoxies, polyurethanes, and alkyds), now have excellent weathering and chalk-resistant properties so that they are only slightly affected by the sun's radiation. Several years of exposure are usually required before an appreciable surface reaction occurs. The same is true for some of the new aliphatic isocyanate-catalyzed polyurethane resins. These materials not only have a high gloss; they also retain the gloss without chalking over a period of several years. Since the late 1970s polysiloxane-modified epoxies and polyurethanes have proven to have even longer color and gloss retention properties along with minimal chalking. From an industrial environment viewpoint, the polysiloxanes have also proven to have better chemical and corrosion-resistant properties than the acrylics that were previously used to modify epoxies for color and gloss retention purposes.

Pigments

The pigmentation of coatings is extremely important in the chalking reaction. The original white pigments, including anatase titanium dioxide (TiO_2), tended to chalk readily and rapidly in almost any coating vehicle. On the other hand, when the rutile TiO2 pigment became available, it had a major impact on the chalking properties of coatings. These materials made possible the use of pastel colors and the mixing of colored pigments with white in order to obtain pastel shades. The combination of the chalk-resistant resins and pigments has made possible the type of automotive finishes that are available today, which last for several years and still maintain their appearance without appreciable attention.

Many coating pigments will tend to catalyze the chalking reaction. There are some black pigments that will remain unaffected in a coating for long periods of time, while others will tend to chalk in a short period, with the black surface becoming dull and easily rubbed away. Blue pigments also tend to bronze and then continue on to the chalking stage. Many other pigments tend to change color on the surface. Figure 14.2 shows the effect of sunlight on a red-pigmented coating, turning it white and chalking it over a relatively short period of time.

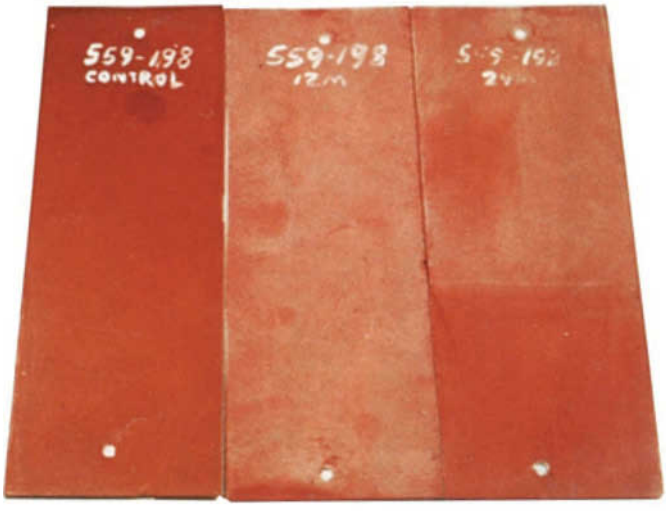


FIGURE 14.2 : Red-pigmented coating specimens chalked and changed color after a short exposure to sunlight.

Pigments also have a positive influence on chalking, as they tend to reduce the chalking by shielding the resin from the sun's rays. This is the action of some of the black pigments and was one of the reasons that the Ford automobiles, when black was the only color available, maintained their appearance over a relatively long period of time. The shading effect is also demonstrated to an even greater degree when coatings are pigmented with aluminum. This is an excellent example of shielding the sun's rays from the binder. The shingle effect of the aluminum platelet type pigment restricts the sun's rays from contacting the vehicle binder. This is the reason that the weather resistance of almost any coating vehicle is improved when the coating is formulated with aluminum pigments.

Figure 14.3 schematically shows the type of orientation developed by a leafing aluminum pigment in a coating film. The overlapping metal flakes provide an opaque shield for the binder resin. Other opaque pigments also shield the resin from the sun, but not as effectively as the orientation of the metal flake.

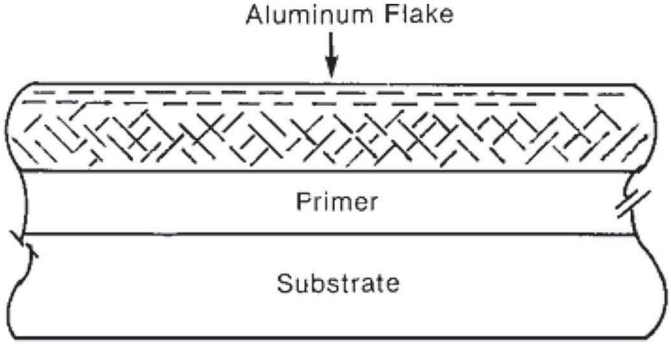


FIGURE 14.3: Orientation developed by a leafing aluminum pigment in a coating film.

The chalking reaction has also been used in a positive manner by a number of coating manufacturers. These manufacturers have formulated coatings with a controlled chalking rate, so that the surface erodes slowly, but still at a sufficient rate for the surface to remain white and clean.

This reaction is regulated through the proper formulation of the coating binder and the pigments, and it reduces the effect of grime and dirt that otherwise might accumulate and adhere tightly to the coated surfaces. In this case, the white remains much more attractive over a longer period of time. In all of these cases, the reduction in the thickness of the coating is controlled so that the thickness reduces slowly, thus allowing the coating to provide the protection needed and still maintain its appearance over a number of years.

Chalking is also considered one of the least objectionable types of coating failure. It is preferred because a clean chalked surface that is free of corrosion provides a good base for additional topcoats which can bring the coating back to its original thickness and effectiveness.

In order to evaluate the extent of chalking, ASTM Standard D659-865 that was withdrawn in 1989 and replaced by ASTM D4214[6] in order to measure the degree of chalking of exterior coatings. Figure14.4 shows the various degrees of chalking failure outlined in this standard. The procedure used here is a simple one; merely wrap a piece of black felt or velvet on a thumb or finger, rotating the finger through a 180-degree angle when pressed against the coating. The cloth can then be removed and the degree of chalking checked against the standard shown. A dark black felt is used for white or pastel coatings, while a white cloth is used for colored coatings.[5] It is a simple yet very effective test for comparing the chalking characteristics of various coatings.

In order to reduce chalking to a minimum, formulations for topcoats based on the acrylics, the acrylic-modified vinyls, the acryl-

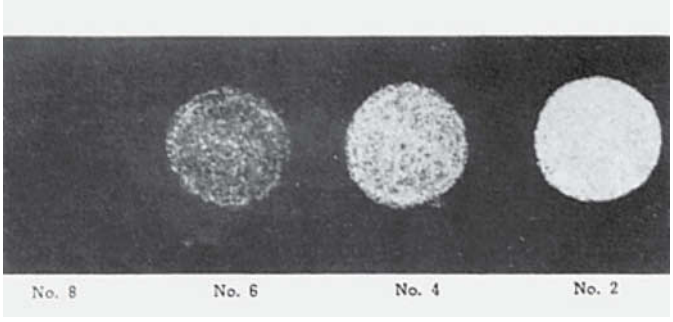


FIGURE 14.4: Standards showing the degrees of chalking failure. Source: Pictorial Standards of Coating Defects, "Chalking Resistance" (Philadelphia, PA: Federation of Societies for Coating Technology).

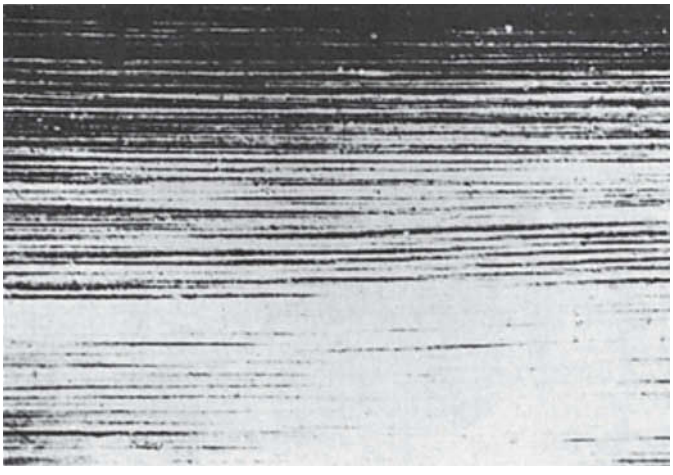


FIGURE 14.5: Erosion by weathering of a brushed coating. The tops of the ridges of the brush marks are worn away first. Source: Pictorial Standards of Coating Defects, "Erosion Resistance" (Philadelphia, PA: Federation of Societies for Coating Technology).



FIGURE 14.6: Macro checking of the topcoat on an interstate sign.

ic-modified epoxies or alkyds, the aliphatic polyurethanes and the polysiloxane modified epoxies and polyurethanes combined with chalk-resistant pigments and such coating additives as ultraviolet absorbers, will provide resistance to chalking or reduction in gloss for a period of several years.

Erosion

Erosion is also a surface reaction usually associated with chalking. It is often seen in brushed coatings where the high ridges of the brush marks show greater erosion than the valley areas. It can also be caused or aggravated by the surface being exposed to heavy rainfall, hail, high winds, or a combination of high winds and rain. Erosion is essentially a wearing away of the coating surface in a gradual manner similar to the chalking mechanism.

There are various types of erosion mechanisms (e.g., sand erosion, which is very common in the western deserts). Automobiles caught in sand storms can have the entire coating on one side of the car eroded by windblown sand within a short period of time. This is because the high winds and sand create a condition much like sandblasting. Sand erosion is also caused by winds on beaches, where the constant movement of the sand against the coating on piling or similar structures will wear it away in the area of impact. Sand erosion by wave action can also take a toll on coated piling or bulkheads.

Generally, however, erosion, as it is considered in the coating industry, is a reaction similar to chalking (i.e., the gradual wearing away of the coating due to weathering action). The resistance to this type of coating failure is also similar to that of chalking, and the use of the same type of resistant resins and pigments substantially reduces the erosion mechanism. Figure 14.5 shows an eroded coating. In this case, the coating has been brushed, and erosion has taken place on the high spots in the coating.

Checking

Checking of a coating can be described as small breaks in a coating surface that are formed as the coating ages and becomes harder and more brittle. Checking is a surface phenomenon and does not penetrate the full depth of the coating. This is important since in many cases a coating may check on the surface soon after it is applied, yet remain in a stable condition, corrosion-free, for a long period thereafter. Some checking of a coating is almost invisible to the naked eye and can only be readily seen under a low-power magnifying glass or microscope. On the other hand, other coatings may check sufficiently to be readily visible. Figure 14.6 shows macro checking on a highway sign. In this case, the topcoat has checked, but the failure does not penetrate through to the substrate.

Checking, for the most part, is a formulation-related reaction. It is, again, a combination of the resins and pigments that are not properly combined, so that, as the coating dries or continues to react, the surface becomes hard and brittle and surface stresses develop in the coating. Certain pigments will catalyze or cause checking to occur. This has been proven by using the same vehicle, yet formulating with different pigments, and having various checking patterns develop from the different pigments. This can range all the way from no checking at all, to severe checking due to the pigmentation.

It was originally stated that checks in the coating do not penetrate to the substrate. However, if the coating is not maintained, it will eventually break down to a point where it cracks, exposing the underlying surface. The surface stress in the coating is aggravated by wetting and drying, heating, cooling, and solar radiation, all contributing to the reactions on the coating and creating a more brittle and less expansive surface.

Since checking is primarily a formulation problem, its prevention is a matter of proper coating selection. The coating should be formulated with very weather-resistant resins, with nonreactive pigments that do not contribute to checking, with some permanent plasticizer, and with reinforcing pigments that reduce the stress in the surface of the coating. Figure 14.7 shows an example of fine yet severe checking of a coating film. ASTM Standard D660[7] provides a method for the evaluation of the degree of checking in exterior coatings. Such a method can be quite valuable in comparing coatings prior to selection for a given project.

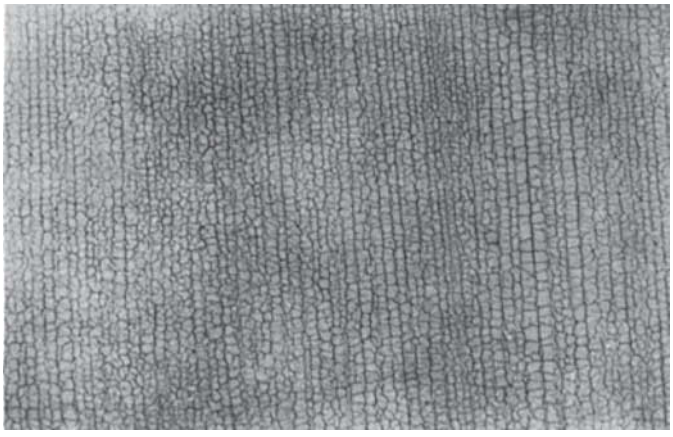


FIGURE 14.7: Severe, fine checking of a coating film.

Alligatoring

Alligatoring can also be considered a checking reaction in which the surface of a coating hardens and shrinks at a much faster rate than the body of the coating itself. Actually, it can be considered a macro checking type of failure caused by stresses set up on the surface of the coating. As in the case of checking, alligatoring usually does not penetrate through the coating, but is a surface reaction. The reaction occurs where a hard, tough coating may be applied over a softer, extensible coating. The harder material tends to shrink and float on the surface of the underlying material, with the surface cracking in large segments (Figure 14.8).

Coal tar coatings, in particular, tend to alligator when exposed to the weather and sunlight. In this case, the coal tar coating hardens on the surface, while the underlying area remains soft. It is a typical coal tar reaction, particularly where the coating is applied rather thickly. It can also occur where harder coatings, particularly oxidizing types, are applied over an asphalt surface. Here again, the harder material, such as an alkyd, may tend to shrink sufficiently to pull it into an alligator pattern over the softer asphalt material.

Alligatoring has also happened where some air drying or chemically cured coatings are applied over a cold surface and then heated from the coated surface side, with a rapid temperature rise curing the surface much more rapidly than the underlying material. Alligatoring, then, is the shrinkage of the surface while at the same time the body of the coating does not change in the same way. Figure 14.9 is a schematic drawing of an alligatored surface, also showing a cross section of the coating. As can be seen, the surface of the coating ruptures due to shrinkage, but the underlying softer material merely pulls while not penetrating to the substrate.

The thickness of the coating has much to do with alligatoring, and, while the thickness is reduced in the checks of the alligator pattern, sufficient thickness usually remains to protect the substrate from corrosion for a considerable period of time. Eventually, failure will occur in these areas due to the thinner coating.

Alligatoring is a formulation-related failure so that prevention is also a matter of coating selection. A coating should be selected that does not have a soft primer under a harder topcoat. The coating, in general, should be reinforced with reinforcing pigments or fibers, and thin coats should be applied and cured before the application of the second coat. It should be a rule of thumb never to apply a hard coating, which oxidizes or requires polymerization, over a permanently softer or more rubbery undercoat.

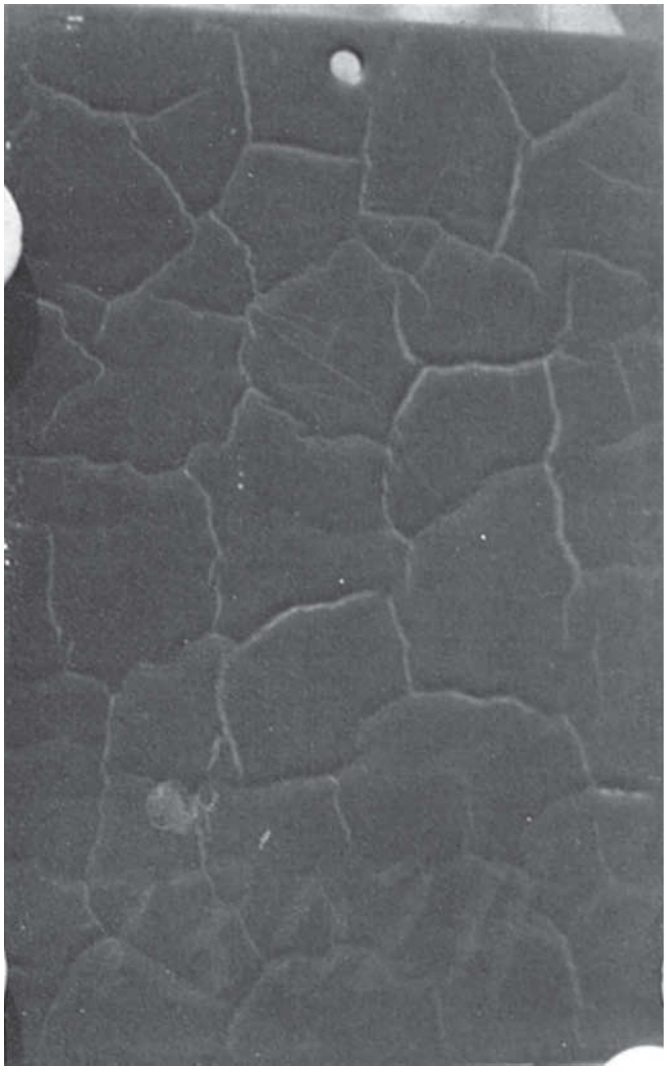


FIGURE 14.8: Alligatoring of a coating.

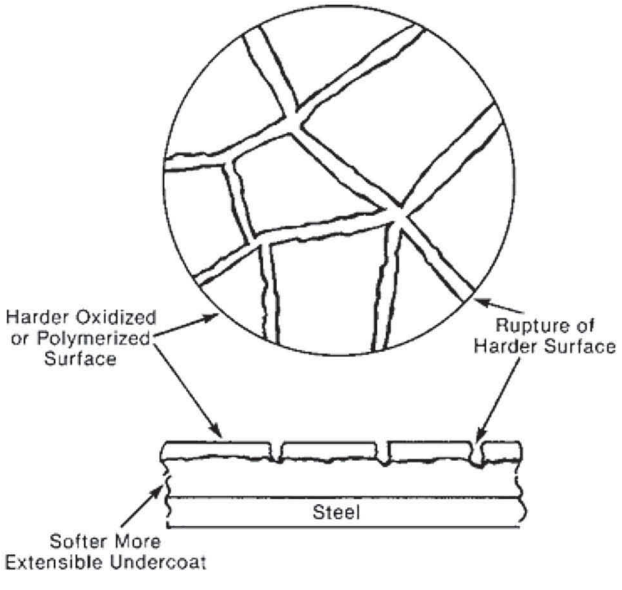


FIGURE 14.9: A schematic of an alligatored surface, showing a cross section of the coating.

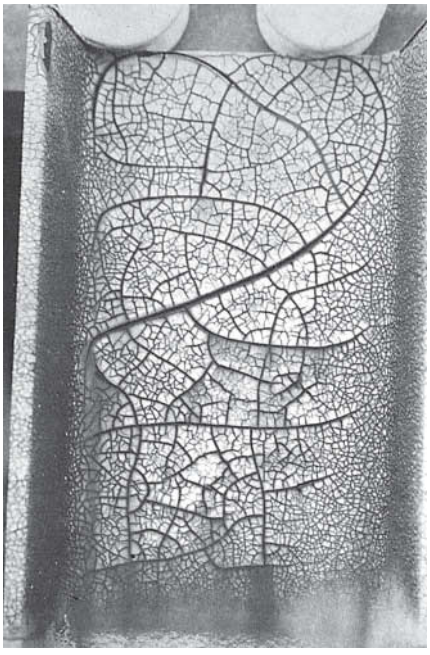


FIGURE 14.10: General cracking of a coating, showing larger cracks in heavily coated areas.

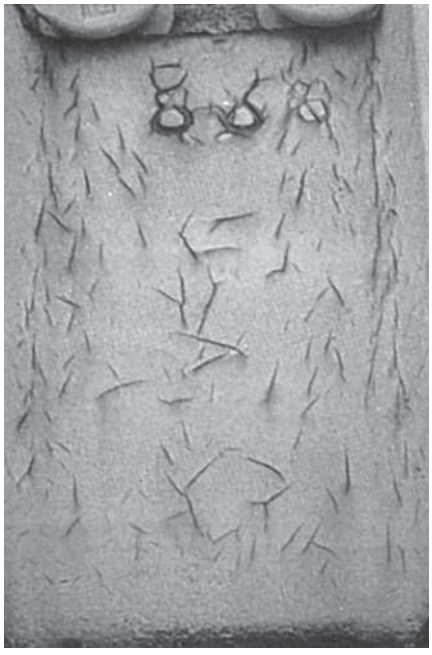


FIGURE 14.11: Cracking of a coating, showing short, non-continuous cracks.

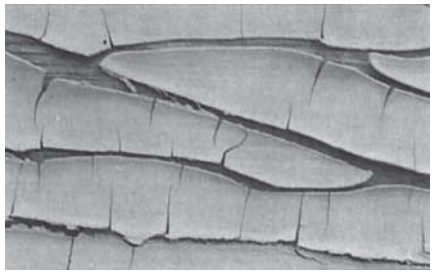


FIGURE 14.12: Severe cracking of a heavy coating film over a wooden surface.



FIGURE 14.13: Cracking of a coating film over a wooden surface, with cracks generally following the wood grain.

Cracking

Under most conditions, cracking is a formulation-related failure and one due to aging and weathering. It is different from checking and alligatoring in that it is not a surface problem, but one where the breaks in the coating extend from the surface through to the substrate. Thus, it is a much more serious type of failure than checking. Both checking and cracking are the result of stresses in the coating film that exceed the strength of the coating. Checking results from stresses on the surface, while cracking is caused by stresses throughout the film and between the film and the substrate.

Cracking can take several different forms. Figure 14.10 shows the cracking of a coating where the coating was applied heavily on the interior of a steel channel. In this case, it is nonlinear, taking a rather circular formation. Figure 14.11 shows a completely different type of cracking where, again, a coating is applied rather heavily on the interior of a steel channel. In this case, the cracking is in relatively short cracks in a heterogeneous pattern over the surface. The difference in configuration is undoubtedly due to the different resin and pigment formulations of the two coatings.

Coatings on wood usually are much more susceptible to cracking than are coatings on metals. This is due to the wood grain. When wood expands and contracts, it does so much more across than along the grain. Therefore, the stress in the coating is greatest across the grain, with the cracking being linear with the grain.

Severe cracking of a coating on wood is shown in Figure 14.12. In this case, there was severe shrinkage of the coating over the wood surface, creating wide cracks between the sections of coating. A more normal cracking over a wood surface is shown in Figure 14.13. Here, the cracking generally follows the wood grain and is caused by the differential expansion and contraction of the hard and soft grains.

Cracking occurs as the coating ages, as it is subject to expansion and contraction, wetting and drying, absorption and desorption of moisture, etc. Epoxy coatings (amine-cured) have been known to crack on steel, which is subject to expansion and contraction due to temperature changes. This is especially true where the coating may be applied in a relatively thick film. The thicker the film, the greater the stress within the film as curing continues.

For instance, an epoxy coating was applied on the exterior of a cylindrical tank that was alternately heated and cooled. The epoxy, as it cured, developed sufficient internal stresses to crack and pull itself away from the surface in large pieces. Lack of adhesion undoubtedly contributed to the failure, even though the coating was in tension due to its outside position on the cylinder.

Cracking can be relieved by the use of proper resins, plasticizers, and pigments. Reinforcing pigments that are fibrous or acicular aid materially in reinforcing the coating against cracking action. The addition of plasticizing resins or plasticizers also aids in softening the coating, allowing it to be more extensible and elastic, and thus tends to reduce the stresses caused by temperature changes, weathering, and continued polymerization. Coatings that continue to polymerize, or which oxidize over a period of time (e.g., oils and alkyds), are more susceptible to cracking failure than are fully polymerized vinyls and chlorinated rubbers.

In order to evaluate the extent of cracking in a coating, reference to ASTM Standard D661-93 (11)[8] is suggested. This provides a standard for the evaluation of the degree of cracking so that coatings can be directly compared where cracking failure is a problem.

Mud Cracking

Mud cracking and alligatoring often seem similar. However, they are caused by quite different sets of circumstances. While alligatoring penetrates only to the more flexible underlying coating, mud cracking goes directly through to the substrate and therefore is a source of immediate corrosion, along with possible chipping and flaking of the coating from the surface. Mud cracking occurs when highly filled coatings are applied rather heavily, which may be the case in runs and sags in the coating. This type of failure is usually found in overly thick areas of coatings. Water-base coatings that are highly filled often fail by mud cracking.

Mud cracking is also a rather immediate reaction, occurring as soon as the solvent or water begins to dry out of the coating. The more rapidly the solvent or water evaporates, the greater the chance that mud cracking will occur. Water-base coatings are usually emulsions or dispersions, and, in this case, the resin is not a continuous phase, but is broken up into small particles or droplets. When these materials dry rapidly, the resin particles do not properly coalesce and the pigment acts like mud in a dried-out pond.

Zinc-rich coatings often tend to mud crack, even though manufacturers have spent much time in formulating to overcome the problem. The reason is the high pigment:vehicle ratio and the nature of the zinc particles. Being spherical, they have poor reinforcing characteristics, and, when this is combined with a high pigment loading and a low tensile binder, an increased rate of shrinkage occurs upon rapid drying, leaving a mud-cracked surface.

The prevention of mud cracking is a combination of coating selection and proper application. Avoid highly filled water-base coatings if fast drying conditions exist. Coatings should have a proper pigment:vehicle ratio for the type and volume of pigment being used. If possible, reinforcing pigments should be included in the coating. Coatings should be applied during drying conditions that are moderate, with the elimination of sags or puddles that can contribute to mud cracking. Apply coats as thinly as possible, using a second pass to develop the required thickness.

Wrinkling

Wrinkling is a peculiar phenomenon and is usually associated with coatings that are applied at too great a thickness, many times occurring in sags and puddles. In place of shrinkage, as is the case with checking and cracking, wrinkling is the result of the swelling of a coating where the surface of the coating expands more rapidly during the drying period than the body of the coating. Wrinkling occurs most often with oil-base coatings, alkyds, and similar materials. It is often seen where a spill may have occurred with linseed oil and the coating is allowed to dry somewhat before cleanup. The surface of the linseed oil expands as it absorbs oxygen from the air, and this causes it to wrinkle over the un-oxidized body of the coating.

Many oil-base materials also contain driers that serve to increase the drying speed. Some driers are used to speed the surface cure and others are used as through-drying materials. If a coating contains an excess of surface drier, wrinkling may occur wherever the coating is slightly thicker than normal. Cobalt materials or cobalt driers are a common type of surface drier. Zinc and lead compounds are classified as the through-drying driers. All of these reactions depend on oxidation, air temperature, surface temperature, and coating thickness.

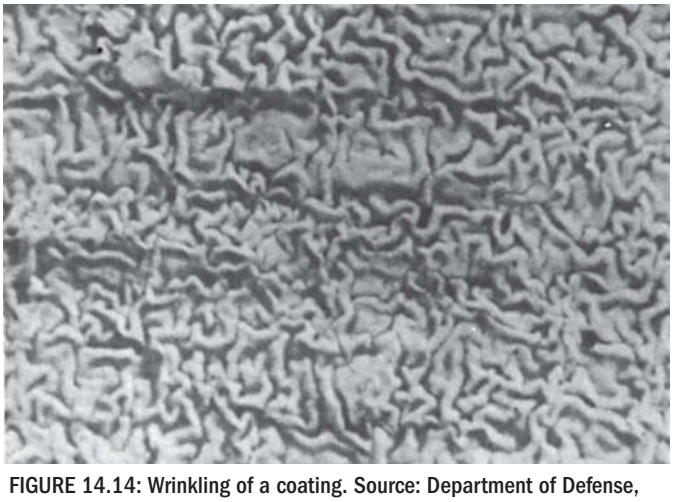


FIGURE 14.14: Wrinkling of a coating. Source: Department of Defense, "Paint and Protective Coatings," Army TM 618 10.5, pp. 5-26.

Temperature has a considerable influence on the problem of wrinkling. Coatings that cure without wrinkling at ordinary application temperatures may wrinkle badly if the curing is accelerated by baking. An increase in temperature tends to cure the surface much more rapidly than the body of the coating. This is particularly true if the coating is formulated with a balance of surface and body driers for curing at a lower temperature. A substantial increase in surface temperature would cause the surface to cure more rapidly and therefore have a greater tendency to wrinkle. Wrinkling can also occur in cold weather when the thickened coating is applied so that a heavy film develops, or in hot weather in the sun when the topcoat dries quickly, but the coating underneath remains wet (Figure 14.14).

Wrinkling is unsightly; however, it may not severely reduce the corrosion resistance of a coating, since the surface swells rather than shrinks. If the coating can eventually through-dry and retain its adhesion, the wrinkling of the surface should not appreciably reduce its effectiveness. As a matter of fact, wrinkle finishes are designed and used as decorative finishes for many small pieces of office equipment or similar metal objects where the need for corrosion resistance is not great and yet a reasonably long-lasting coating is required.

One type of wrinkling that does affect the corrosion resistance of a coating occurs when aliphatic polyurethanes are applied late in the afternoon and the surface goes through the dew point in the evening before the polyurethane has cured sufficiently. The minimal effect will be loss of gloss in spots, but a more severe effect will be wrinkling to the point that the surface is soft and rubbery. It must be removed and reapplied, otherwise it will eventually crack and flake or peel off the underlying coat.

In coatings that have a tendency to wrinkle, such as oil-base materials and alkyd coatings, care should be taken during the application to make sure that several even, thin coatings are applied and that there are no areas of excessive thickness, such as sags or puddles. The elimination of all heavy areas in a coating application materially reduces the possibility of wrinkling.

Biological Failure

Bacteria and fungi are the primary microorganisms that can act on coatings. There are two types of action. One is the activity of a microorganism due to dirt and contamination on the coating. In this case, the bacteria or fungi merely live on the surface of the coating and do not necessarily affect its resistance. The second type is where the microorganisms actually use the coating for food and derive their energy from it. Under certain conditions, coatings can be rapidly disintegrated by this type of action. These latter coatings are all organic (e.g., alkyds, polyamide epoxies, and coatings that use biodegradable plasticizers). In these cases, the portion of the coating that is used for food is the cause of the difficulty, even though the resin portion of the coating might be inert under other circumstances.

One example of this is polyamide epoxy coatings, which are used under sewage conditions or under other conditions where moisture, bacteria, and fungi are active. Coal tar epoxy coatings are particularly effective under sewage conditions. However, when polyamide curing agents are used, they tend to fail quite rapidly. If amine-type curing agents are used, the coal tar epoxies have excellent resistance to sewage conditions.

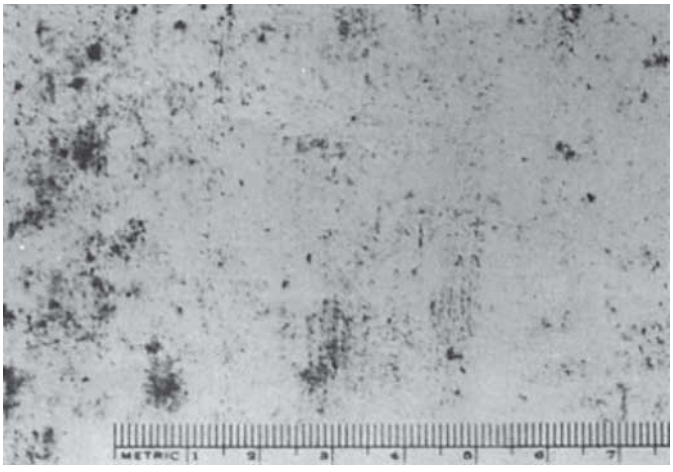


FIGURE 14.15: Fungus growth on a coating film, with fungus colonies covering most of the surface. Source: *Pictorial Standards of Coating Defects*, Mildew Resistance (Philadelphia, PA: Federation of Societies for Coating Technology).

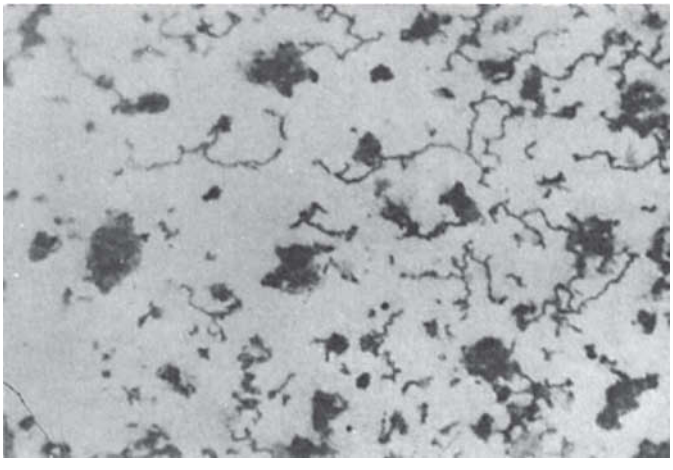


FIGURE 14.16: Photomicrograph of fungus growth on a coating. Source: *Pictorial Standards of Coating Defects*, "Mildew Resistance" (Philadelphia, PA: Federation of Societies for Coating Technology).

The area where fungus attack is most obvious is on coatings that are exposed to a highly humid atmosphere, particularly in the northern hemisphere on the north sides of tank surfaces and buildings. These areas remain damp for much longer periods of time than the sunny side, and, if the coating can be used for nutrients, ugly, dark, blotchy areas can form on the coating that make it very unsightly. Sooner or later, the coating's corrosion resistance is affected because of the breakdown of the film by the fungus attack (Figure 14.15).

When observed under a microscope, the black discoloration on the coating can be seen as black fungus colonies, and, unlike surface dirt, they are difficult to wash from the surface. Figure 14.16 is a photomicrograph of the fungus colonies on the surface of a coating. Note how the organism grows from a central spot out over the surface.

Such a failure does not occur when coatings based on very inert resins (e.g., vinyls, chlorinated rubbers, and acrylics) are used. Even with these materials, if they are plasticized, the plasticizers should be inert, non-biodegradable plasticizers as well. Where other types of coatings are used, the fungus growth can be largely or completely eliminated by the use of zinc oxide (ZnO) as part of the pigmentation, together with the addition of fungicides, bactericides, or a combination of all three in the basic formulation.

Where such a condition exists, the fungus or mildew should be removed from the surface of the coating by abrading the surface, by scraping, by power sanding, or by a light blast. In order to prevent the fungus from continuing its growth, the surface should then be washed with a solution composed of trisodium phosphate (Na_3PO_4), a detergent, and sodium hypochlorite (NaClO). The hypochlorite will both kill and bleach the fungus growth. Following such treatment, the area should be fully rinsed with clear water and thoroughly dried before recoating.

Discoloration

The discoloration of a coating may not seem like a major failure mechanism; however, appearance is a part of the coating's purpose. If its appearance is poor, the coating is generally considered unsatisfactory. Thus, coatings that fade, discolor, or become unsightly a short time after application can be considered to have failed. This is primarily a formulation-type failure. On the other hand, under certain conditions, particularly in recoating a surface, the previous material may bleed through the new topcoat, also creating a poor appearance. Materials such as wood treated with creosote preservatives, copper naphthanate, or previous coal tar or asphalt coatings can easily bleed into the new topcoats. If such materials exist, care should be taken to apply a coating that will not dissolve these materials and allow them to bleed through the new material.

Some dyes and pigments will also cause bleeding. More often, however, the resins that are used to formulate the coatings are the cause of discoloration. Some epoxy resins tend to yellow in the dark, as will linseed oil coatings. Polyurethane resins tend to yellow in the light. Vinyl chloride acetate coatings, for example, if improperly pigmented, may turn yellow or brown. Many clear coatings tend to discolor rather rapidly. This is due to the resins containing photosensitive groups on the molecules which, when exposed to strong sunlight radiation, become dark, yellow, or otherwise discolor.

Discoloration of aluminum flake pigmented epoxy mastic coatings may be considered an aesthetic failure because the color specified in the contract does not meet the color of the applied coating due the laminating action of the aluminum flakes. The platelet like leafing aluminum pigments (flakes) are also mixed with non-leafing aluminum pigments during the manufacturing of the epoxy mastic coating and the proportion of leafing vs. non-leafing pigments affects the final color. Rarely is this considered a corrosion-related failure, but it could be considered a failure to meet the contract specifications.

Pigments also cause color changes. Many colors, especially the brighter ones, fade and turn dull with time. Tinted coatings may chalk and become light colored. Orange pigments may be color-reactive and darken to a dull brown. Other yellow pigments may tend to gray or whiten. The lead pigments are susceptible to darkening in sulfide atmospheres and may even turn very dark or black. Some black and blue pigments tend to bronze and turn brown. It is obvious that pigments such as these should not be used in formulations for high-performance coatings, where they are to be exposed to severe weather conditions. Proper inert pigments of many colors and shades are actually beneficial and will help shade the resin used for the coating and prevent discoloration. For the most part, the best preventive solution to discoloration is experience based on actual operating conditions.

Inorganic Coatings

Up to this point, the discussion of formulation-related failures has been primarily oriented toward organic coatings, which is where

most such failures occur. On the other hand, inorganic coatings are also susceptible to some formulation related failures.

One of the principal causes of formulation problems with inorganic zinc (IOZ) coatings is the fact that they are made with silicate vehicles, either alkali silicate or organic silicate such as ethyl silicate. Neither of these materials is a good film former in the sense of film formation by organic materials. When unpigmented, these materials usually form a brash, clear deposit on the surface that tends to check and crack and to have little coating strength. It is only after the reaction with the zinc pigmentation that these materials form a film that has both adhesion and strength. Under these conditions, it is obvious that formulation is critical, and small variations in additives or pigmentation can cause the coating to be soft, poorly adherent, or to have generally poor film characteristics.

Checking

Because of the character of IOZ coatings, they are particularly subject to checking if the formulation is not proper. In addition to the fact that the silicates in themselves are poor film formers, IOZ coatings are highly filled with powdered metallic zinc and other pigments. The ratio of pigments to binder is high, and under these conditions, particularly where drying is rapid, fine surface checking can occur.

Formulations often include fibrous pigments to help prevent the checking, as well as the incorporation of slower solvents and mixtures of silicates to aid in controlling the drying rate and the checking. As with organic coatings, the checking is usually a surface reaction, and as such, with otherwise properly formulated IOZ coatings, the small checking imperfection can heal due to the continuing curing reactions that occur within the zinc silicate film. Checking can also be prevented by proper application techniques. Thin, multiple-pass coats are often helpful. Application of the coating under less severe drying conditions, or under cover in order to keep the surface cool, improves the checking problem.

Cracking

Cracking or mud cracking also occurs with IOZ coatings. It often occurs rapidly and, again, is related to the rapid drying of the coating as well as the coating thickness. On the other hand, the high pigment:vehicle ratio is the basic cause. Where the coating is applied heavily and allowed to sag or puddle, mud cracking easily occurs, particularly where drying conditions are rapid. Its appearance is similar to that of the mud in a puddle of water that begins drying out. As the water evaporates, the finely divided soil particles contract and form mud cracks, which is where the name of this reaction originated.

Mud cracking usually occurs prior to the time that any chemical action of the silicate and the zinc occurs, so that when the coating is heavily applied, it is much like a heavy slurry. As it dries, it shrinks and the film cracks. Many times, the cracked area is curved up from the surface in chips or flakes. On the other hand, IOZ coatings have been applied as much as 1/8 in (3 mm) thick, and still maintained excellent film characteristics and adhesion without any evidence of checking or mud cracking. It must be stressed, however, that in this case the curing conditions of the coating were ideal, with just the right humidity, temperature, and evaporation rate for the water or solvent.

Primarily, the elimination or prevention of this problem is in the application of the coating (i.e., applying a relatively thin film, with additional passes if necessary, in order to obtain the thickness recommended by the manufacturer.

Pinpoint Rusting

Pinpoint rusting usually occurs where a coating has been in service for a long time, nearing the end of its useful life. However, if a coating is improperly formulated, pinpoint rusting can begin even a few days after application. This has occurred in a number of instances with some of the zinc coatings with a low zinc loading. (These are the lower-priced coatings, intended to be very competitive.) It has also occurred in some of the coatings where pigments have been added to provide a pastel color to the IOZ coating.

In one instance, the zinc was removed and colored pigment was added in sufficient volume to mask the zinc so that the zinc became ineffective as an anticorrosive pigment. Figure 14.17 shows the condition of such a zinc coating after only a few weeks in service. In such cases, the only remedy is proper coating selection. Personal knowledge of the coating or testing prior to use is the best procedure.



FIGURE 14.17: Pinpoint rusting of an IOZ coating shortly after application.

A summary of formulation-related failures giving the failure appearance, general cause of the failure, and the usual remedy for the failure appears in Table 14.1.

Failures Due to Coating Selection

Since Chapter 12 deals exclusively with coating selection, most of the information that might be covered here is covered in that chapter. However, since failures due to improper coating selection can be catastrophic, some discussion of failure due to improper coating selection seems worthwhile.

Mixed Surfaces

One area where coating selection can be difficult is where a coating extends from one type of surface to another (e.g., structural steel in a concrete foundation). The coating selected for the steel surface in the particular atmosphere might be entirely adequate. However, because of the entirely different surface presented by the concrete, the coating could fail quite rapidly over the concrete in a severe corrosive condition. The corrosive liquid or atmosphere could then attack the steel at the concrete/steel interface. In this case,

TABLE 14.1: Formulation-Related Failures

Organic Coating Failure	Failure Appearance	Cause of Failure	Remedy
1. Chalking	Surface soft and powdery. Easily removed by wiping surface.	Surface disintegration by actinic rays of sun on the organic resin binder; improper pigmentation.	Select coatings formulated with radiation-resistant resins (acrylics) and noncatalytic, nonchalking pigments.
2. Erosion	Similar to chalking. Surface removed on high spots and brush marks to base coating or primer.	Chalking mechanism with coating surface removed by weathering.	Select chalk-resistant coating with good flow out to a smooth film.
3. Checking	Surface phenomenon—uneven, small, noncontinuous fissures in coating which do not penetrate to the substrate.	Surface stresses caused by shrinkage due to weathering and continued surface polymerization and oxidation.	Select coating formulated with weather-resistant resins and inert reinforcing pigments in addition to noncatalytic colored pigments.
4. Alligatoring	Very large macrochecking, generally cross-hatched pattern.	Internal stresses where surface shrinks more rapidly than body of coating. Hard topcoat applied over soft undercoat.	Apply thin coats and thoroughly dry before adding additional coats. Never apply hard topcoats (epoxy) over soft undercoats (asphalt).
5. Cracking	Small breaks in coating to substrate. May be linear, cross-hatched, or curved. Cracks may or may not be continuous.	Stress set up in coating due to continued polymerization and oxidation; improper pigmentation.	Select coating formulated from nonreactive weather-resistant resins, reinforcing pigments, and nonreactive colored pigments.
6. Mud Cracking	Large macrocracking. Coating may curl at cracks and lose adhesion.	Rapid drying of highly filled coatings, especially water-based materials (water emulsion paints).	Use coatings with strong adhesion. Apply coatings under proper drying conditions and prevent sags, puddles, or areas of excess thickness.
7. Wrinkling	Furrows and ridges in coating surface. May be linear or random pattern. Wrinkle may be fine or quite large.	Surface reaction where surface of coating expands more rapidly during drying than does the body of the film.	Choose coatings with even, thorough drying characteristics. Apply evenly; avoid excessive thickness.
8. Biological Failure	Softening or slime reaction of coating. Blotchy brown or black spots on coating surface causing poor, dirty appearance.	The biodegradation of the coating by bacteria or fungii. The coating is used as a source of nourishment.	Select oil-base coating that contains permanent fungicides, bacteriacides. Nonoil coatings should use non-biodegradable modifiers.
9. Discoloration	Yellowing, greying, or darkening of coating.	Resin or pigment color change due to weather or chemical action.	Select coating formulated with both color stable resins and pigments.
Inorganic Coating Failure	**Failure Appearance**	**Cause of Failure**	**Remedy**
1. Checking	Usually fine visible or microscopic checks. Do not penetrate to the substrate.	The zinc pigment to binder ratio is high; rapid drying conditions cause surface checking.	Formulation should include reinforcing pigments. Apply coating as thin as recommended. Second coat, if necessary. Apply under favorable drying conditions.
2. Mud Cracking	Fine to fairly large segments (1 in.) flaking from surface.	Application of coating too heavy. Rapid drying conditions.	Apply coating at no more than recommended thickness. Apply under favorable drying condtions.
4. Pinpoint Rusting	Pinpoint spots of corrosion progressing from a few per square feet to almost continuous. Early failure can be catastrophic.	Zinc pigment mask by other pigmentation or improper zinc/binder ratio. Uneven coating thickness; thin coated areas show first failure.	Usual remedy: remove coating and reapply more satisfactory zinc coating. Apply maintenance coat at first sign of pinpoint failure.

Source: *Steel Structures Painting Manual*, Causes and Prevention of Paint Failure, Chapter 23, "Good Painting Practice," Vol. 1 (Pittsburgh, PA: SSPC, 1982).

the selection of a coating for one surface would not be adequate for the second surface. Where situations like this occur, it is best to consider both surfaces, and to select either a coating that is adequate over both surfaces or a coating for each surface, extending one or the other out over the coating on the other surface in order to thoroughly seal the joint between the two surfaces.

Chemical Exposure

Selection of a coating that is inadequate for the subsequent chemical exposure of the film is a common occurrence. Many times, this is due to minor chemical contaminants in the atmosphere or solution that were not taken into consideration during the coating selection process. One example occurred in an alcoholic beverage rectifying plant, which formulates alcoholic beverages such as sloe gin. The coating that was applied to one of the large mixing vessels was tested and found to be thoroughly resistant to alcohol, which is the primary ingredient. Shortly after the mixing tank was placed in service, it was noticed that on one side of the container the coating had disappeared.

Upon investigation, it was found that the area where the coating had disappeared was the area where the workers added the special additives and flavorings to the alcoholic solution. In this case, they were adding a rather high boiling aldehyde that was very penetrating and that actually dissolved the coating in the area where it ran down the tank. Obviously, all of the conditions of the atmosphere in which the coating was to operate had not been taken into consideration during the coating selection.

Tank Linings

Another area where there have been failures due to coating selection has been in tank linings, tank car linings, and tanker ship linings, where combined service causes difficulties. Tank cars and tanker ships are frequently subject to alternate cargoes of quite different materials. While a coating may be entirely satisfactory for one of the cargoes, when a second loading follows the first, the coating may fail. This has actually happened many times under alternate loading conditions. In one instance a vinyl coating was used as a lining for

TABLE 14.2: Compatibility and Adhesion Properties of Coatings and Paints[1]

Existing Painted Surface *(Aged 12 mos. min.)*	Long Oil	Med. Oil Alkyd	Short Oil Alkyd	Silicone Alkyd	Oil Modified	Phenolic Modified	Amine	Polyamide	Coal Tar Epoxy	Chlorinated Rubber	Solution Vinyl	Moisture Cured	Catalyst Cured	Coal Tar	Asphalt	Latex
Long Oil	G	G	F	G	G	G	X	X	X	X	X	X	X	F	G	G
Med. Oil/ Alkyd	G	G	F	G	G	G	X	X	X	X	X	G	F	F	G	G
Short Oil/ Alkyd	G	G	G	G	G	G	X	X	X	X	X	G	F	F	G	G
Silicone Alkyd	G	G														
Epoxy Ester																
Oil Modified	G	G	G	G	G	G	X	X	X	X	X	G	F	F	G	G
Phenolic Modified	G	G	F	G	G	G	X	X	X	X	X	G	G	F	F	G
Catalyzed Epoxy																
Amine	X	X	X	X	X	X	X	X	X	X	X	X	G	X	X	X
Polyamide	G	G	G	G	G	G	G	G	G	G	G	X	G	G	G	G
Coal Tar Epoxy	X	X	X	X	X	X	G[2]	G[2]	G[2]	F[2]	X	X	F	G	G	G
Chlorinated Rubber	G	G	G	G	G	G	X	G	X	G	G	F[2]	F	G	G	G
Solution Vinyl	G	G	G	G	G	F	X	G	X	G	G	F	F	F	G	G
Zinc Rich																
Inorganic	X	X	X	X	X	X	G	G	F	G	G	F[2]	G[2]	G	G	G
Organic	X	X	X	X	X	X	G	G	G[2]	G	G	G	G	G	G	G
Coal Tar	X	X	X	X	X	X	X	X	X	X	X	X	X	F	G	F
Asphalt	G	G	G	G	G	G	X	X	X	X	X	X	X	X	G	G
Latex	G	G	G	G	G	G	G	G	G	G	G	X	X	G	G	G
Urethane																
Moisture Cured: Type II	F	F	F	F	F	F	X	X	X	X	X	F	G	X	X	X
Catalyst Cured: Type IV	G	G	G	G	G	G	G	G	G	G	F[2]	G	G	G	G	G

G = Good—always work. F = Fair—will work; some exceptions. P = Poor—will not work; some exceptions. X = Not recommended.

[1]This table should be used only as a guide, and as stated in the text, a test patch must be used to confirm satisfactory performance of the intended coating or coating system.

[2]Application critical.

[3]Properties will be same as for binder shown for existing paint.

Source: NACE Technical Committee Report, "Combating Adhesion Problems When Applying New Onto Existing Finish Coats of Paint," T-6H-27 (draft) (Houston, TX: NACE, 1982).

a refined oil tank in a tanker. The coating stood up well to gasoline, diesel fuels, lube oils, and similar products. However, when toluol was included as a lading, the entire tank lining blistered. In fact, the blistering was sufficient for the lining to be considered a total failure. In this particular case, however, the ship went back into gasoline and diesel service. After 10 years of service, the lining had still prevented any corrosion in the tank, in spite of the blisters that still remained.

Tank cars and tanker ships are also often steamed or washed with hot water after unloading one material and prior to loading another. While the coating may stand up well under the original material, if there is some absorption of the material by the coating, the hot water and steaming can often cause blistering as well. Alternate ladings are a difficult service, because of the varying kinds of chemicals to which the coating may be subjected from one trip to the next, and coating selection is critical in making sure that any coating used will not only be satisfactory for the various ladings, but will withstand many of the tank washing procedures as well.

Repairing and Recoating

Coating selection is even more of a problem when recoating is being considered. In this case, not only is it necessary to determine the properties of the coating from the standpoint of the exterior exposure, but also the coating must be satisfactory over the existing coating on the structure. Many failures have occurred due to a lack of attention to the properties of the undercoat and adhesion characteristics of the new repair coating. Table 14.2 shows some of the compatibility and adhesion characteristics of coatings when one material is applied over another. This table, developed by NACE Technical Committee T-6H, is a good general reference for the compatibility

of some generic materials.[9] If there is ever any question, a test area of the new material should be applied on the old in order to make sure of the adhesion and compatibility of the new material, as well as the retention of adhesion of the old material after recoating.

Substrate-Related Failures

Chapter 8 stressed the importance of the substrate in its relation to coatings. However, some additional points should be emphasized from the standpoint of failures due to substrate reaction.

Steel

Steel is probably the most important substrate because of the volume of steel surface that requires coating. While steel may be the easiest surface to coat because of its dense, impervious nature, steel is also reactive to many different environmental conditions, and can thus become a significant factor in coating failures.

There are also many different types of steel surfaces over which coatings may be applied. Hot-rolled steel with its mill scale surface is certainly one of these, and when overcoated, mill scale can be a major cause of coating failure due to its delamination from the steel surface and the ability of corrosion to undercut a mill-scaled surface. Mill scale is also cathodic to bare steel, and as such aggravates the coating breakdown through the action of a massive cathode and a small anode. Previously corroded steel also presents a very different surface from new, clean steel. When rust has occurred and coatings are subsequently applied, even though the surface is blasted clean, the coatings will fail more rapidly in these areas than over the virgin metal due to contamination.

Cold-Rolled Steel

Cold-rolled steel is vitally important because of the many millions of square feet of surface that are coated. This includes most appliances, automobiles, and many other similar pieces of equipment. Cold-rolled steel is particularly difficult to coat with an organic material because of its smooth character. There are many coatings that will adhere to it; however, the same coatings will adhere and retain their adhesion much better if the surface is lightly blasted to increase the tooth.

One way in which cold-rolled steel is improved is to treat the surface with a zinc phosphate. Most automotive and appliance surfaces are treated with zinc phosphate to reduce underfilm corrosion of the applied coatings. Robert Iezzi and Henry Leidheiser, in a paper on the treatment of cold-rolled steel,[10] indicate that carbon contamination of the steel surface is a major factor in the adhesion and effectiveness of the zinc phosphate treatment. They state:

> Samples with low surface contamination have high electrochemical reactivity and a high surface area available for zinc phosphate nucleation. This combination results in nearly complete zinc phosphate coverage with low porosity and good adhesion to the steel surface.
>
> Samples with high surface contamination have a less electrochemically active steel surface and a reduced area for zinc phosphate nucleation. Nucleation of zinc phosphate crystals grow laterally over contamination, but coverage is incomplete and the bond is poor. Samples with high surface contamination fail much more rapidly than those with low surface contamination because of the lower bonding area of the zinc phosphate layer to the steel surface and the consequent higher oxygen and moisture availability to the steel surface due to the incomplete coverage of the zinc phosphate layer, i.e., porosity. This greater oxygen and moisture access to the steel surface promotes the cathodic delamination reactions and accelerates paint failure.[11]

This is a considerably different surface condition than exits for most structural steel. However, it demonstrates the different types of surfaces that steel can present as a substrate for coatings.

We've previously seen how the same coating can act very differently on one surface as compared with another. This is an important finding, since there is a tendency, when a coating works satisfactorily in an atmosphere and over a specific surface, to then apply the same coating over other surfaces that may be in a similar atmosphere.

A good example of this is the use of coal tar epoxy coatings subject to a sewer atmosphere. Coal tar epoxy applied over steel provides a good corrosion-resistant material, and will fully protect the steel surface if it is properly applied. When the same coating is applied over concrete, because of the inherent porosity of the concrete itself and the difficulty of obtaining a continuous film, the coal tar epoxy coating can fail quite readily.

Going a step further, if the coal tar epoxy is applied over wood, early failure may be expected because of the continual contraction and expansion of the wood due to changes in atmospheric moisture. In this case, since the coal tar epoxy is somewhat brittle, it would soon crack over the wood surface, allowing penetration of whatever materials are in the atmosphere.

Aluminum

Aluminum has become a much more common metal surface over which to apply coatings. In many ways it is a good coating surface, particularly where the metal surface is broken up by a light abrasive blast. Vinyl coatings that have been applied to aluminum surfaces have remained on the surface for more than 35 years, maintaining satisfactory protection and excellent adhesion.

Aluminum is often attached to steel in order to provide a lightweight superstructure. While such a combination of metals may be good from an engineering standpoint, it may create difficulties from a coating standpoint. Unless the junction of the steel and aluminum is insulated so that there is no actual bimetallic contact, a galvanic corrosion cell is easily established. This is particularly true if the coating has a tendency to crack at the junction of the two materials.

Lightweight deck houses have been seen on steel ships where the coating on the aluminum was undercut for several inches away from the junction of the two metals due to the penetration of seawater at the junction and the rapid corrosion of the aluminum in that area. Also, the adhesion to the aluminum was not as effective as it would have been had the aluminum itself been blasted prior to the application of the coating. While the steel substrate adjacent to the aluminum was well protected, the combination of seawater, aluminum salts, and alkali buildup at the cathode caused the coating to peel away from the junction of the two metals.

Zinc

Galvanized steel attached to ordinary steel can also cause similar problems under many corrosive conditions. Zinc, as previously seen, is an excellent surface over which to apply many coatings. On the other hand, other coatings tend to fail fairly rapidly over a zinc

surface because of their reactivity with that surface. Oil coatings, alkyds, and other coating materials that contain drying oils, often react poorly over a galvanized surface or over an IOZ surface due to the reactivity of these materials with the zinc salts that form between the coating and the substrate.

Figure 14.18 provides an example of the failure of a coating over a galvanized surface. In this case, an alkyd coating is cracking and spalling away from the zinc surface in large pieces. This indicates the bond between the zinc and the coating is deteriorating due to chemical reactions between the zinc and the coating. No corrosion exists because of this galvanized steel surface.

Zinc surfaces oxidize and react with the atmosphere quite readily, and many times the zinc surface is allowed to react with the atmosphere before the coating is applied. Any coating that goes over a zinc oxide or zinc carbonate surface must be thoroughly compatible with these zinc salts; otherwise, early adhesion problems develop.



FIGURE 14.18: Coating failure over galvanized steel.

Used Surfaces

Used surfaces are much more difficult to coat than new ones, and the failure of a coating over a used surface is much more probable than one applied over a new original surface. Surfaces that have been subject to sulfides are a particular problem, and coatings have failed extensively over such surfaces. In this case, the metal surface, even though it apparently is blasted free of corrosion products, contains enough iron sulfide (FeS) and iron oxide (Fe2O3) to create a substrate that is less than satisfactory for the application of coatings.

Figure 14.19 is a schematic drawing of a corroded area on a piece of steel where minute microscopic contamination remains even after blasting. That these areas exist after blasting has been demonstrated several times with both chlorides and sulfides being identified. After the surface has been blasted, and with high humidity, these minute areas that are invisible to the naked eye soon become visible by absorbing moisture from the air. When this happens, these tiny areas of contamination turn dark and become pinpoint rusted areas. If these small areas are coated over, they become focal points for coating failure, and thus are one of the primary causes for continuing failure in the same area where coatings had failed previously and where corrosion existed.

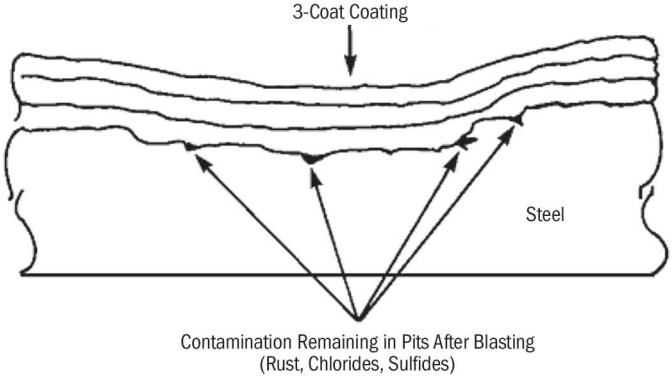


FIGURE 14.19: Contamination remaining in a corroded area of steel after blasting.

Such a substrate is difficult for most organic coatings to cover and remain intact for long periods of time. (Chapter 8 on surface preparation covered this problem in more detail.) One of the options that has proven satisfactory in many areas is the application of IOZ coatings. In this case, the iron ions that are present in the tiny spots of contamination are reacted into the coating, helping to nullify the contamination. The problems involved with used steel surfaces should not be underestimated in any way. Untold failures of coatings have occurred because the problem of prior use of a substrate had not been recognized.

Wood and Concrete

Similar problems are not necessarily found with wood or concrete surfaces, although they are definitely affected by previous use. The problem with these surfaces is that they absorb and retain soluble or reactive materials that are difficult to remove without removing part of the actual surface of the concrete or wood. The contamination that has been absorbed will cause blistering, lack of adhesion, and coating failure. Previously used surfaces of all types should be given extra care during their preparation in order to make a satisfactory substrate for the coating.

Cleanliness

Cleanliness of the surface is part of the substrate problem and is vitally important to the life of the coating. It can be stated as a rule of thumb that any coating applied over a perfectly clean surface will last longer and be more effective than the same coating applied over a less than clean surface. This not only applies to concrete and wood, but to all types of metal as well. The best coating available will fail rapidly if it is applied over a surface that has not been properly prepared to receive the coating. This is true even when it can be proven that the coating material itself can resist the environment and protect the metal. The probability of coating failure over a surface is directly proportional to the amount of contaminant left on the surface.

The substrate is important, since otherwise there would be considerably less emphasis on surface preparation throughout the coating field. The problem of substrate preparation is recognized by several corrosion-related organizations (NACE, SSPC, ISO, ASTM) that have established standards for the preparation of surfaces and the cleanliness of the substrate over which a coating is to be applied. Table 14.3 provides a summary of substrate-related failures.

Surface Preparation-Related Failures

It is little wonder that improper surface preparation is the cause of a sizable number of coating failures. There appears to be a psy-

TABLE 14.3: Substrate-Related Failures

	Coating Failure	Failure Appearance	Cause of Failure	Remedy
1.	Previously Used Steel	Blistering, rust, tubercles, loss of adhesion in areas where steel was previously exposed to corrosive conditions	Retention of minute amounts of corrosion product or contaminant along grain boundaries of the steel surface, even though blasted to white metal	Wash-blasted surface with water or dilute phosphoric acid solution and reblast. Apply an anticorrosive primer with strong adhesion. Where applicable, an inorganic zinc primer may provide a good base coat by reacting with the minute surface corrosion after the first blasting.
2.	Galvanized or Metallic Zinc Surface	White zinc corrosion product forming under the coating or actually breaking through the coating	Formation of zinc salts (oxide, sulfide, oxychloride, zinc soap) underneath coating.	Brush blast zinc surface or treat with commercial zinc treatment. Apply a nonoil base, inert, strongly adherent primer.
3.	Aluminum	White Corrosion product causing pinpoint failure in coating; loss of adhesion because of very smooth surface. Possible blistering.	The very smooth aluminum oxide surface. No physical adhesion.	Very lightly dust blast the aluminum surface, or where applicable, treat with commercial aluminum treatment. Apply a primer with known compatability and strong adhesion to aluminum surface.
4.	Copper	Grey-green corrosion product; loss of adhesion.	Very smooth copper oxide surface. No physical adhesion.	Brush blast copper surface or etch with commercial copper treatment. Apply a primer with known high adhesion to copper.
5.	Wood	Checking and cracking of coating. Flaking from hard winter grain. Dense coatings with a low MVT rate may blister due to absorption and evaporation of moisture from the wood.	Expansion and contraction of wood due to varying temperature and humidity. Differential expansion summer and winter grain. Very hard dense winter grain combined with soft porous summer grain, causing a variation in adhesion.	Start with a slean, newly sanded wood surface. Apply low molecular weightly, highly penetrating paint, preferably oil base, with sufficient elasticity to expand and contract with the wood surface. Paint should have relatively high moisture porosity to allow wood to breathe.
6.	Concrete	Blistering of coating. Formation of calcium salts under coating, forcing coating from the surface. Loss of adhesion and peeling.	The chemical reactivity and moisture content of concrete. Its nonhomogeneous very porous structure. Pinholes, water, and air pockets in poured concrete surfaces.	The concrete should be clean and the surface dry. It may be acid etched or lightly blasted to obtain proper surface condition. Use a low molecular weight, highly penetrating primer with strong alkali resistance (liquid epoxy). Primer should be heave bodied and thixotropic to fill imperfections in concrete surface.

Source: Federation of Societies for Coating Technology, Pictorial Standards of Coating Defects, Chalking Resistance, Erosion Resistance, Mildew Resistance, Philadelphia, PA.

TABLE 14.4: SSPC Surface Preparation Specifications

	Method of Surface Preparation	Specification No.
1.	White Metal Blast Cleaning	SSPC-SP 5
2.	Near White Metal Blast Cleaning	SSPC-SP 10
3.	Commercial Blast Cleaning	SSPC-SP 6
4.	Acid pickling	SSPC-SP 8
5.	Industrial Blast Cleaning	SSPC-SP 14
6.	Brush Off Blast Cleaning	SSPC-SP 7
7.	Power Sanding	SSPC-SP 3
8.	Power Wire Brushing	SSPC-SP 3
9.	Chipping and Hand Wire Brushing	SSPC-SP 2
10.	Solvent Cleaning	SSPC-SP 1

chological block with painters of all types when it comes to proper surface preparation. However, there is no substitute for proper surface preparation, as previously discussed in Chapter 8, if long life is expected from a coating.

When applying a repair coat over a previous material, even greater care is necessary to make sure the surface is prepared properly to accept the repair coating. Compatibility of the repair material, as well as proper cleaning of the surface, is the key to a satisfactory repair job. Intercoat contamination as well as outside contamination of a properly prepared surface before coating application is often a cause for coating failure. Such contamination can come from many sources (e.g., from the chemical plant next door to the air used to sandblast the surface). Many air compressors that have had poor maintenance may pass small quantities of oil into the air, which can often contaminate an otherwise clean, blasted surface, causing the applied coating to blister wherever a minute oil droplet remains.

There are a number of methods of surface preparation available. SSPC has prepared a list of surface preparation specifications covering most of the common methods of preparing steel.11 This list is given, in a descending order of effectiveness, in Table 14.4.

As one goes down the list in Table 14.4, the method of surface preparation leaves increasing amounts of contamination on the surface and therefore creates an increasing chance of coating failure, with the method at the bottom of the list (solvent cleaning) being almost a sure failure with any of the high-performance coatings. This method is effective must be selected to go with each of these methods in order to obtain even reasonably good life from the coating. The high-performance coatings, which are those with which most corrosion engineers are familiar, should not be used with a primary surface preparation less effective than number 5 on this list.12

There are coatings that are specially formulated for application to rusty hand-cleaned surfaces. Some of these do a good job, but only where used in a light to very moderately corrosive atmosphere. Where a severe corrosive atmosphere exists or where the coating must withstand immersion, only the best surface preparation is satisfactory. Any techniques following acid pickling (Table 14.4) leave too

much contamination on the surface to prevent coating failure. Even within the group of the first six, failures can easily occur because of the use of poor abrasives during blasting or sloppy pickling techniques.

Abrasives

There are literally hundreds of abrasives used to prepare metal surfaces. These range from the very good silica materials, such as garnet, flint, silica sand, etc., to river sand. The unwashed river sands usually contain considerable amounts of clay. When this is impacted on the surface, it not only creates a large amount of dust, which makes for poor visibility, but when it is driven on the surface, the impact of the clay makes it tightly adhere to the surface. In fact, it is almost impossible to remove by blowing or brush blasting. Thus, application of a coating over such a surface is almost a sure failure. There is little that can be done with it other than to wash the surface with clean water and scrub it to remove the clay from the surface profile. Even this is a less than satisfactory procedure.

The abrasives also have a broad range of particle size. The optimum abrasive size is believed to range from 16 to 30 mesh. This will produce the most uniform surface and surface profile, and is effective for the greatest number of coatings. While there are heavy-bodied coatings that require heavy surface profiles, they represent the exception more than the rule.

All of the different abrasives provide a different anchor pattern and profile on the surface. As mentioned above, it is believed that the silica sand using a 16 to 30 mesh sand produces a universally satisfactory profile. Since silica sand is no longer allowed in many countries, garnet in the same mesh size has achieved very broad acceptance for a universally satisfactory profile. Steel shot and steel grit provide a completely different profile from that of the sand, and coatings that may be entirely satisfactory over the sandblasted surface may not perform as well and may fail faster over a steel shot- or grit-blasted surface. On the other hand, there are other coatings that perform equally well, if not better, over the cut profile of steel grit. There are dangers here, however, from too great a roughness of the surface caused by either too great a size in either the sand or the steel grit.

For instance, the exterior of a steel pipe had such a heavy profile that it was necessary to go over the surface with an emery cloth prior to coating application. The surface in this case was essentially the same as a heavy rasp or file. There have also been ship bottoms blasted with silica sand with a grain size up 1/8 to 3/16 in (5 mm). In this case, the profile was extreme and was not satisfactory for most ship bottom coatings. There are other cases where there is insufficient surface profile or pattern on the surface where the blasting has occurred too rapidly so that there are many areas of plain surface in between the impact areas of the steel or shot. This has been seen particularly in automatic blasting units where the steel has passed under the unit at too rapid a pace. Blasting such as this can leave sizable particles of mill scale, as well as rust and contamination, all of which make for early coating failures.

Inhibitors

At the present time, with the increase in wet abrasive blasting and water jetting, there are a number of different inhibitors used, along with a number of different methods used for treating steel surfaces to prevent them from changing color. Citric acid and some of the citrates have been used for this purpose. A number of tests have been made using such materials. In many cases, the adhesion of coatings over such treated surfaces was considerably less than a plain white metal blast when tested in seawater for several months. This was true for both organic and inorganic coatings.

There are also many phosphates used, with the phosphate being applied during water jetting or during and after blast wash. Again, it is suggested that these be used with caution, since many coatings do not adhere as well to such a treated surface as they do over a standard abrasive blast. Coating failures are more probable, therefore, when inhibitors are used than when the same coating is applied over a dry abrasive blasted surface. If a coating is to be immersed, or where it is used in an area of high humidity or condensation, metal surface inhibitors should be used with caution, and the coating thoroughly tested over such a surface prior to making a full-scale application.

Application-Related Failures

Chapter 10 was dedicated entirely to the importance of and techniques involved in coating application. Nevertheless, there are a number of failures that are a direct result of improper application, and thus should be addressed in any discussion of coating failures. Almost all application-related failures are due to carelessness and poor workmanship. For instance, the surface may not be sufficiently clean, with dirt, dust and many more obvious types of surface contamination (e.g., sand or steel grit left from blasting operations, gum wrappers, cigarette butts, tobacco juice, and even, on occasion, urine). All of these things have been coated over during coating application, resulting in failure once the coating was put into service. Most of the above contaminants are not so much the result of poor workmanship as of plain carelessness, with the applicator and inspector overlooking items that will obviously cause prompt coating failure.

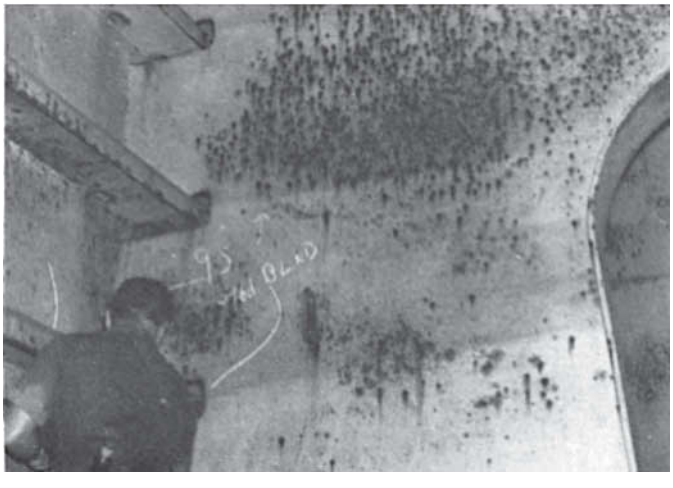


FIGURE 14.20: General failure of an epoxy coating in a ship's tank due to poor and inconsistent coating application.

Poor workmanship refers to improper coating application by being too close to or too far away from the surface, or by spraying the surface at angles that cause coating imperfections. All application-related failures are due to lack of care, lack of an understanding of coating fundamentals, or poor workmanship, which may be the result of poor training in the application of high-performance coatings or little pride in proper workmanship. Figure 14.20 shows a general coating failure as a result of poor application procedures. Areas in the same tank where application was consistent showed no failure whatsoever.

Brush Marks

The failure that occurs when pronounced brush marks are left in a surface is due to the hills and valleys left in the coating by the brushing technique. There are many heavy-bodied coatings that are difficult to apply and that leave pronounced brush marks. However, these can be overcome through the use of proper application techniques. The failure starts as pinpoint rusting in the low, thin areas of the coating, which soon undercut, and, because the low areas of the coating are rather close together, rapid, total failure results.

Runs and Sags

Failures that are due to runs and sags are usually a result of too great a coating thickness. Many of the internally reacted or catalyzed coatings continue to cure over a considerable period of time, and, in areas where the coating is heavy (e.g., runs and sags), they often check and crack, leaving the substrate open to rapid coating failure. Runs and sags are also a result of careless application. In brushing, it means that the material was not brushed out sufficiently to eliminate overly thick areas in the coating and that the curing was sufficiently slow that these areas sagged. With spraying, improper gun adjustment can cause sags or runs, or merely the overly heavy application of the coating at any one spot. This can be caused by the gun being held too close to the surface and not moved rapidly enough over the surface in order to obtain a uniform film.

Inorganic coatings often crack and scale in runs and sags. While corrosion may not begin immediately, it will proceed more rapidly in these areas than in the smooth, evenly coated areas. Also, if such areas are overcoated with organic coatings, these rough areas are focal points for the breakdown of the organic coating. Runs and sags should be eliminated soon after the application of the coating, and before the coating has dried sufficiently so that the sags cannot be removed.



FIGURE 14.21: A thin coating area showing both pinpoint and general corrosion after a period of exposure.

Improper Coating Thickness

There are two types of failures that occur from improper coating thickness. One, as with runs and sags, is a result of the coating being too thick, and the other is a result of the coating being too thin. Where a coating is applied too thickly, particularly with a lacquer-type coating, the coating may not dry properly and may have an excessive retention of solvent in the coating. Retained solvents may cause blistering and poor adhesion to the substrate because the underlying coating is softer and because of the retained solvents close to the substrate. Where the coating is catalyzed or internally cured, the coating may have internal shrinkage because of the thickness, which causes checks, cracks, and even scaling. Where this occurs, rapid undercutting of the coating may result from the poor adhesion of the overly thick film.

In the case of thin coatings, failure is primarily due to rapid application that does not leave enough material on the surface. The type of failure that occurs in these areas is due to pinpoint rusting, with the pinpoints gradually becoming larger until the entire coated area is undercut in the thinnest spots. This is a common type of coating failure and can easily be overcome by careful workmanship on the part of the applicator, and by careful checking on the part of the inspector to ensure that the proper thickness of the coating is applied.

Figure 14.21 is an example of improper coating thickness on the thin side. The area above the weld is corrosion free, while the area of the pile below the weld was undoubtedly done at a different time by a different worker, who applied an inconsistent and thin coat resulting in both pinpoint and heavy rusting.

Where coatings are applied over wood, excessive coating thickness can result in cracking and scaling as the alkyd or oil coating continues to oxidize in the air. Again, this is a common type of failure and the remedy is simply the application of thin coats in order to obtain a thorough cure before application of additional coats.

Holidays

Regardless of their size or description, holidays are essentially a discontinuity in a film of coating. The discontinuity can be limited to one or more layers of an applied film or it can be down to the substrate. Holidays are also related to coating thickness. Holidays are areas where the applicator has missed coating the surface, or where an extremely thin spot remains after the coating is applied. These can be on plane surfaces where the coating was not overlapped sufficiently. They are more often found in difficult-to-coat areas, such as interior corners, along welds, around bolts and rivets, or wherever there are rapid changes in the direction of the surface. The type of failure resulting in these areas is an early pinpoint rusting of the area, followed by the formation of rust scale and the undercutting of the coating adjacent to the holiday. Again, this is a common type of failure and is due to lack of care during coating application. A 50% overlap of each pass of the coating is recommended in order to ensure against holiday-type failure.

Figure 14.22 shows a typical holiday after the coating has been in service. The coating in this area was not overlapped sufficiently to make a continuous film. The failure ranges from pinpoint rusting to continuous rust in the thinnest area of the holiday.

Overspray

When overspray is allowed to remain on the coating, and additional coats are applied, the coating generally will not penetrate around the overspray particles, but will leave imperfections in the coating at this point. Pinpoint rusting then occurs, with the rust growing to where the coating is undercut, resulting in a complete failure of the area.

Overspray is a common type of coating failure, particularly where fast-drying coatings are used. However, even heavy-bodied epoxies and similar materials will cause overspray as a result of improper application. Overspray, in general, is a result of poor application techniques, a result of either poor gun adjustment or application of the coating at too great a distance from the surface and not applying an even, wet film to the surface. Overspray can be prevented by proper gun adjustment and careful application.

Figure 14.23 shows a typical overspray failure (i.e., pinholing around or adjacent to the rough overspray particles). In this case, it can be seen that the lower part of the surface had been given a cursory wipe before the second coat was applied. There is no corrosion where even this minimum cleaning was done. On the other hand, above the wiped area, heavy pinhole rusting has occurred where the second coat was applied over the rough overspray of the first coat.

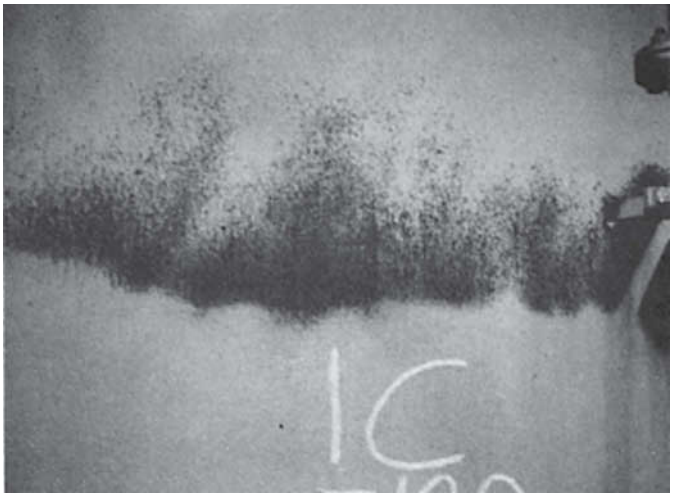


FIGURE 14.22: A typical holiday that is readily visible only after the coating has been placed in service. Both pinpoint and general corrosion are evident.

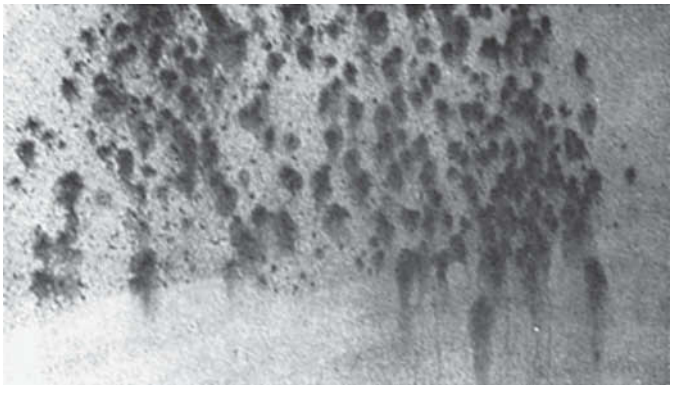


FIGURE 14.23: Typical overspray failure, showing pinholing adjacent to rough overspray particles.

Pinholes

Pinholes are also discontinuities in an applied film of coating, and can exist in one or more layers of a coating film or all the way down to the substrate. Pinholes in a coating can result from overspray. For the most part, however, they result from heavy application of a coating, with air being blown into the coating surface during the application. As with overspray, pinholing can be caused by improper gun adjustment, where the gun does not atomize properly and air is entrapped in the coating. It can also be caused by the application of the coating too close to the surface, creating an area in the center of the fan where too much material is applied and where air bubbles are entrapped in the wet coating. The air bubbles remain, unless the coating is a very slow drying one, creating a pit that may go to the substrate or entirely through any one coat of the coating. In any case, the coating is thinner at these spots than in the body of the coating, and these are focal points for rapid coating failure. Pinpoint rusting occurs first, followed by undercutting of the coating around the pinhole. This is also a common type of coating failure caused by improper application and can be prevented by careful workmanship.

Figure 14.24 shows a typical pinholed coating after being in service. The one streak of pinholes is undoubtedly due to a pass of the gun that was too close to the surface, with air being blown into the wet coating. In this case, the coating was a heavy-bodied epoxy and was sufficiently thixotropic so that once the air bubbles were blown into the coating, they remained, creating the pinholes as shown.



FIGURE 14.24: Pinholing failure of a coating, with the pinholes being somewhat isolated in comparison with those found in overspray failure.

Spatter Coat

Spatter coat is much like a holiday or other workmanship defect. It is an area where the coating is not applied as a continuous film, but is applied sufficiently fast and in a small enough volume so that the coating reaches the surface not as a wet film, but as a series of discrete droplets with bare areas in between. This is a common application problem, and is the basis of most "holidays." The coated area may look like it is covered, but on close inspection, the droplets are visible, as are the bare substrate areas in between. The coating is thin, which is easily detected by a thickness gage. If such areas occur during an application, they are easily repaired by the application of an additional coat. If the coating is placed in service without repair, spatter coat areas are the first to fail.

Cratering

Cratering (or bug-eyeing or crawling) may be either an application problem, a material problem, or both. It is sometimes labeled as pinholing. Some materials that have a high surface tension have a greater tendency to behave in this manner than those with a lower

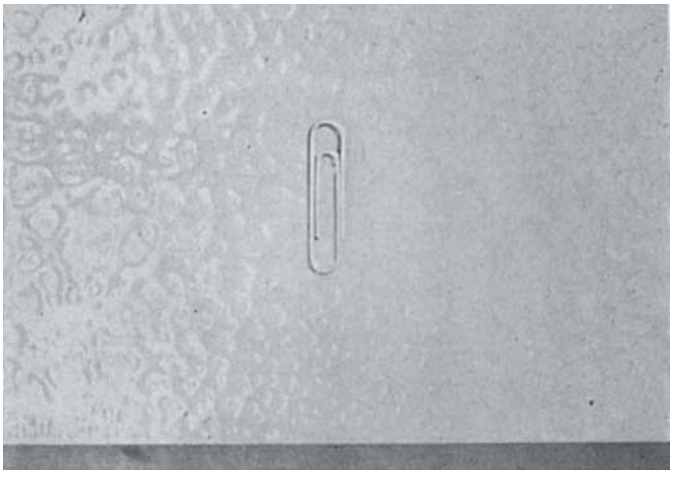


FIGURE 14.25: Cratering or crawling of a thermosetting coating.

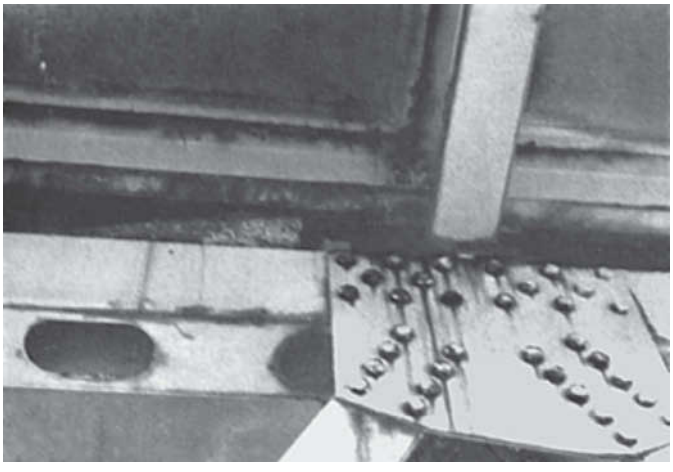


FIGURE 14.26: Edge corrosion in a marine atmosphere after approximately two years of exposure, with nearly all edges showing corrosion and undercutting of the coating.



FIGURE 14.27: Edge corrosion on a coated panel exposed to a marine atmosphere.

tension. Much cratering is due to contamination and dirt that may be on the surface or that falls into the wet coating during application. When a vehicle has some cratering tendency, minor contamination can seriously aggravate the problem. Oil in abrasive blast or atomization air is one source of such contamination and can be removed by proper oil and water filters on the application air line.

Cratering occurs before the coating dries, and as such can be eliminated during application. Often, the wet coating must be removed and reapplied. If the coating cures with the cratering in place, the coating surface, particularly in the cratered area, must be roughened sufficiently to break the surface before another coat is applied. The repair coat should be brushed to work the new coat into the previous one. The coatings most susceptible to this problem are those which thermoset (e.g., epoxies, phenolics, polyurethanes, etc.).

The areas of a coating where a crater forms are thin and are therefore focal points for coating failure. Without repair during application, pinhole corrosion can occur. Figure 14.25 shows the cratering or crawling of an epoxy coating and the uneven appearance that results.

Application failures are due to human and not mechanical or material failures. Application failures are often blamed on the material, poor equipment, lack of time, and many other similar excuses. Application failures, generally, are due to lack of care and poor application techniques on the part of the applicator and not to any other cause. Application-related failures are summarized in Table 14.5.

Design-Related Failures

Design and its effect on corrosion has been covered in several previous chapters. However, it is an important subject in terms of coating failures because it is difficult to change an existing design, and design does contribute to the corrosion resistance (or lack of resistance) of a structure.

Edges

The failure of coatings on edges is important since this is the area where corrosion usually first begins. The edge provides a sharp break in the coating and is also subject to more damage than flat areas. Edges invariably seem to be a problem, unless special care is taken during the application of the coating to these areas.

Figure 14.26 shows the failure of a coating on the edges of structural steel that obviously had not had any particular attention during application. Edges also represent critical areas of the structure, and continued failure can result in cracking from a decrease in steel thickness. Areas such as those shown in Figure 14.26 are quite typical, particularly in the marine area where structural steel shapes are welded and riveted together to form the overall structure. Note that almost all edges in the figure show some edge corrosion. In this particular case, the coating was only two years old.

Figure 14.27 shows the typical edge effect on a panel exposed to a marine atmosphere. While the plane surface is unaffected and the coating is fully protecting the surface, the edges are seriously corroded, with the coating gradually being undercut. Coating failures on corners and edges can be expected, unless additional care is taken on these areas during application.

Corners

Exterior corners can be considered the same as edges, and the same corrosion occurs on exterior corners as would be expected on edges. This is shown on the corners of the box beams in Figure 14.26. Interior corners, however, are quite different. These are generally two types of failure that can be expected on interior corners. The first is the shrinkage of the coating away from the interior corner, causing a blistered area or an area where the coating bridges the corner. In this case, corrosion starts under the lifted area of the coating in the corner and spreads from that point out. The other common type of coating failure in a corner is due

to dirt and trash accumulation in the corner that is not removed during the coating process. In this case, the coating is discontinuous over the contamination, and corrosion begins very quickly.

Figure 14.28 shows a column in which contamination was coated over and where early corrosion started after only a few months of exposure. In the case of this type of interior corner failure, the only remedy is to remove the contaminated coating and recoat. The best way to eliminate the failure is to improve the workmanship of the applicator.

Welds

The failure of coatings on welds is very common. There are several causes, the primary one being that the weld is a rough and discontinuous surface area on a plane surface. On the other hand, many welds are tested for leaks, after which a soap solution is applied over the weld. In many cases, the coating is applied over such a surface, with early failure of the coating resulting over the soaped surface. Many welds are cleaned less than perfectly, and weld slag and similar contamination can cause early coating failure. Figure 14.29 shows a typical weld failure on a plane surface. In this case, the weld was not given the proper attention and the coating failed over the rougher weld area in a short period of time.

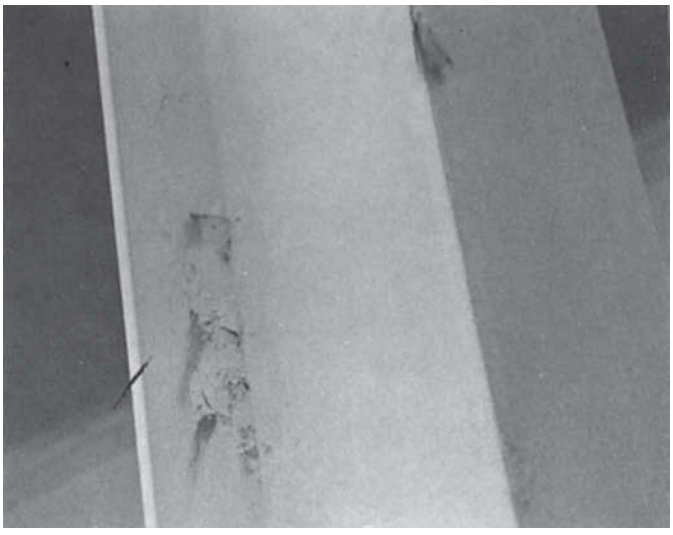


FIGURE 14.28: Corrosion in the interior corner of an H- beam due to contamination that was allowed to remain on the surface and therefore caused a non-continuous coating.

TABLE 14.5: Application-Related Failures

	Coating Failure	Failure Appearance	Cause of Failure	Remedy
1.	Poor Workmanship	Dirt, dust, grime on surface and in coatings. Holidays, overspray, pinholes, runs, sags.	Lack of care in application.	Better training for workmen. Instill sense of pride in work.
2.	Runs, Sags, Curtains	Heavy areas in coating which flow down vertical surface in streaks or curtains.	Lack of care in application.	Remove runs and sags with a brush prior to initial set of coating. Smooth area with light spray coat.
3.	Brush Marks	Linear hills & valleys in coating. Considerable difference in coating thickness from hills to valleys. Rusting starting in valleys.	Poor workmanship. Very heavy bodied (thixotropic) coating.	Train workmen to brush smoothly. Brush coatign out well, finishing by light brushing in one direction.
4.	Improper Coating Thickness	Areas of pinpoint corrosion between areas of solid coating. Where coating is over thick. Possible checking and cracking.	Thin areas, spatter coating, holidays. Runs, puddles, excessive number of spray passes in areas where coating is difficult.	Careful application. Even spray passes with each pass overlapped 50%. Use cross spray technique.
5.	Overspray	Very rough coating surface. May appear like sand in coating. Some dry coating, like dust, on surface. Pinpoint corrosion throughout rough areas.	Improper spraying technique. Uneven spray passes with gun too far from surface.	Apply coating with care and with even wet spray passes overlapped 50%. If overspray occurs, remove before overcoating.
6.	Pinholes	Discontinuities in coating film. Holes generally appear in concentrations with a random distribution. Pinpoint corrosion in pinholes.	Improper spray technique. Spray gun too close to surface with air bubbles being forced into coating. Spray pot pressure too high with atomizing air pressure too low. Pinholes may exist in the substrate (concrete).	Apply coating with care with spray gun at the optimum distance from surface. Make sure gun is properly adjusted. If pinholes already exist, apply coating by brush, working it into surface.
7.	Holidays	General corrosion in bare or thin areas of surface which were uncoated by the painter. Most often in difficult areas to coat.	Poor, inconsistent application. Lack of care.	Apply coating in careful, consistent manner, making certain that no areas remain uncoated. Overlap each pass 50%.
8.	Spatter Coat	Pinpoint rusting in area of thin coating, usually at end of spray pass or around a complex section of structure. Small spots of coating which are noncontinuous over substrate. In poor light may seem continuous.	Discrete coating droplets that are not continuous over surface. Inconsistent t spray passes not overlapped 50%. Spray gun flipped at end of spray pass.	Apply coating with care. Use even, wet spray with each pass overlapped 50%. Use cross spray technique.
9.	Cratering	Pinpoint rust forming in thin areas of bug eyes, fish eyes, or craters randomly dispersed over coated area. May be more prevalent in thicker sections.	Improper solvent mixture, oil in atomizing air, surface contamination, particulate fallout during application, high surface tension.	Once cratering occurs, sand or roughen crater area. Apply second coat by brush, working coating into cratered area.

Source: *Steel Structures Painting Manual*, Causes and Prevention of Paint Failure, Chapter 23, "Good Painting Practice," Vol. 1 (Pittsburgh, PA: SSPC, 1982).

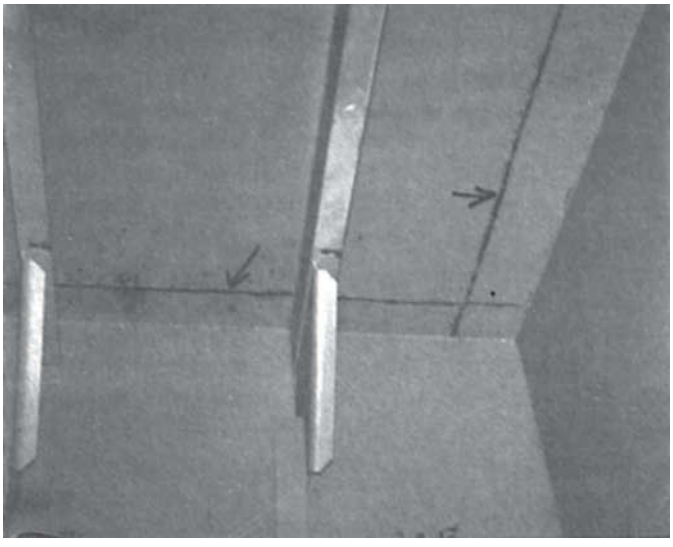


FIGURE 14.29: Typical coating failure over a weld on a plane surface.



FIGURE 14.30: Coating failure of the weld area on a pipe.

Figure 14.30 shows another weld failure. Again, it is a change in direction of the surface, with the weld being considerably rougher than the plane surface adjacent to it. Extra attention was not given to such a weld, as recommended in previous chapters, and therefore the weld is the first area to fail.

Welds are almost always the first area in a structure to show failure. Main construction welds in tankers have been known to fail after one year, with the coating completely corroded across the weld area, even to the point of heavy scale developing on the weld. The cause was purely lack of attention to the weld area during the coating process. As stated in previous chapters, welds should be given proper attention and an extra pass for each coat applied.

On the other hand, weld areas in ships can turn out to be the best areas of the entire tank, primarily because of extra attention given the weld during coating application. In some cases, the primer is brushed on the weld and an extra pass applied to the weld during each coat on the flat surface.

Nuts, Bolts, and Rivets

Corrosion on nuts, bolts, rivets, and similar construction fasteners is almost inevitable, unless extra care is taken during the application of the coating. This is due to the many edges and corners that are present in a bolted structure. Figure 14.31 shows a critical bolted joint, with heavy corrosion occurring on the bolts and joint after only a few months of service. This is typical of many bolted areas and only leads to the conclusion that extra care is necessary wherever such a bolted joint is used. Bolt heads also can be coated effectively, as shown in Figure 14.32. Even in this case, damage occurred to some of the bolt heads and edges, causing early corrosion. Extra care in application is a requirement wherever bolted or riveted structures are used. IOZ coatings as a base coat for such areas have vastly improved the corrosion resistance of such joints.

Overlapping Joints or Plates

There are always critical corrosion areas whenever bolted or riveted structures are used. Failure of the coating in these areas is, in many cases, rapid and is due to the crevice between the two plates and the rapid change in direction of the coating in the joint. The coating in the joint often cracks, with moisture, salts, and similar contamination penetrating the overlap and causing rapid corrosion.

An excellent remedy is the use of IOZ coatings on the faying surfaces (i.e., the surfaces being joined) prior to bolting or riveting. In this way, the coating is carried underneath the plate and is protected for long periods of time. Figure 14.33 shows an overlapped joint and the corrosion that can occur when proper care is not taken in the application of coatings over such areas.

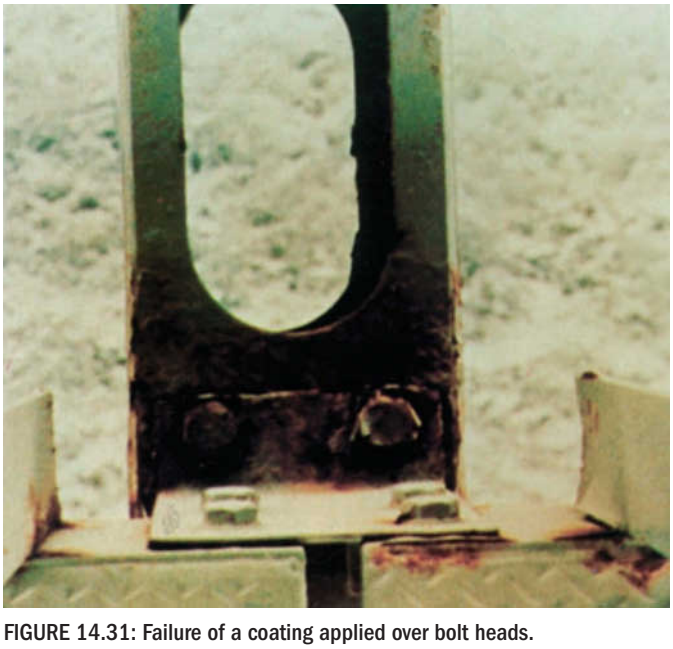


FIGURE 14.31: Failure of a coating applied over bolt heads.



FIGURE 14.32: Bolted structures can be effectively coated when proper care is taken during application.

Construction Aids

Construction aids, hold downs, and similar areas are areas where corrosion is usually initiated and coating breakdown is quite rapid. The cause is that these aids to construction are temporary and are usually welded rapidly, without particular care during the welding process. The welds are also usually quite rough. The metal pieces that are welded to the structure are rough cut and may be skip-welded or only welded on one side. This allows easy access to moisture and salts with resulting corrosion. These temporary aids are too often left on the surface as well.

Figure 14.34 shows a construction aid that was left on a main piling of an offshore structure and the type of failure that can occur, even though the coating was applied over the construction aid during the original application. Unfortunately, application to these temporary aids is also usually less than the best. Corrosion starts at the weld and at the cut edges of the angle.

The remedy for such problems is to remove the construction aid once it has served its purpose, properly smoothing the cut edges, and, where the aid is removed, preparing the surface properly and applying the proper number of coatings in the repair area. While corrosion in such areas may seem trivial, once the coating has broken down and corrosion begins, pitting can occur, and if such aids are in a highly stressed area, failure of the structure can occur because of cracking beginning at the pit.

Pipe Structures

The failure of coatings on pipe structures is usually due to two principal causes. One is the welding of the pipe itself, with the failure of the coating occurring on the weld. The second is due to holidays left in the coating where the coating has not been properly overlapped during the coating process. In this case, the failure areas are usually longitudinal with the pipe and take the form of areas where there is first pinpoint rusting, followed by expansion of the corrosion over the whole thinner area, out to the point where the coating is applied at full thickness. These represent a typical type of failure on a pipe and are easily seen and recognized on pipe structures. The remedy is to overlap each pass of the coating as it is applied to the pipe by at least 50 in order to overcome the uneven surface.

Adhesion-Related Failures

As reiterated throughout the discussions on coatings, adhesion is one of the key factors in the effectiveness of a coating. Conversely, lack of adhesion can be the cause of a number of major coating failures. Without adhesion, a coating is merely a film on the surface, subject to all types of disruption and damage caused by exterior forces. The coating must adhere to the substrate if the substrate is going to be protected from corrosion. Any factor that prevents or reduces coating adhesion will subsequently create coating failures of one type or another.

Blistering

One of the most common types of failure related to adhesion is that of blistering (Figure 14.35). Blisters can be large or small, although generally they are round, hemispherical projections of the coating from the surface and are either dry or liquid filled.

The size of the blister usually depends on the degree of adhesion of the coating to the surface and the internal pressure of either gas or liquid within the blister, stretching the coating to the point where the internal pressure is balanced against the degree of the coating adhesion. The usual cause for blistering is the penetration of moisture through the coating into areas of poor adhesion. The moisture vapor may condense and form a liquid blister, or the vapor pressure of the moisture at the interface between the coating and the surface may be sufficient to lift the coating away from the substrate. There are generally two types of blisters:

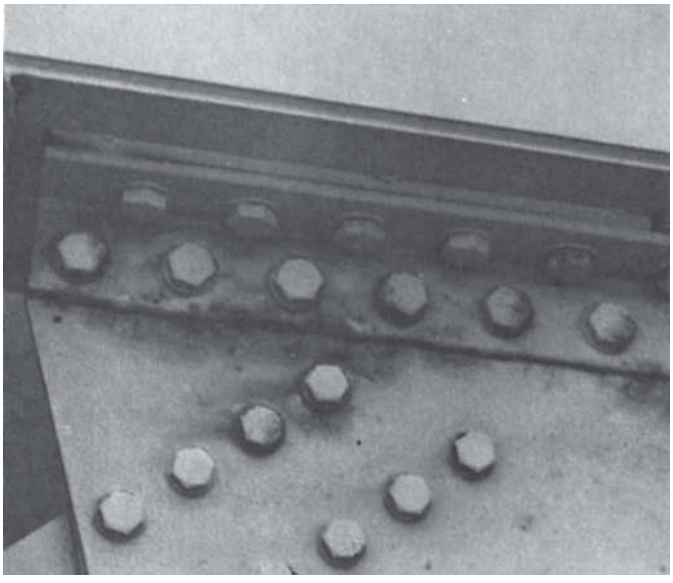


FIGURE 14.33: Typical overlapping joint, with corrosion beginning in the joint and with undercutting of the coating on each side of the overlap.

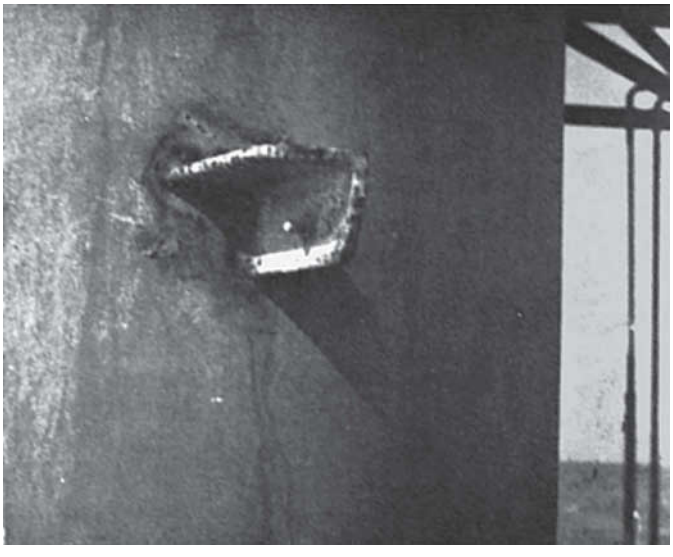


FIGURE 14.34: Coating failure on a typical bracket or scaffolding support which served as a construction aid.



FIGURE 14.35: A typical blistered surface, showing mostly hemispherical projections without breaks in the coating.

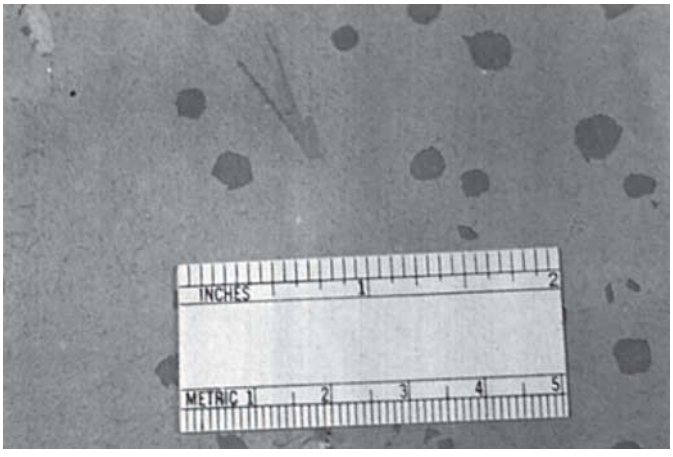


FIGURE 14.36: Broken blisters in a topcoat that is incompatible with the base coat.

(1) those that are formed from the substrate, with the coating separating from the substrate, and (2) those that are formed between coats and where the topcoat separates from an undercoat, forming circular blisters.

Figure 14.36 is an illustration of a topcoat blistering from the undercoat. In this case, the blisters were removed, showing the round areas where the blisters formed. There is little adhesion of one coat to the other, as indicated by the scratch between blisters. In this case, the topcoat chips and flakes away from the undercoat with no apparent adhesion between blisters. This type of failure indicates a complete lack of compatibility between coats. To repair such a condition, the entire topcoat must be removed and re-coated with a coating that is more compatible with the undercoat.

Both of the above types of blisters, whether they are from the substrate or between coats, may be either dry or filled with liquid. Blistering can be caused by a number of different conditions.

Soluble Pigments in the Primer

Soluble pigments in the primer have been a cause for many blistering failures. In this case, the soluble pigments absorb moisture vapor as it passes into the coating, creating a rather concentrated solution. At that point, the phenomenon of osmosis occurs, pulling water through the coating into the areas where the pigments have been dissolved. This is the reason why impervious types of coatings (previously described) are recommended for highly humid or immersion service. This same phenomenon can occur if there are soluble salts contaminating the substrate or contaminating the surface between coats of the coating. Osmosis is the transfer of moisture through the coating in the direction of the most concentrated solution. When there are soluble materials on or within the coating, blistering is almost inevitable. Blisters, in this case, would be liquid filled from the osmotic action.

Blistering can also be caused by contamination of the surface by materials (e.g., oils, waxes, dust, etc.) that will not allow proper adhesion of the coating. Again, the moisture vapor transferring through the coating is the cause for the blistering. The moisture vapor tends to concentrate in these areas of low adhesion, with the vapor pressure causing the blister to form. In this case, the blisters are so-called "dry" blisters.

Shop Primers

Blistering can also be caused by the selection of an improper primer for the surface. This can often be the case when a shop primer is used on surfaces that are later overcoated with a high-performance coating. The primer does not have the necessary adhesion or physical properties to provide adequate adhesion for the high-performance coatings. Also, under some circumstances, the solvents in the high-performance materials will cause this shop primer to disbond from the surface.

Shop primers are always suspect where a high-performance material is to be applied over them. Unless the shop primer is designed as an undercoat for epoxies, vinyls, and similar coatings, it should be removed before the high-performance material is applied. Where primer failure is involved, the blistering is usually from the surface of the substrate.



FIGURE 14.37: Blistering in a water area of a petroleum tank, indicating the basic incompatibility of the topcoat with the IOZ base coat.

Incompatibility

Incompatible coatings often have poor adhesion that causes blistering between coats. Figure 14.37 shows an incompatible topcoat over an inorganic base coat. In this case, the topcoat had very poor adhesion, as indicated both by the blistering on the surface and the areas where the blisters have been broken, and by the area where the coating flaked away from the surface. The blistering occurred primarily in areas where a water layer was involved. Higher areas in the tank, exposed to oil only, were not affected in such a dramatic way, even though basic adhesion was poor.

Retained Solvents

Blistering failure also can be caused by poor or inadequate solvent release by the coating. Solvents retained by the coating act like plasticizers, making the coating softer and more flexible, and, depending on the water sensitivity of the solvent, can increase the water absorption and moisture vapor transmission of the coating. If the basic adhesion of the coating is at all marginal, the decrease in water resistance can cause adhesion release and blistering failure.

Where there is solvent retention and the coated surface changes in temperature, the solvent itself may create a sufficient vapor pressure to cause blisters to form in the coating. The most serious of these types of blisters are those caused by the moisture vapor passing into the coating and combining with the solvent, in some cases dissolving into the solvent, and causing a com-

bined vapor pressure with resulting blistering of the coating. Solvent odor is usually connected with retained solvents, and under many conditions, solvents are detectable even after months and years of service. The blisters caused by solvent evaporation alone usually occur shortly after the coating has been applied, and, for the most part, can be relatively easily repaired.

Blisters of the solvent type may also occur where a topcoat is applied over a porous substrate or a porous undercoat. Such blistering often occurs where an organic coating is applied over an inorganic base coat and the temperature of the surface is quite warm. Blisters of these types rise rather quickly, often breaking and leaving a bare area where the blisters formed. This type of blistering can be prevented by a very penetrating prime coat flowing into the more porous substrate or base coat. The primer is usually applied in a relatively thin but wet film, so that is dries quickly yet has time to penetrate the surface. Changing the time of application to one when the surface is relatively cool may overcome this type of blistering as well.

Cathodic Protection

Blistering is often caused where cathodic protection (CP) and coatings are used to supplement each other. This type of blistering is most often caused by hydrogen gas being formed on the metal substrate underneath the coating in sufficient volume so that the hydrogen vapor pressure pushes the coating off of the surface. Figure 14.38 shows blistering of this type, where excess CP caused blistering in the neighborhood of a scribe or damaged area of the coating. Cathodic disbonding is not unusual where coatings have less than the best adhesion.

Previously corroded surfaces can also cause blistering where salts or oxides remain in the surface pores of the substrate, creating focal points for rusting and blistering. Blistering can also be caused by a corrosive gas (e.g., hydrogen sulfide [H_2S], hydrogen chloride [HCl], or carbon dioxide [CO_2]) passing through the coating or being absorbed by it and pushing the coating from the surface. Such strongly active penetrating materials can react with the surface, causing a gas pressure with resultant blistering. Coatings used in fermentation tanks often blister because of the passage of CO_2 through the coating into an area where the coating adhesion is less than adequate.

Any blistering of a coating is serious. If it is localized from surface contamination, the coating can be removed and repaired. If it is general, the entire coating should be removed from the surface, the surface re-prepared in order to obtain adequate adhesion, and if the coating selected is satisfactory for the service, it should be reapplied.

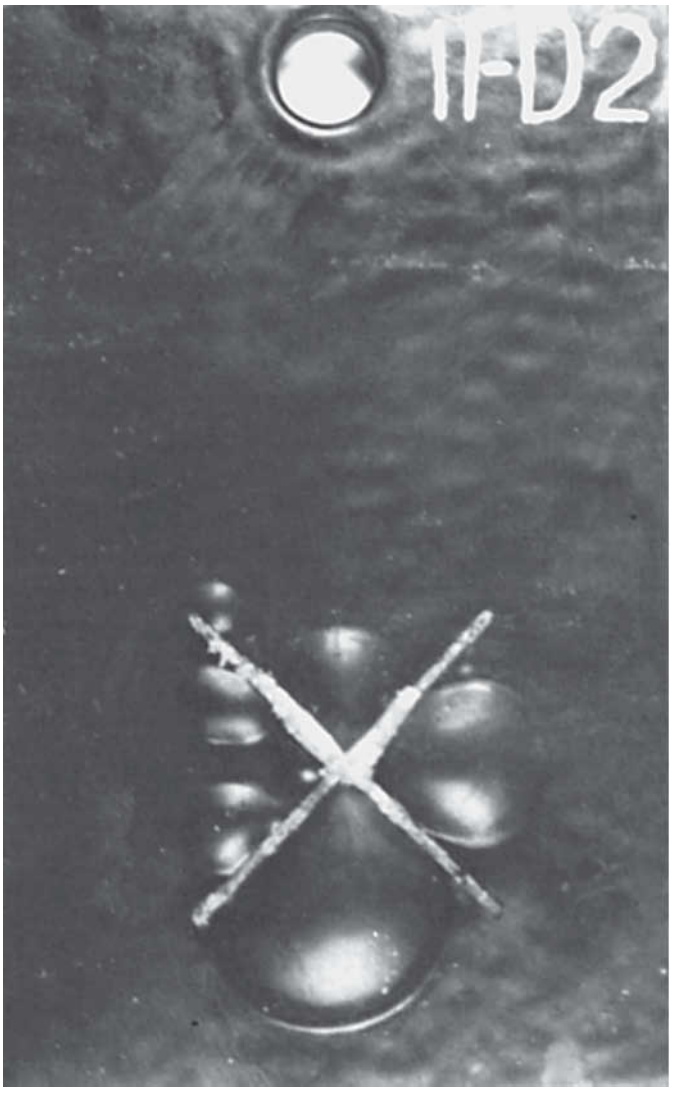


FIGURE 14.38: Blistering of a coating subject to CP.



FIGURE 14.39: Peeling of a coating because of surface contamination or the incompatibility of the topcoat with the undercoat.

Peeling

Peeling is definitely an adhesion-related failure. It includes peeling from the surface or peeling between coats. It is generally caused where the tensile strength of the coating is higher than the adhesive strength or bond strength. This may be caused by poor surface preparation that reduces the bond of the coating to the surface. It can also be caused by contamination between coats, where the topcoat then peels from the surface; or it may occur when the thickness of the coating is too great, causing a film that is stronger than its adhesive characteristics.

Figure 14.39 shows the peeling of a topcoat from an undercoat, which is due either to surface contamination or to lack of compatibility of the topcoat with the under coat. Figure 14.40 demonstrates an area of poor adhesion, where the coating originally blistered and the blisters were broken, after which the coating was easily peeled from the non-blistered surface. In this case, the coating was non-adherent to or incompatible with the substrate.

Flaking

Flaking is also an adhesion-related failure, and is much like peeling, with the exception that the flaked coating is usually hard and brittle and tends to pull itself away from the substrate. Once the coating cracks, the edges may tend to curl away from the surface, creating



FIGURE 14.40: Peeling due to poor adhesion.



FIGURE 14.41: Flaking of a heavy organic coating from a metal surface because of poor adhesion.



FIGURE 14.42: Flaking of an oxidized organic coating from a wood surface due to the coating's obvious lack of penetration of the wood surface.

the flaking tendency. Figure 14.41 shows a relatively heavy, hard coating flaking away from a metal substrate. Coatings applied over wood have a strong tendency to flake because of the working of the wood surface. Oftentimes, coatings are applied quite heavily over a wood surface, and, as it oxidizes and cures, the film becomes quite hard and brittle and tends to shrink. Figure 14.42 shows the coating as it is flaking away from a wood surface.

Intercoat Delamination

Delamination is the loss of adhesion between coats and is a common type of coating failure. The failure occurs most often where repair or maintenance coatings are being applied over existing coatings that have been in service for some period of time. Under these conditions, the original coating usually is chalky, has dirt embedded in the surface, or has oxidized or cured on the surface to the point of complete insolubility and impenetrability. Whatever the cause, the repair coating has difficulty wetting and establishing bond areas over the previous surface.

There are many causes for intercoat delamination. Incompatibility of two coating materials is one. It is always preferable to put the same kind of a topcoat or repair coat over a previous coat since there is less chance of incompatibility with similar materials. This is an area where mixing coating systems or mixing suppliers can cause some serious problems. Unless the two coatings are of the same generic type, or unless tests have been made to determine that the coatings are compatible, the mixing of coating systems is not a recommended procedure.

Contamination

The contamination of a surface is always a possible cause of delamination. Coatings that have been in service for some time and are being repaired accumulate dust, dirt, grease, chemicals, and similar contamination that must be thoroughly removed prior to the application of an additional coat. This can often occur quite quickly, even during the original application of a coating system. In areas where there is considerable atmospheric contamination from chemical fallout, dust, or similar materials, sufficient contamination can fall on the original coat to the point where a second coat may not adhere to the first coating. Although this is a difficult situation at best, the application of fast-drying, resistant coatings such as vinyls or chlorinated rubbers can help eliminate the rapid contamination between coats. In this case, the second coat should be applied as quickly as possible after the first coat, even within minutes.

Chalking

A chalky surface is a difficult one over which to apply any coating. Some are much more susceptible to delamination from chalking than others. On a chalky surface, it is recommended that it be thoroughly scrubbed or pressure washed with surfactant-type water-based cleaners prior to the application of any additional coats. Even with the substrate scrubbed to remove the chalking as much as possible, a coating that will wet the chalked surface is preferable, since it will penetrate any chalk and adhere to the original coating. Some materials are much more satisfactory for this type of exposure than others. Emulsion-type coatings are particularly poor for application over a chalked surface, and quick peeling or delamination can occur.

Over-cured Surfaces

Over-cured surfaces occur with many coatings, particularly those that react with air or are internally cured. Oil-base materials, such as linseed oil, alkyds, epoxy esters, and some similar materials, oxidize sufficiently so that over a period of time, if an additional coat is required, intercoat delamination may be a problem. It is always recommended that the surface of highly oxidized materials be broken or abraded by sanding or lightly blasting to allow mechanical adhesion, as well as some access of the new coat to the lesser-oxidized body of the coating.

The same applies to epoxy coatings. However, in this case, they are internally cured, and many amine-type epoxies cure sufficiently hard so that the application of a second coat to the first coat that has cured may be difficult, making delamination possible. Coal tar

epoxy coatings are even more difficult than epoxy coatings. The combination of the two materials, coal tar and epoxy, apparently creates a coating that will cure rapidly on the surface, sufficiently so that even a few hours curing will cause delamination between coats.

As discussed previously, when coal tar epoxy coatings are exposed to sunlight, the sunlight will catalyze the curing of the surface to the point where additional coats will not adhere properly. Both amine- and polyamide-cured coal tar epoxies react in this way. This is not an uncommon problem, and has occurred in some extensive applications of coal tar epoxy. In fact, it has occurred on large applications where the coating was exposed to both sunlight and condensation. Massive delamination occurred even before the unit could be placed in service.

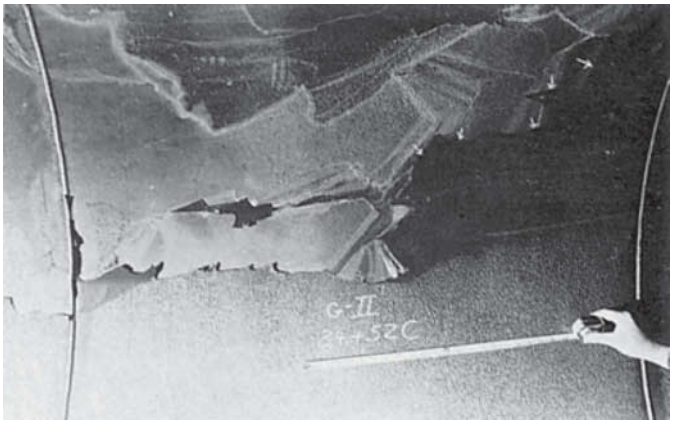


FIGURE 14.43: Delamination of a coal tar epoxy coating on the interior of a large pipe.

Another cause of delamination with coal tar epoxies is the exposure of the surface to moisture, such as condensation or dew, rain on the surface, and, of course, dust or dirt. In the case of Figure 14.43, the coal tar epoxy suffered massive failure, with extensive delamination covering many thousands of square feet, even though the coating was plant-applied and the second coat applied within 48 hours. The problem, therefore, can be a major one that must be taken into consideration during the application of coal tar epoxy coatings. The one answer to this problem is the use of some of the newer high solids coal tar epoxy coatings that can be applied at a dry film thickness of 20 to 25 mils per coat. A single coat over a primer is often adequate and eliminates the delamination problem.

Polyurethane coatings are also highly polymerized, with a high-gloss surface. The combination often causes problems when applying additional coats. In every case where epoxy, coal tar epoxy, or polyurethane coatings are to be given more than one coat, the second coat should be applied prior to the time that the first coat has cured to insolubility on the surface. This may be within a few hours, under many circumstances. If this is not possible, or the original coating has aged, breaking the surface by a light brush blast, hand sanding, or light belt sanding is recommended to eliminate intercoat delamination.

The application of too great a thickness of a coating can also lead to delamination. It can cause delamination not only down to the substrate, but also between coats. The shrinkage stresses in a heavy coating can increase until they exceed the force of the adhesion between coats, and the heavy coat will actually pull itself apart and away from the surface. This is something that often occurs with heavy-bodied epoxy coatings where excessive thicknesses are applied. This is particularly true where there is a substantial temperature variation of the coated surface.

Chemical attack can also cause delamination. Volatile acids, such as acetic, hydrochloric, or nitric, often are sufficiently penetrating to cause delamination between coats. They also will often cause delamination from the substrate for the same reason. Where coatings are subject to strong solvents, the solvent may also separate the various coats, even though the coats appear tightly bonded to each other. If there is a distinct interface, solvents will often penetrate sufficiently so that delamination occurs.

As discussed, the oxidized or internally polymerized coatings are much more difficult from a delamination standpoint than materials that are permanently soluble in their own solvents such as lacquer-type coatings, vinyls, chlorinated rubbers, etc. Materials that are permanently soluble in their own solvents have less of a problem, since the solvents strike into the original coating and allow some penetration and mixing of the coating at the interface. This is one of the advantages of the vinyl and chlorinated rubber-type high-performance materials. Where delamination is a possibility as a result of exposure, aging, or contamination, vinyl and/or chlorinated rubber coatings should be considered.

Correcting delamination failures depends on a number of things. If the delamination is spotty and is limited to certain localized areas, repair of these areas is often possible. Where the delamination is extensive, it usually is preferable to remove the entire coating down to the substrate, starting out with a clean surface and reapplying the coating, while making certain that the factors causing the initial delamination have been eliminated.

Undercutting

Undercutting of a coating is the action of rust under the coating, usually forming around a small break in the coating. This precondition is not necessary, however, if the coating has been applied over a previously corroded surface or one that may be contaminated with chlorides. In the latter case, depending on the coating (particularly those that cure by oxidation), corrosion can occur underneath the coating, undercutting the coating prior to any actual break.

It is often difficult to see minor abrasions that may be sufficient to cause undercutting in a coating. Figure 14.44 is an example of the type of undercutting that occurs because of minor abrasions on the coated surface. Figure 14.45 is a close-up of a more massive coating failure, showing the growth of the corrosion under the coating. Each of the round, blister-type spots is a growth of iron oxide underneath the coating. In both cases, corrosion has penetrated the coating and is building up under the coating at the interface between the coating and the metal.



FIGURE 14.44: Undercutting of a coating due to corrosion of small surface abrasions.

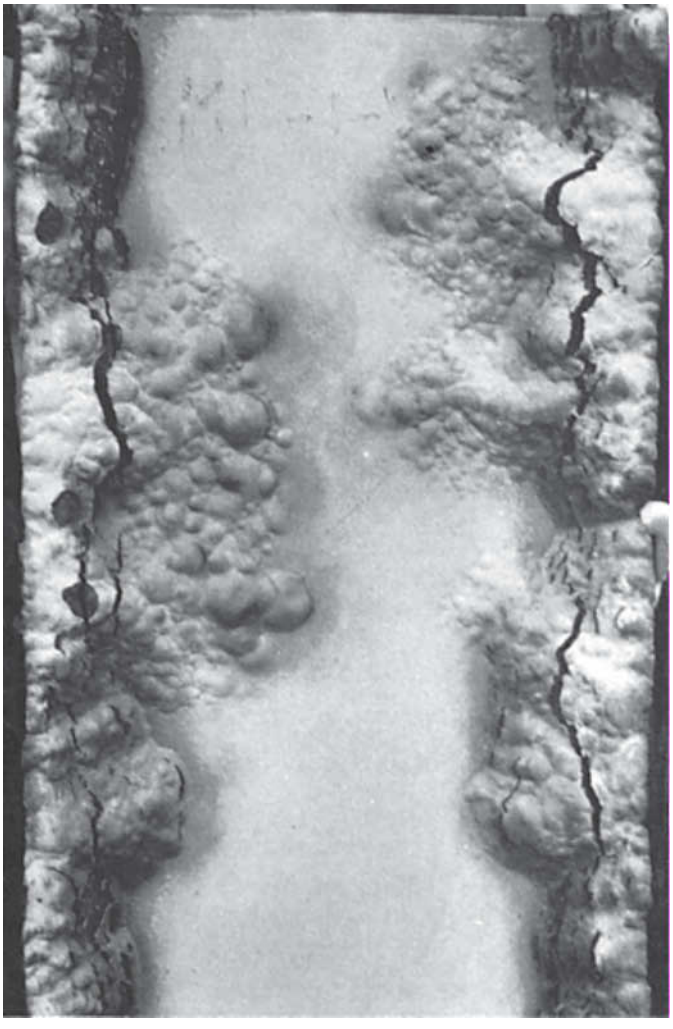


FIGURE 14.45: Undercutting from the edges toward the center of a panel exposed to a marine atmosphere.

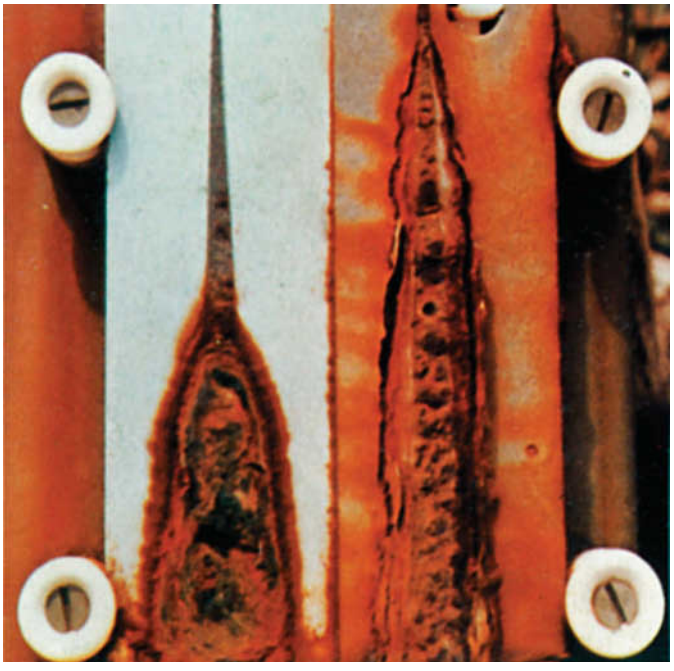


FIGURE 14.46: Undercutting beginning at a break in the coating.

Corrosion occurs quite rapidly under such conditions, inasmuch as the corrosion product will retain moisture and/or salts, creating an ideal corrosion cell.

A coating that has been applied over mill scale is susceptible to undercutting, since once a break in the coating occurs, corrosion can begin between the mill scale surface and the steel, and corrosion can spread rapidly between the two surfaces. Moisture and oxygen both penetrate the coating and react at the scale/metal interface and at the coating interface, causing a loss of adhesion, with progressive corrosion beneath the mill scale and the coating.

Undercutting is also common where a coating is applied over a smooth surface, since the adhesion between the coating and the surface is marginal because of this condition. Here again, the corrosion, once started, acts as a wedge, pushing the coating away from the surface and building up corrosion product between the surface and the underside of the coating. Figure 14.46 is a good example of the undercutting of a coating from a break in the coating. Note that the panel on the right shows an extremely heavy corrosion product at the break and that the coating is actually being turned up at the sides of the break as the corrosion product works underneath.

Undercutting is a serious problem, and very deep pitting can result from the corrosion that builds up underneath a coating. Undercutting is definitely adhesion-related. The greater the adhesion, the less tendency for the coating to undercut. This is one of the reasons why the use of an IOZ base coat under organic coatings has been so successful in eliminating undercutting. In any area where there are general serious corrosive conditions, such as in marine areas, industrial plants, refineries, etc., an in- organic base coat should be seriously considered for any coating project so as to eliminate the possibility of undercutting and serious corrosion.

Failures Due to Exterior Forces

In many ways, it can be said that all types of failures are due to exterior forces, since it is the environment in which a coating operates that is the primary cause of coating failure. If the environment was always benign, there would be no coating failure, even though there are coating imperfections. Nevertheless, there are certain types of exterior forces that cause coating failure that are over and above the ordinary atmospheric types of exposure to which the coating is expected to be resistant.

Chemical exposure is one of the principal types of exterior forces that can cause coating failure. Not only is the chemical industry one of the largest industries in the world, but it is also of a broad scope, covering many different types of chemical exposure. Chemical attack on coatings can be by simple solution, where a solvent for the coating material dissolves the coating and removes it from the surface. Even though the solvent may not remove the coating, but only tend to swell it, in many cases it opens the coating to attack from the atmosphere by making it more porous.

Volatile acids are particularly damaging to coated surfaces since they are highly penetrating. In fact, acetic acid acts as both a solvent and an acid, so that easier and greater penetration of many coating materials is possible. Hydrochloric and nitric acids are very penetrating, and under many circumstances will pass through a coating as a vapor, attacking the substrate without appreciably damaging the coating itself. Once the penetration has occurred, the corrosion takes place underneath the coating, forcing it off from the surface and increasing the corrosion possibilities.

The caustic chlorine industry is a difficult one in terms of coatings. Not only is there strong caustic available, but chlorides are also



FIGURE 14.47: Star cracks due to reverse impact.

present, and chlorine gas is a very penetrating oxidizing material as well. The combination makes this industry a difficult one for coatings, although there are a number that effectively resist the corrosion.

Chemical transport is another industry that is difficult from a coating standpoint. Not only are there many different chemicals involved, but there may be abrasion involved as well, so that breaks in the coating increase the possibility of coating failure in this service.



FIGURE 14.48: Anchor-chain abrasion on a ship's hull.



FIGURE 14.49: Erosion and abrasion of the coating on a ship's rudder.

Reverse Impact

Reverse impact is an area that can be particularly damaging to coatings (Figure 14.47). As can be seen in the figure, the coating is heavily star cracked because of the impact on the exterior of the coated surface. Reverse impact is a difficult problem for many coatings, and in some cases it is used as a test for coating adhesion. Actually, because the coating is heavily stressed, it is not only a test of adhesion, but a test of extensibility as well. Reverse impact is much more difficult for a coating to resist than is direct impact on the surface. There are coatings that are designed to have extremely good adhesion as well as extensibility and that will resist the reverse impact shown in Figure 14.47.

Abrasion

Abrasion is another common cause of coating failure. Floors and similar surfaces are one of the major areas where abrasion is a problem. Wheel traffic, foot traffic, sliding of heavy objects—all cause abrasion on floors and severely damage the coating. In order to resist such forces, the coating must have the ability to resist abrasion, but, at the same time, have sufficiently strong adhesion to the substrate so that, as the coating is worn away, it does not flake or chip, but wears down to an even, feathered edge. Good adhesion is essential for an abrasion-resistant coating.

Ships and other marine structures are subject to considerable abrasion. Figure 14.48 shows the hull of a ship where the anchor chain has scraped over the surface. This type of abrasion is called riding the anchor, and coatings must be particularly abrasion-resistant and have good adhesion to reduce to a minimum the corrosion caused by such abrasion. Such abrasion actually cuts into the steel itself. How- ever, with a coating with high adhesion and abrasion resistance, the damage is reduced to a minimum, and repair can be made

with a minimum of effort during dry docking. IOZ base coats have been a major factor in holding this type of coating abrasion to a minimum as a result of their strong adhesion, malleability, and corrosion resistance.

Figure 14.49 shows the rudder of a ship and the abrasion that occurs directly behind the propeller. Notice, in this case, the zinc anodes that are used to help reduce the corrosion caused by the abrasion of the coating in this area. In this case also, a very abrasion-resistant and highly adherent corrosion-resistant coating is required in order to minimize the corrosion caused by the abrasion.

Faying Surfaces or Joint Movement

Failures can occur where joints in a steel structure are fastened by riveting or by the use of high-strength bolts. Such joints are common throughout industries of all types and are used on many steel structures, such as bridges. Faying surfaces are designed to resist movement. However, at this point there is a change in direction of the coating where cracking will often occur. When this happens, coating failure occurs at the junction of the two metal surfaces, resulting from excess moisture and atmospheric contamination. Most coatings are unsuitable for faying surfaces because of the fact that the coefficient of friction is not sufficient for the bonding of the joint. Fortunately, IOZ coatings are satisfactory for use on these surfaces and are an answer in protecting the overlapping surfaces from corrosion.

Summary

Coating failures, then, may be caused by many different factors, ranging from the characteristics of the coating itself to its formulation and the materials from which it is made. Failure can occur from the underlying surface when improperly prepared, by the application of the coating over the surface, by incomplete coverage of the surface, and because of the basic design of the structure itself.

There is no set manner in which to deal with coating failures. Each problem is a unique one and must be analyzed as such in order to overcome that particular type of failure. Once the failure has occurred, repair is usually possible. On the other hand, unless the repair is done very carefully, continuing corrosion can occur in the repaired area. Massive failures can only be repaired by removing the coating, re-preparing the surface, and reapplying a coating that will be more resistant to the particular source of corrosion. Any generalization on the prevention of coating failure can be made only by proper analysis of the exposure and the structure, and specifying a material that will completely resist the exposure. No compromise should be made, either in the coating or with its application, since repair of failures are much more costly than proper application of the original material.

Once a material has been selected, a specification should be written, covering not only the material, but its application as well. The specification should be detailed, making certain that all possible causes of coating failure are taken into consideration and eliminated. Following the specification, a thorough inspection of the coating should take place during its application, as well as upon its completion. There is no substitute for proper material selection, complete specifications both for the material and its installation, and a strong follow-up inspection to ensure that it has been properly applied. These three points can do more to ensure against coating failure than any others known.

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15 Coating Repair and Maintenance

Introduction

The maintenance and repair of coatings is one of the corrosion engineer's primary responsibilities. This is particularly true when dealing with critical structures where corrosion is a constant threat (e.g., boats, ships, offshore structures, refineries, chemical plants, paper plants, and sewage treatment plants). Linings for the interior of tanks, chemical reaction vessels, leaching tanks, transportation equipment, and even food processing and storage vessels are also included, since maintenance is an important procedure in the protection of both the structure and the contained liquid. Since coatings represent the first line of defense in the protection of these structures, they must be kept in the best possible condition for the longest period of time to guarantee proper protection over their intended life span. Therefore, both coatings and linings need to be maintained and repaired on a continuing basis to ensure their maximum usefulness.

A subtle difference exists between the terms maintenance and repair. Maintenance means preservation, conservation, safeguarding, upkeep, or to hold or keep in a particular state. Repair means to fix, recondition, renew, rebuild, patch, or restore to a sound state. As defined, maintenance is a much broader term referring to the protective management of the surface. This does not simply mean the periodic touch-up of a few damaged spots, but rather the management of the coatings process from the beginning of the original application to its present as well as future state. It includes the inspection, record keeping, and observation of the coating and its condition. It also requires material studies and the establishments of limits of failure, beyond which repair and recoating are automatic procedures.

Repair, on the other hand, refers to the actual act of reconditioning, rebuilding, and restoring a coating to its proper condition and protection standard. Thus, proper repair is a part of good maintenance and coating management. One such general maintenance procedure is described in a Department of Defense manual on paints and protective coatings.[1]

> Programmed painting is a systematic process for establishing when painting is required, what painting should be done, by whom, with what materials, at what time, and in what manner. Paint systems deteriorate and will lose their protective ability unless the film is intact. The principal objective of painting is to prevent deterioration of the substrate at a minimum cost per square foot per year. One procedure frequently used for providing protection has been to completely repaint after the original coating has failed. This failure results in an unsightly surface, expensive preparation before repainting, and possible deterioration of structural members. Another procedure is to completely repaint by applying two and even three coats at arbitrary intervals. This may be too late in cases where deterioration has already taken place, but completely unnecessary in others. Extensive surface preparation will be required in the first case, and film thickness will eventually become excessive in the latter case, leading to early failure by cracking and peeling. The most practical method of protection, therefore, is a continuous program of inspection, and painting as necessary. By means of programming and careful record keeping, a history of past performance is accumulated which aids materially in selection the best paint systems and painting procedures. Applied paint systems do not deteriorate uniformly, even when skilled painters apply them; some pinholes, holidays, and breaks at sharp edges or seams are often present. Left untouched, corrosion and deterioration will start at these points, eventually undermining the coating and then spreading to adjacent areas. Furthermore, as corrosion increases, it does so at an accelerated rate until large areas of the surface are left unprotected. Programmed painting enforces inspection and work scheduling to provide for relatively easy spot-painting of these minor breaks in the film long before any serious harm is done. Spot painting describes the painting of only the small or localized areas in which the coating has begun to deteriorate. Not only does spot painting save costly surface preparation and repainting of large areas, but the life expectancy of the paint system and structure can be extended considerably. Furthermore, when repainting is desired to achieve adequate film thickness or for uniform appearance, it can be accomplished economically with the minimum number of coats, since the surface will be in sound condition. An added advantage derived from preventive maintenance is the detection of faulty structural conditions or problems caused by leakage or moisture before they become serious due to oversight.[1]

The repair and proper maintenance of coatings is equally as important as application of the original coating. In fact, the repair of coatings is actually a more difficult procedure than coating a new structure or one that has been completely abrasive blasted. One of the principal reasons is that coating repair carries its own psychological barrier. People just generally do not like to do it. It might be different if the process could be done quickly and with no preparation. Unfortunately, any repair job done in this manner would not last long. The delay seems to be the surface preparation that is needed to do the job right. For example, how often have you put off painting the kitchen because you knew the ceiling would have to be washed first? The same problem exists on industrial jobs where a coating has failed on tank roofs or corroded structural steel. However, if these areas are not properly prepared, the repair effort will be wasted and have to be repeated after a short period of time. For example, ships have been repaired by giving them what is called a quick

"shave and haircut," only to have the coating wash away from the surface when the ship was refloated in drydock.

The timing of any coating repair is critical. Recoating before it is required is uneconomical and eventually results in a heavy, thick film buildup, which leads to deterioration of the coating system by delamination, cracking, chipping, and so on. For instance, a ship was coated after every round trip of approximately two months in order to maintain the best possible appearance of the ship for public relations purposes. However, when the time came to remove the coatings and begin from scratch, it was found that various areas of the coating had delaminated, both between coats and from the surface, and in many areas the thickness of the coating was from ¼ to ⅜ in (6.3 to 9.5 mm) thick. On the other hand, re-coating scheduled at overly long intervals results in costly surface preparations and may be responsible for damage to the structure, which also may require extensive repairs.

Results from a NACE report on "Industrial Maintenance Painting Programs"[2] shows that the frequency of inspection and therefore repainting in severe environments was six months to a year in about half the plants reporting; about one third of the plants with moderate or normal corrosion rates reported inspections at six months to a year intervals without necessarily requiring any repair. The tendency for longer intervals inspections increased as the atmospheric corrosion rate diminished.[2]

Spot painting should be done before any appreciable amount of rust appears. Where inorganic zinc (IOZ) primers are used, spot painting should be done only when the second coat (primer, where used) is exposed and before the zinc primer is exposed. If repainting is done before rust appears, surface preparation costs can be significantly reduced. If more than 10% of the surface3 needs spot painting, it is more economical to paint the entire surface. While more material will be used, less labor will be required. Labor for spot painting with a brush costs approximately six times as much as the material used.[3]

When is it time to recoat? The coating of equipment or structures that are already in poor condition should not necessarily receive top maintenance priority. Since such a coating is already disintegrated, the structure is corroded and the overall coating not salvageable. A few months more or less at this point would probably make little difference to the basic structure. On the other hand, a tank or structure that is weathered to the point where the primer may be showing through in a few spots, but where no active corrosion has occurred, can yet be salvaged. Here, with proper cleaning and additional topcoats, a continued trouble-free life of many years can be expected. Once this surface has been brought up to an "as good as new" condition, the repair of the badly disintegrated coating can begin.

Primary Repair Considerations

Once the decision is made to repair a coating, there are a number of items that must be considered in making decisions as to the type of repair, the amount of the repair, the coating to be used, and the number of coats. Several of the most important considerations are:

1. Type of failure
2. Extent of failure
3. Adhesion of existing coating
4. Type of coating
5. Type of substrate
6. Area of coating use

Type of Failure

The preceding chapter on coating failures discusses the major types of failures. Nevertheless, since coating failure is the primary reason for maintenance or repair, a brief summary of failure types in this context follows.

Undercutting

Corrosion undercutting and buildup of corrosion beneath the coating is one of the most common causes of coating failure and deterioration. The cause of undercutting is inherently an adhesion problem stemming from the original coating or its application. This type of failure is most often found on structural steel, bridges, open steelworks, construction in the chemical industries, offshore structures, and in the marine industry in general. Actually, it is common to most industries to one extent or another.

Blistering

Blistering is certainly one of the more common types of coating failure that should be considered in relation to coating repair and maintenance. It occurs in immersion service, in areas of splash and spray, and in high humidity. Therefore, it is a broad range type of failure and may be found in almost any industry. However, it may be more common in the marine industry due to a greater amount of immersed surface and surface exposed to splash or spray and high humidity. Blistering is usually caused by poor adhesion, a lack of proper surface preparation, cathodic disbonding, and various types of surface contamination.

Pinpoint Rusting

Overall, pinpoint rusting is probably the most common type of coating failure. Where repair of a coating is contemplated, pinpoint rusting is the first sign of coating failure. It is usually found first where the coating is thin and not fully protecting the surface. It occurs in both organic and inorganic coatings, and is the first sign of thin areas or holidays that may have occurred during application. Pinpoint rusting is a type of failure found throughout most industries in which high-performance coatings are used. It is the aging type of failure for zinc coatings such as galvanizing, IOZ, and even organic zinc-rich coatings. It is the type of failure that is often overlooked for a considerable period of time, to the point where it becomes sufficiently widespread to require major repair operations. However, pinpoint rusting is probably the easiest type of failure to repair, if observed in time and followed by prompt repair procedures.

Delamination

Coating delamination is not quite as common a problem as some of the previously described failures. Nevertheless, it can prove serious from a repair standpoint. Delamination is essentially a lack of adhesion between coats. While a small area may blister or otherwise be pushed from the surface, if that small spot is recoated, additional delamination usually occurs around the repair due to the original lack of adhesion between coats. This type of problem is usually found where thermosetting type coatings are encountered. Even oil

paints can be considered in this category since they are essentially thermoset once they are strongly oxidized. The amine- or polyamide-cured epoxy coating is one of the most common of this type of coating. These materials, as well as other epoxies and urethanes, cause delamination problems where over-cured between coats by heat, sunlight, or water exposure. In this latter instance, the surface becomes dense and insoluble, making it difficult for additional coats of the same material to adhere. This problem can occur in almost all industries.

Chalking

Chalking is an extremely common type of failure for all except a few coatings. It is an ultraviolet related surface difficulty; therefore, it is normally found on the exterior surfaces of buildings and structures and is common to all industries.

Checking

Checking is similar to chalking. It is a weather-oriented problem, and occurs on the surface only, rather than penetrating through the coating.

Extent of Failure

The extent of coating failure is one of the most important items to determine when a coating is to be repaired. The extent of the failure determines to a considerable degree the method as well as the extent of the repair. In order to know the extent of the repair, it is necessary to rate the condition of the coated surface so as to know when and how to recoat. Weaver, in his book Industrial Maintenance Painting,[3] describes four states of coating failure, as follows.

1. Thin finish coat. Some primer showing, rust negligible.
2. Thin finish coat. Considerable primer showing, 10% of surface containing rust, loose scale, and loose paint film.
3. Finish coat is thoroughly weathered and is blistered badly. Approximately 30% of the surface contains rust with pitting and hard scale.
4. Badly pitting surface with rust nodules.[3]

This series of coating ratings, however, is not adequate to properly describe the extent of failure on the surface. If 10% of the surface is showing rust or other failure, repair is undoubtedly necessary. In most cases, the method would be to completely remove all of the coating, unless the corrosion was sufficiently localized to allow easy repair of the corroded areas while the remainder of the surface remained completely corrosion-free.

ASTM has attempted, by a series of standards for types of coating failure, to evaluate the extent of the failure numerically, in a way that can be reasonably duplicated by more than one person. The ASTM standards that are most useful in determining the extent of coating failure are as follows.

1. ASTM Standard D610-894 (2012), "Evaluating Degree of Rusting on Painted Steel Surfaces"
2. ASTM Standard ASTM D4214-07,[5] "Evaluating Degree of Chalking of Exterior Paint Films"
3. ASTM Standard D660-936 (2011), "Evaluating Degree of Checking of Exterior Paint"
4. ASTM Standard D661-937 (2011), "Evaluating Degree of Cracking of Exterior Paint"
5. ASTM Standard D662-938 (2011), "Evaluating Degree of Erosion of Exterior Paint"
6. ASTM Standard D714-029 (2009), "Evaluating Degree of Blistering of Paint"
7. ASTM Standard D772-8610 (2011), "Evaluating Degree of Flaking (Scaling) of Exterior Paint"

Each of these standards for evaluating coating failure includes a photographic standard, which serves as a useful tool in rating the extent of failure. The ASTM standards generally use a rating of from 10 to 0, with 10 being perfect and 0 being completely corroded, blistered, or other such failing. This is considered a good method since the scale of 10 to 0 is discrete enough to accommodate accurate reporting of the condition. In some cases, where a more general scale is needed, it can be modified to proceed from 10 to 8, 6, 4, 2, and then 0, which allows more leeway between the numerical values.

Figure 15.1 shows the scale and gives a description of the rust grades outlined in ASTM Specification D610. This standard is designed to rate the condition of the coating as a percentage of the surface rusted. However, it can also be used for blistering, scaling, and similar types of failure.

While the percentage method is a good one, it can be simplified using the same approach as shown in Figure 15.1. If, for instance, in place of the percentage rating, the rating of the number of corrosion spots or blisters per ft^2 were used, results would be easier to visualize in a report. If each one of the squares in Figure 15.1 were considered to be one ft^2, then the following rating would result. A rating of 9 would equal 1 or 2 pinpoints of rust per ft^2. A rating of 8 would equal 3 to 6 pinpoints of rust per ft^2. A rating of 6 would equal plus or minus 30 pinpoints to $^1/_{32}$ in rust spots per ft^2. This would then scale up rapidly to the point of complete failure at 0.

This alternate rating method is suggested because experience in reporting failures via written reports has led to the conclusion

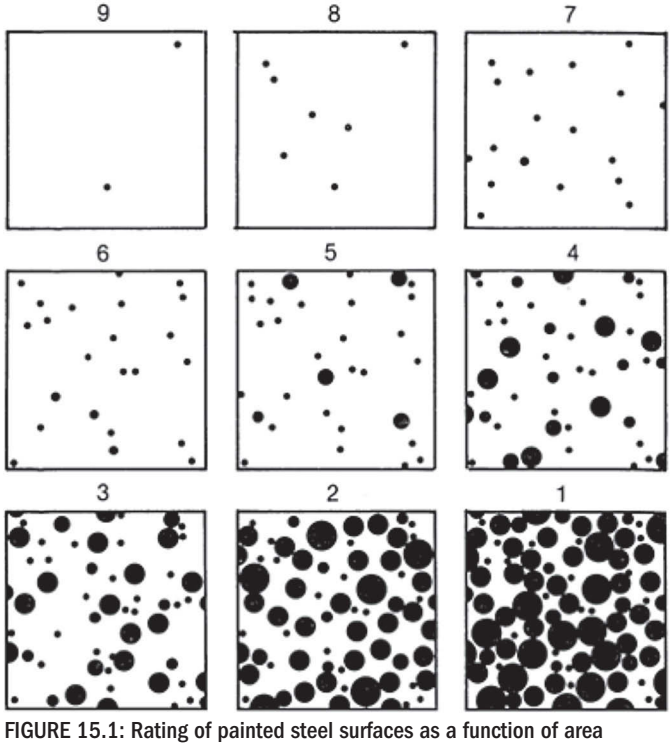


FIGURE 15.1: Rating of painted steel surfaces as a function of area percent rusted. Source: ASTM-D610/SSPC-Vis 2 (West Conshohocken, PA: ASTM).

TABLE 15.1: Scale and Description of Rust Grades

ASTM Rust Grades	ASTM Description	Alternative Description
10	No rusting or less than 0.01% of surface rusted	No corrosion
9	Minute rusting, less than 0.03% of the surface rusted	1 or 2 pinpoints of rust per square foot
8	Few isolated rust spots, less than 0.1% of surface rusted	3 to 6 pinpoints of rust per square foot
7	Less than 0.3% of surface rusted	±20 pinpoints of rust per square foot
6	Extensive rust spots, but less than 1 % of surface rusted	±30 pinpoints of rust per square foot
5	Rusting to the extent of 3% surface rusted	±30 pinpoints to 1/16 in. rust per square foot
4	Rusting to the extent of 10% surface rusted	±50 1/32 to 1/8 in. of rust spots per square foot
3	Approximately 1/6 of the surface rusted	Approximately 1/4 of the surface rusted with 1/32 to 1/8 in. rust spots
2	Approximately 1/3 of the surface rusted	Approximately 1/3 of the surface rusted with 1/32 to 1/4 in. rust spots
1	Approximately 1/2 of the surface rusted	Approximately 1/2 of the surface rusted with 1/32 to 1/2 in. rust spots
0	Approximately 100% of the surface rusted	Approximately 100% of the surface rusted

Source: ASTM Description from ASTM Stand D-610-69, Evaluating Degree of Rusting on Painted Surfaces, Philadelphia, PA, 1982.



FIGURE 15.2: Complete blistering of coating (ASTM Rating 2, Dense). Source: "Pictorial Standards of Coatings Defects, Blistering" (Philadelphia, PA: Federation of Societies for Coating Technology).

that it is easier to visualize 2 pinpoints of rust per ft^2 than it is 0.003% of surface rusted. For instance, in the case of a rating of 8, it is easier to visualize 3 to 6 rust spots per ft^2 as compared with a rating of less than one tenth of one percent of the surface rusted.

Table 15.1 shows the ASTM rust grades and their descriptions, combined with the alternative descriptions suggested above. These alternative descriptions can be related to Figure 15.1 for a visual evaluation of the rating. ASTM and SSPC have photographic standards corresponding to the various ratings, which can be obtained from them or from the Federation of Societies on Coating Technology.[11]

The ASTM standard for evaluation of rust on painted steel surfaces provides the basis for the rating of the other types of coating failure that have been discussed. The evaluation for the degree of 8 being pinpoint blisters, 6 being blisters up to 1/16 in (1.6 mm) in diameter, 4 being blisters up to 1/8 in diameter, and 2 being blisters up to 3/8 in diameter or larger. In addition to the size of the blisters, the quantity of the blisters is also rated. In this case the rating is none for no blistering, few for one or more blisters per unit area, medium for several blisters per unit area, medium dense for an area with many blisters but with some flat space between the blisters, and dense for continuous blisters over the surface.[4] Figure 15.2 shows blisters with a rating of number 2 dense. Other ASTM ratings for degree of coating failure are as follows.

1. ASTM-D659-65,[12] "Evaluating the Degree of Resistance to Chalking of Exterior Panels," has been consolidated with ASTM D4214-07. The D4214 rating is determined by the amount of reflectance of chalk compared to the photographic standards prepared by Kronos-Titan GMbH, Leverkusen, West Germany. Examples of these chalk ratings are given in Table 15.2. ASTM D4214 rating is based on photographic reference standards prepared by ASTM. Chalking is the powdering of the surface of a coating, and in the ASTM photographic reference is evaluated as 10 where there is essentially no chalking and 0 where the chalking is extremely heavy. The method of rating is to take a dark wool cloth, press it against the surface, and twist it under your thumb for 180 to 360 degrees. With a rating of 10, there is no discoloration on the dark cloth; 8 leaves a slight discoloration, while 2 results in a completely opaque white surface.
2. ASTM-D660-93 (2011), "Evaluating the Degree of Resistance to Checking Exterior Paints." In this case, checking means a break in the surface that does not penetrate to the substrate. This means checking is a surface condition. The rating system is from 8 to 0, with 8 being minor checking, 6 being moderate checking, 4 being nearly continuous checking, down to 2, which is a completely checked surface. Reference standards describe the types of checking as Irregular Pattern, Line and Short Parallel, Switch, Crow Foot, Mosaic, Shrinkage, Short and Random, and Sigmoid.
3. ASTM D661-93 (2011), "Evaluating the Resistance to Cracking of Exterior Paints." The differentiation between cracking and checking is that cracking is completely through the coating film down to the substrate. The appearance may be quite similar, but cracking is a much more severe type of disintegration, with corrosion often occurring in the cracks. In other words, cracking is a step beyond checking from the standpoint of severe coating failure. The rating system is essentially the same as for the previous ASTM standard on checking, but the reference types are limited to Irregular, Line, and Sigmoid.
4. ASTM-D772-86 (2011), "Evaluating the Degree of Flaking (Scaling) of Exterior Paint." Flaking may be considered a continuation of the previous cracking failure. Flaking can be considered a cracked surface where the small areas between the cracks have lost adhesion and are curling or popping from the surface. The rating system is similar with 10 meaning no scaling, 8 meaning 1 to a few small flakes per unit area, 6 meaning moderate flaking, and 2 meaning 40 to 50% of the surface flaking.

Table 15.2 summarizes the ratings for evaluating the above failures. In connection with the evaluation of coatings, it must be kept in mind that there are photographic standards for the various degrees of failure, which can aid immeasurably in evaluating the type and

TABLE 15.2: Standard Coating Ratings

Standard	Scale	Description
ASTM D714-56, Evaluating the Degree of Blistering Paints	**Size of Blister**	**Description**
	10	No blister
	8	Pinpoint
	6	Pinpoint to 1/16 in.
	4	1/8 in.
	2	3/8 in. or large
	Frequency of blisters	
	10	None
	8	Few
	6	Medium
	4	Medium-Dense
	2	Dense
ASTM D659-44, Evaluating Degree of Resistance to Chalking of Exterior Paints (wool cloth pressed on the surface and turned 180°)	10	No chalk or discolor of cloth
	8	Slight discoloration
	6	Light discoloration
	2	Completely opaque chalk
ASTMD660, Evaluating Degree of Resistance to Checking (checking is a break in the surface not penetrating to the substrate)	10	No checking
	9	Very minor checking
	8	Few checks
	6	Moderate
	4	Almost continuously checked
	2	Completely checked
ASTM D661, Evaluating the Degree of Resistance to Cracking of Exterior Paints (cracking extends through coating to the substrate)	10	No cracking
	9	Very minor cracking
	8	Few cracks
	6	Moderate
	4	Almost continuously cracked
	2	Completely cracked
ASTM D772-47, Evaluating the Degree of Flaking (Scaling) of Exterior Paint	10	No flaking
	8	Few flakes
	6	Moderate flaking
	4	20 to 25% of surface flaked
	2	40 to 50% of surface flaked

Source: C.G. Munger, Repairing Protective Coatings: Effect of Coating Types, *Plant Engineering*, Feb. 17 (1977).

amount of coating failure.

As previously stated, it is important to know the degree of coating failure in order to determine the type of repair that is needed. If the amount of failure is relatively minor, with a rating of 8, the surface can usually be repaired without completely removing the entire coating from the surface. If the rating is much less than 8, it is usually more economical to remove the entire coating and begin from scratch. While this may seem somewhat drastic, preparation of individual spots of failure is often much more difficult and time consuming than removal of the entire coating.

Adhesion

It is extremely important to know the adhesion of the original coating wherever repairs are to be made. The adhesion of the original material can make the difference between success and failure in the application of a repair coating over that surface. For example, in the case of the undercutting of a coating by corrosion products, if the undercutting is localized to a break in the coating or to an edge, and the adhesion beyond the undercutting is good and continuous, then the undercut areas can be satisfactorily prepared, the area patched with the original number of coats, and an overall coat provided over the entire surface.

On the other hand, if the adhesion is only marginal beyond the area of undercutting, it is quite probable that the addition of an overall topcoat over that surface may further decrease the adhesion and create areas for blistering or for further undercutting. Also, in the case of blistering, if the coating on the plane area beyond the blister has poor adhesion, then the entire coating must be removed. If the adhesion between the blisters is strong, the blistered areas often can be repaired with an overall coating over the remainder of the surface. Without the strong adhesion between the blisters, however, this would not be practical.

TABLE 15.3: Common Coating Types and Areas of Use

Area of Use	Coating Type	Environment
Exterior Iron and Steel	Oil	Rural-Mild
	Alkyd	Industrial
	Urethane	
	Oil-Based Phenolic	High Humidity, Mild Industrial
Interior Iron and Steel Metal	Alkyd	Mild Industrial
	Urethane	
	Epoxy Ester	
	Vinyl Epoxy	Acid or Other Corrosive Fumes
	Chlorinated Rubber	Dust Fallout
Interior Storage Tanks, Chemical Solutions	Vinyl	Sal Solutions
	Epoxy Phenolic	Dilute Acid
	Epoxy	Alkalies
Interior Water Tanks	Vinyl	Water Immersion
	Epoxy	
	Chloinated Rubber	
	Coal Tar Epoxy	High Humidity
	Coal Tar	
	Asphalt	
Interior Concrete, Tanks or Reservoirs	Vinyl	Water Immersion
	Epoxy	High Humidity
	Chlorinated Rubber	
Interior Solvent Storage Tanks	Inorganic Zinc	Solvent Immersion
	Epoxy Phenolic	Fumes—Condensation
	Epoxy	
Exterior Concrete Plaster—Masonry	Cement	Mild—Industrial
	Acrylic	
	Vinyl Acetate	
	Vinyl	Corrosive
	Epoxy	Humidity
	Chlorinated Rubber	
Exterior Wood	Oil	Rural—Mild
	Alkyd	Industrial
Interior Plaster or Wall Board	Acrylic	Mild—Industrial
	Alkyd	
	Chlorinated Rubber	
Wooden Floors	Alkyd	Mild—Industrial
	Polyurethane	
Concrete Floors	Epoxy Ester	Mild—Industrial
	Polyurethane	
	Chlorinated Rubber	Spillage Water—Dilute Chemicals
	Vinyl	
	Epoxy	

Source: C.G. Munger, Repairing Protective Coatings: Effect of Coating Types, *Plant Engineering*, Feb. 17 (1977).

In the case of cracking, the coating may have strong adhesion except at the crack. If the coating is generally cracked, and corrosion has started on the substrate within the crack, then the only recommended procedure is to remove the entire coating from the surface. If the adhesion is good, and there is little or no corrosion starting, repair by additional coats may be practical. Since chalking and checking are surface coating phenomena, adhesion generally is not affected by either one of these types of coating failure. Thus, these types of coating failure can usually be remedied by the proper application of a topcoat over the existing material. With chipping or scaling, however, adhesion to the surface is usually questionable, so that unless the failure is restricted to local areas, it is generally preferable to begin repair from the substrate out by removing the existing coating.

Type of Coating

Any repair program must take into consideration the type of coating that already exists on the surface; otherwise, the entire repair job may result in early failure. For instance, a topcoat that is incompatible with the existing coating can create adhesion problems, blistering, delamination, wrinkling, and other similar problems, any one of which can cause the repair material to fail within a short period of time.

It is often difficult to determine the type of the original coating. This is particularly true where no record has been kept of the original material and its application. Table 15.3 shows many of the common coating types and areas where they are commonly used. However, even with this type of information, it is difficult to determine the character of the previous coating. The table does, however, help eliminate many of the possibilities that need to be explored.

For example, on the interior of storage tanks for some types of chemical solutions, the principal material on the surface may be a vinyl, an inorganic zinc (IOZ), an epoxy, an epoxy phenolic, or a novolac epoxy. With this information, and by knowing the particular characteristics of these coatings, some deduction can be made as to the actual type of coating on the surface. A practical determination of compatibility can then be made by cleaning several ft^2 of the coated surface, treating the surface with the proper surface preparation, then applying the repair coating material over that surface. In doing this, it will be possible to determine (1) if the coating is going to damage the previous one (i.e., cause it to swell, dissolve, or lose adhesion); and (2) whether or not the new topcoat will have adequate adhesion to the previous coating. If it does not, the new coating can generally be peeled from the older surface within a reasonable period of time after the new coating has been applied (e.g., after an overnight dry). Even if the new topcoat cannot be physically peeled from the surface, if it shatters, pops, or scales from the surface when cut with a knife, it is obvious that the new material is incompatible with the original coating.

Although the new topcoat may appear to satisfactorily adhere to the undercoat, it often tends to decrease the adhesion of the original coat to a substantial degree. Again, if a knife is used to cut the surface and the entire coating tends to pop, shatter, or scale from the surface, the basic adhesion of the previous coat has been damaged and future failure can be anticipated.

TABLE 15.4: Common Coating Types—Maintenance Procedure

Class of Coating	Type of Vehicle	Maintenance
Air-Reactive Coating	Oil Varnish Enamel Alkyd Oil-Modified Phenolic Epoxy Ester	1. Remove all oil or grease. 2. Wash/scrub with clean water. 3. Power sand or light brush blast. 4. Brush first coat on repair areas NOTE: If general surface has heavy or medium chalk, sanding may be eliminated.
Internally Reactive Coatings (Catalyzed)	Epoxy Amine Epoxy Polyamide Epoxy Phenolic Coal Tar Epoxy Urethanes Polyester	1. Remove all oil or grease. 2. Wash/scrub with clean water. 3. Power sand or light brush blast. 4. Brush first coat on repair areas NOTE: Surface of coating must be abraded for proper topcoat adhesion.
Moisture-Reactive Coating	Moisture Cure Urethane	1. Same as Internally Reactive Coatings.
Solvent Drying	Vinyl	1. Remove all oil or grease. 2. Wash/scrub with clean water. 3. Reapply solvent dry coatings
Lacquers	Vinyl Acrylic Coal Tar Asphalt Nitrocellulose	1. Remove all oil or grease. 2. Wash/scrub with clean water. 3. Reapply coatings
Water-Based Coatings	Vinyl Acetate PVA Vinyl Acrylic Acrylic Coal Tar Emulsion Asphalt Emulsion	1. Remove all oil or grease. 2. Wash/scrub with clean water. 3. Reapply water-based coatings
Inorganic Zinc	Water-Based Silicate Solvent-Based Silicate	1. Remove all oil or grease. 2. Wash/scrub with clean water. 3. Power sand or light brush blast. 4. Reapply coating. NOTE: Light abrasion of surface is necessary to open up new zinc. NOTE: Inorganics will not adhere to any organic/oil-grease coating.

Source: C.G. Munger, Repairing Protective Coatings: Effect of Coating Types, *Plant Engineering*, Feb. 17 (1977).

While such tests do not indicate the exact type of the existing coating, they do indicate the compatibility of the new topcoat over the previous coating. If the test shows none of the possible difficulties, there is a good chance that the two coatings are compatible and that the new topcoat will make a satisfactory repair over the previous coating.

Another procedure has been developed, however, which provides a much more definite identification of the previous coatings than the simple test indicated earlier. It consists of a series of tests developed at the Naval Civil Engineering Facility at Point Hueneme, California that provides a chemical identification of the unknown coating on the surface. When this procedure is used, a reasonably accurate identification can be made, and selection of the coating can proceed from that point.[13]

Table 15.4 lists a number of different common types of protective coatings and the areas where they are generally used. These may be combined into various general coating categories that usually can be treated in a similar manner when repair is necessary. While the various classes of coatings listed in Table 15.4 are all described in previous chapters, they nevertheless should be reviewed in terms of their repair characteristics.

Solvent-Drying Lacquers

Solvent-drying lacquers are made from resins that are fully polymerized prior to being formed into a coating. There is no change in the resin after the coating is formed, and they remain permanently soluble in their original solvent. The drying process is merely one of the solvents evaporating from the coating, leaving the fully polymerized resins and pigment on the surface. These coatings are thermoplastic coatings, indicating that they are softened with heat and usually provide a tough, semi-rubbery, partially extensible film. Hard, internally polymerized coatings are therefore generally not recommended for repair of these materials.

The coatings that come under the classification of solvent-drying lacquers are generally single-package coatings, since they require no catalyst. They include vinyl coatings, chlorinated rubbers, cellulose lacquers, phenoxy coatings, vinyl acrylics, as well as coal tar and asphalt cutbacks. As discussed, all of these materials are soluble in their own solvents, even after several years of exterior exposure. Repair coatings of similar types, for example, a vinyl over a vinyl, will soften the previous undercoat, and will allow some softening of the old material at the interface between the new and the old coating. Thus, the new material generally has good adhesion to the old undercoat. This is an important characteristic of the thermoplastic-type of coating since it eliminates many of the difficulties caused by the interface between the new and the old coatings. Intercoat adhesion is generally good because of the permanent solubility of these materials.

The general repair procedure suggested for the lacquer-type coatings is as follows.

1. Remove all oil and grease or similar contaminant with water-soluble hydrocarbon removers that will not damage the surface.
2. Wash the surface of the coating thoroughly with water and detergents, scrubbing with brushes or sponges or power washing at a minimum of 1,000 psi to physically remove the surface contamination.
3. Rinse the surface with clean water.

4. Allow the surface to dry thoroughly after which a similar type of lacquer coating should be applied over the clean surface.

The repair coating thus applied should have all of the properties of the original coating, and the renewal will substantially increase the life span of the coating.

Thermoset, Internally Reactive Coatings

In the classification of thermoset, internally reactive coatings, all coatings revert to insolubility as a result of internal condensation or polymerization shortly after application. They are, for the most part, two-part coatings that have to be mixed just prior to application. They change from a liquid to a solid due to the internal polymerization reactions. Once formed, these materials are insoluble in most common solvents, and therefore the solvents in a repair coat would not necessarily strike into the previous coatings and allow adhesion in a way similar to lacquer-type coatings. Many coatings in this classification are of a high solid type. Nevertheless, there is usually a resin-rich layer on the surface that makes the penetration of the topcoat much more difficult. This surface layer is not necessarily any more highly polymerized than the remainder of the coating, but, because of the thin resin-rich surface, it makes penetration difficult. Thus, the topcoat must be completely compatible with this surface.

The coatings that are usually included in this classification are amine epoxies, polyamide epoxies, phenolic epoxies, coal tar epoxies, bitumen epoxies, two-component polyurethane coatings, and some polyester coatings. These coatings are mostly thermosetting, and provide a hard, somewhat brittle film over the surface. Polymerization may continue for some time with this type of coating, making it more resistant after it has been exposed for a long period of time.

The recoating of these internally reacted coatings usually involves the following procedure.

1. Remove all oil and grease and similar contaminants from the surface.
2. Wash the surface, using a sponge, brush, or power wash with at a minimum of 1,000 psi, with clean water to remove the water-soluble contaminants from the surface, as well as any chalk or similar surface material.
3. Allow the surface to dry, and abrade it lightly by brush-off blast cleaning (NACE No. 4/SSPC-SP 7/ ISO SA 114) or by hand or power sanding. This step is necessary for this coating classification to break up the surface of the coating and allow some mechanical adhesion in addition to the normal adhesion of the compatible topcoat. Coatings in ambient service that have begun to chalk may be cleaned with surfactant-type cleaners without the necessity of abrasive sweeping or hand sanding. Spot tests of adhesion after cleaning are recommended.
4. If possible, it is preferable to brush the first coat of the repair material over the surface since this aids in wetting the surface with the new coating.

Using this procedure, the topcoats of these coatings generally have good compatibility with the old coating being repaired, and a continuing life span of the total coating can be expected following repair.

Air-Reactive Coatings

Air-reactive coatings comprise a comparatively large group of coating materials due to the many variations available. Most of these materials are based on drying oils, or are resins combined with drying oils that have similar air-curing properties. Air-reactive coatings have the characteristic of hardening and polymerizing through reaction with oxygen from the air. This reaction first occurs on the surface, and then, as the oxygen penetrates the surfaces, passes on through the depth of the coating. Due to the surface reaction, the surface is often more highly polymerized and more highly insoluble than the underlying coating, which is less reacted. This surface layer is relatively insoluble, particularly in the mild solvents generally associated with these coatings, and therefore the repair coating must not only be compatible with, but must also thoroughly wet, the previous material in order to obtain satisfactory adhesion. It cannot rely on solvent softening of the previous coating for its adhesion. Coatings in this classification are enamels, linseed oil paint, medium and long-oil alkyds (as well as alkyds that are modified with chlorinated rubber), silicones, acrylics, phenolics, and epoxy esters.

The repair recommendations for air-reactive coatings are as follows.

1. Thoroughly remove any oil, grease, or other similar contamination from the surface.
2. Wash the surface with clean water, using a sponge, brush, or power wash with at a minimum of 1,000 psi. This not only removes soluble contamination from the surface, but also helps remove any chalk or dirt that has accumulated on the surface over a period of years.
3. Lightly power or hand sand the surface of the coating in order to break up the surface and allow penetration of the new coat. The surface may also be lightly sweep blasted with fine abrasive to gently abrade the surface.
4. Apply the compatible topcoat material to the lightly abraded surface, preferably by brush or roller.

These coating materials generally have good wetting characteristics. Nevertheless, the physical working of the coating into the old surface aids in that wetting property. Because these materials react with oxygen from the air, some time is required for them to cure sufficiently for additional coats to be applied. The proper drying of each coat after it is applied is important in the resistance of these materials.

Moisture-Reactive Coatings

The most common type of coating in the classification of moisture-reactive coatings is the moisture-cured polyurethanes. The main characteristic of this coating type is that it has a tightly cross-linked and polymerized surface. This surface is usually a glossy one, with the gloss being retained over long periods of time, indicating a resin-rich surface. This surface is very insoluble so that it is necessary to break up the surface and allow mechanical, as well as chemical, adhesion. The general repair procedure with the urethane-type coatings is similar to that outlined for the thermoset, internally reactive coatings.

Water-Based Organic Coatings

Water-based organic coatings are usually emulsions of different resins. Some of them are water dispersions or emulsions of polyvinyl acetate, polyvinyl acrylic copolymers, acrylic resins, coal tars, or asphalts. They also include water-based thermosetting-type coatings, such as epoxies and coal tar epoxies. The thermoplastic-type materials have characteristics somewhat similar to the lacquer-based ma-

terials. The epoxy emulsion coating, and even some water-based alkyd, have some of the characteristics of the thermoset type coatings. Although these characteristics are quite different, all of these materials must coalesce out of the water dispersion and form a film prior to its final reaction.

Water-base organic coatings are not as dense and do not have the same type of film as that formed from a solvent-based coating. Some of these materials do tend to chalk, and, because of their water base, tend not to wet the chalky surface as well as some other coating classifications. However, these coatings can usually be repaired and recoated with little difficulty. The repair procedure, as follows, is reasonably simple.

1. Remove oil and grease from the surface.
2. Scrub the surface with clean water to remove all of the soluble dirt and chalk.
3. Allow the surface to dry and then reapply the water-based coating.

Inorganic Zinc Coatings

IOZ materials are of a completely different class than the organic coatings. They may be water-based (composed of soluble sodium, potassium, or lithium silicates), or they may be the solvent types, which are solvent solutions of organic silicates such as ethyl silicate. When these coatings are cured to insolubility, there is little difference between the two types of films, except for the amount of zinc and the various fillers that may be added to the coating.

When applied without topcoats, these materials usually remain on the surface several years before requiring repair. The surface at that time is a hard, rock-like zinc surface that is no longer soluble in either water or the solvents of the solvent-based inorganic. As mentioned, these coatings continue to react over long periods of time with oxygen and carbon dioxide (CO_2) from the air. The CO_2 and oxygen reaction products gradually penetrate throughout the coating to form both zinc oxide (ZnO) and zinc carbonate ($ZnCO_3$) on the surface and within the coating. The resulting product is hard, with the zinc particles encapsulated in a matrix of zinc silicate (Zn_2SiO_4) combined with ZnO and $ZnCO_3$.

It usually is not satisfactory to apply an IOZ coating over an old IOZ film without lightly abrading the surface to break up the Zn-CO_3-ZnO film on the surface, and to expose the zinc in the old film so as to allow it to combine with the silicates in the new vehicle. In this way, the old or original zinc coating combines with the new repair coating, creating a chemical bond between the two. If the surface is properly abraded, good adhesion between the new and the old coatings usually results.

The recommended procedure for recoating the IOZ coatings is as follows.

1. Remove oil and grease from the surface.
2. Wash the surface free of any contamination with clear water, using brushes or other means to release the contamination on the surface. (Any organic type of contamination will prevent the proper adhesion of the repair coating.)
3. Once the surface is free of contamination, it should be lightly abraded, preferably by sweep blasting the surface with a fine abrasive. The surface may also be abraded by hand or power sanding. Since IOZ coatings are generally 3 to 4 mils thick, even after several years in the atmosphere, the abrasion should be light, yet sufficient to remove the carbonate film from the surface while not re- moving the zinc coating itself.
4. Once the surface of the coating is abraded, the new repair coat of IOZ may be applied.

In the discussions of the various coating types, it has been assumed that the original coating is a continuous film with no general corrosion breaking through the surface. If there is corrosion on the surface, the repair procedure is much more complicated.

Type of Substrate

As previously discussed, the substrate is an important part of any coating system. This continues to be true where coatings need to be repaired, since the substrate may be exposed at any break that occurs in the coating. There usually are breaks in the coating where not only the coating substrate interface is exposed, but also where there is active corrosion and perhaps undercutting of the coating. In this case, the repair coating must not only be compatible with the previous coating, it must be compatible with the substrate and must thoroughly wet, penetrate, and adhere to any area of the substrate that is pitted or corroded.

The principal substrates encountered are steel, cast iron, galvanized steel, aluminum, wood, and concrete. Each of these corrodes or disintegrates in a different manner, and each presents a different surface over which the repair coating must be applied.

Steel

Steel is the most commonly coated substrate. Coatings are the primary method of protecting steel, so that much coating maintenance and repair involves steel surfaces. Where a steel surface has been coated, and where the coating has been in service for a considerable period of time, there is usually some degree of corrosion and coating failure taking place. Rust tubercles form wherever there are breaks in the coating, even at minor breaks such as pinholes. The rust spot may be small, even pinpoint in size, or it may cover an extensive area. Pitting corrosion may be undercutting the coating, with corrosion building underneath the coating. In each of these cases, the basic steel substrate will be pitted.

Where repair is necessary, the corrosion products at the breaks in the coating must be completely removed. The pit must be cleaned free of corrosion so that the repair coating can properly adhere to the steel surface. However, whether large or small, the coating surrounds each one of these areas. Thus, in order to make the repair, the corrosion product and the coating must be removed from the surface back to the point where the coating is solid, intact, and tightly adhering to the surface.

The removal of the coating around the corroded area is extremely important, since the adhesion of many coatings is released in the areas of corrosion, and unless the loose, poorly adhering coating is removed, failure will continue at the same spot. It is also essential that the coating be tapered from the corrosion area out to the solid coating, creating a feather edge at the junction between the steel and the old coating. This provides a transition area where the repair coating extends from the corroded steel surface out over the existing coating. This is not only necessary for proper repair, but also gives the repair job a much better appearance, since there are no jagged, rough edges to give the appearance of a patch job.

The repair of coated steel surfaces is a difficult and time-consuming task. Unfortunately, many plant managers, maintenance per-

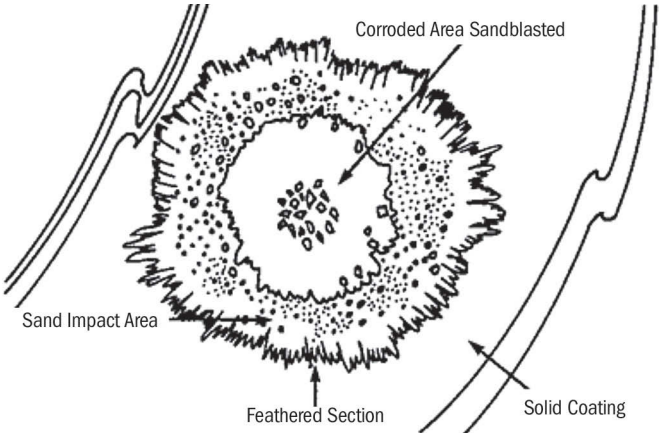


FIGURE 15.3: Interface between blasted area of corrosion and solid coating, with feathered area between. Source: C.G. Munger, "Practical Aspects of Coating Repair," *MP* 19, 2 (1980): p. 46.

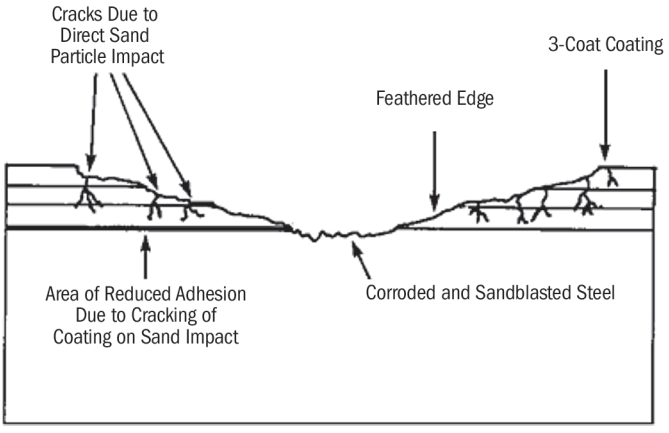


FIGURE 15.4: Cross-section of coating showing a corroded area that has been sandblasted. Note the tapered, feathered edge and the star cracks caused by heavy sand grain impacts. Source: C.G. Munger, "Practical Aspects of Coating Repair," *MP* 19, 2 (1980): p. 46.

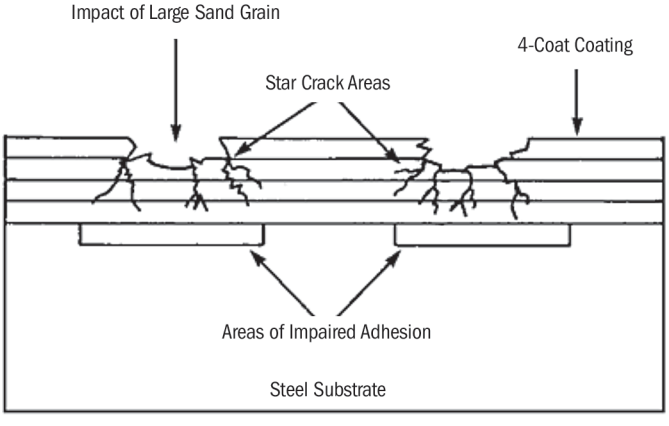


FIGURE 15.5: Star cracks caused by the impact of heavy sand particle. Source: C.G. Munger, "Practical Aspects of Coating Repair," *MP* 19, 2 (1980): p. 46.



FIGURE 15.6: The edge of a repaired coating after blasting and recoating. The 1.8-mil area was blasted free of the original coating. Heavy impact areas can be noted above the 5.5-mil area where the original coating was chipped and star cracked by heavy blast media.

sonnel, marine operators, and applicators too often take coating repair for granted. If there is coating damage (e.g., blisters, rust, undercutting), the immediate reaction should involve chipping and scaling, or brush blasting to remove some of the corrosion products and failed coating, and to apply additional coats of the same material over these areas. In situations where there may be some areas of pinpoint rusting or undercutting while the remainder of the coating is in good condition, the repair is often a stopgap measure to provide some immediate improvement in appearance, while the primary problem may be aggravated by damage to the original coating from the repair procedures used. There are many difficulties and hazards in repairing coatings over steel surfaces that should be understood before any repair procedure is followed.

Many repair difficulties stem from the methods of repair used. Most of these methods go back to lessons learned about the application of coatings over original surfaces where the surface is cleaned to white or near-white metal and then the coating applied. Abrasive blasting is the preferred method of obtaining such a surface, so, when it comes to repair, the first thought is to abrasive blast the damaged areas of the coating and then reapply the original coating over the clean surface. Unfortunately, the preferred procedure for new work can prove damaging where a coating is to be repaired. First, the steel structure, tank, ship, or bridge now exists as a completed unit, so that blasting must be done by hand, using various abrasives, and usually from some sort of a scaffold. Spot hand blasting is therefore included in many specifications where a coating is to be repaired.

There are, however, repair problems associated with spot blasting. First, the blasting procedure uses impact as the method of cleaning the surface and removing the coating. The impact of the abrasive particle, and the scouring as it disintegrates on impact, provides the cleaning process. Impact of the abrasive particle is one of the inherent problems of coating repair. The procedure often outlined in the specification is to spot blast the rusty area, feather the edge of the coating surrounding the area, and sweep blast the rest of the coating to remove dirt, chalk, and other surface contaminants, in addition to lightly abrading the surface of the coating. This light

abrasion is necessary for alkyds, epoxies, and polyurethanes where the surface requires some tooth or mechanical advantage when the repair coating is applied. The blasting procedure to remove the area of rust is good. However, to be most effective, all corrosion products must be removed (white metal) since the corroded area is more sensitive to continued corrosion than the original metal underneath the remaining solid coating.

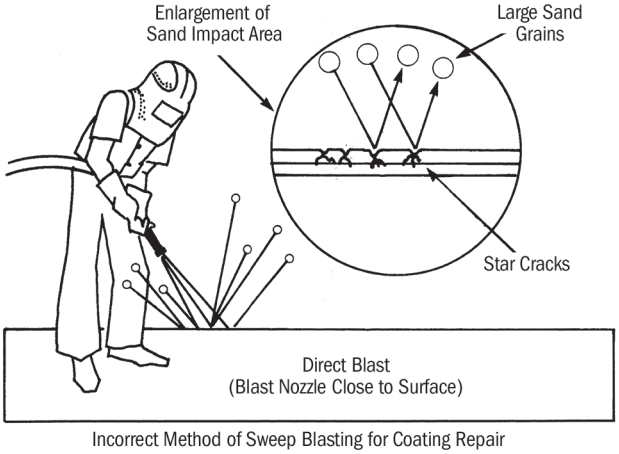
The repair problems primarily occur at the area of the interface between the blasted areas and the old coating where the edge is supposed to be feathered and the coating beyond that slightly roughened (Figure 15.3). In these areas, the impact of the abrasive particles (particularly where highly cross-linked and brittle coatings are involved) can cause fractures of the coating on impact and have a tendency to loosen the adhesion of the coating in the area of impact (Figure 15.4).

This poor adhesion is often evident when the repair coating is applied. The edges of the coating swell and curl, creating an area of questionable effectiveness, as well as one of poor appearance. The feathered edge is the most subject to this action, since it is the part of the coating most subject to abrasive action other than the corroded area itself. There also may be star cracks in the coating area just beyond the feathered edge from impact of the abrasive. This makes a porous spot in the coating and an area of questionable adhesion (Figure 15.5). These spots can then become focal points for the failure, as evidenced by the fact that many such repaired sections soon fail again, beginning not where the previous rust occurred, but in a circle surrounding the area where the old coating was feathered (Figure 15.6).

Much of the failure of organic coatings is due to the impact of the blasting media impairing the adhesion of the original coating. This is combined with the difficulty of the repair coating to sufficiently penetrate the original film at the star cracks, and in the feathered area, to gain new adhesion to the substrate. The feathered area is also a transition zone between the abrasive blasted area and the solid coating beyond the feathered edge. As the coating dries and cures, stress may further reduce the adhesion in that particular transition zone, which often curls the edge of the old coating.

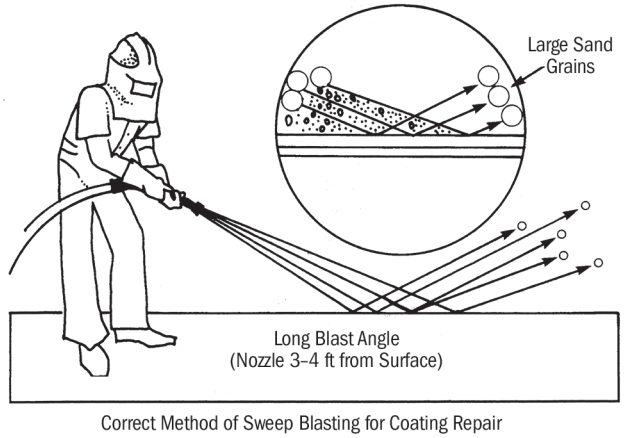
Considering these difficulties, the following repair procedure is recommended. Use very fine abrasive, such as 60 to 80 mesh, so as to eliminate the impact of large particles on the coating.

1. Blast the corroded area clean, preferably to white metal, by normal blasting procedures. Following this, however, back off the blast nozzle to 3 or 4 ft (0.9 or 1.2 m) from the surface and blast the feathered edge from this distance at an oblique angle to the surface. This further reduces the impact of the abrasive on the coating and tends to wear the coating away in the feathered edge area.
2. To clean and slightly roughen the solid coating surrounding the repair, continue to use the very fine abrasive, sweeping the existing coating both at a distance from the surface and at an oblique angle to prevent direct impact of large abrasive particles. The incorrect procedure is shown in Figure 15.7. With the blast nozzle held close to the surface, any heavy abrasive particle can star crack the coating, causing a spot of incipient failure. The heavy impact is satisfactory for removing corrosion deposits. However, for feathering edges and slightly roughening existing coated surfaces, the blast nozzle should be removed to a distance of 3 to 4 ft from the surface, and the blasting done at an angle oblique to the surface, as shown in Figure 15.8.
3. Apply a very liquid, highly penetrating primer to the surface to penetrate any possible edge areas of poor adhesion in the feathered area, and any possible star cracks in the body of the coating. Such a primer should be, if possible, a low viscosity and low molecular weight material that is thoroughly compatible with the existing coating and steel surface, and which has high wetting characteristics for each.
4. Mechanical application of the primer (preferably by brush) aids in the wetting and penetration of the primer into the porosity of the feathered section of the coating.



Incorrect Method of Sweep Blasting for Coating Repair

FIGURE 15.7: Incorrect blasting procedure.



Correct Method of Sweep Blasting for Coating Repair

FIGURE 15.8: Correct blasting procedure.

Depending on the severity of the coating breakdown, other methods of surface preparation can be used. If the coating has only started to show minor failure in isolated spots, blasting might cause more damage to the solid coating by abrasive ricochet and accidental impact than the benefit gained. Power sanders, while not leaving the metal surface as clean as abrasive blasting, can be used to effectively clean and feather isolated corrosion spots (i.e., pinpoint rust spots or small coating breaks) without damage to the large surrounding areas of solid coating. A rotary power sander does an excellent job of feathering the edge of the coating around a break, particularly when equipped with impregnated fiber discs or flapper wheels. Impact tools, such as needle guns, are effective for small complex corroded areas (e.g., rivets, bolt heads, welds, etc.), but are not as effective in feathering the coating edge as a rotary power sander. The combination of both tools may be more effective than either one used alone. Should the mechanical method of cleaning be used, it is essential that a highly penetrating primer be brushed into the repair area for the most effective results.

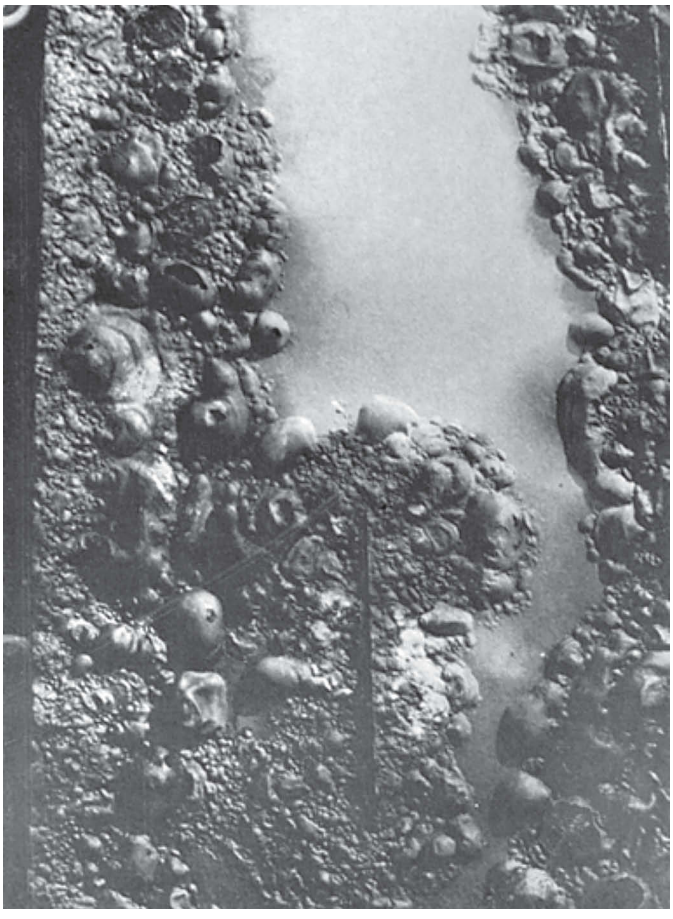


FIGURE 15.9: Typical edge corrosion and undercutting of a coating in a marine atmosphere.

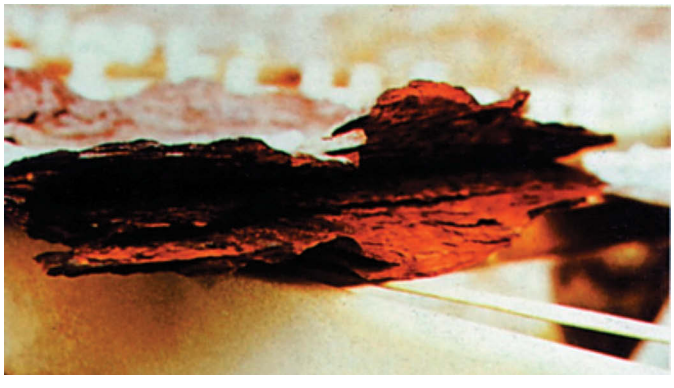


FIGURE 15.10: Unsupported edge of a coating where the steel substrate had completely disintegrated. Repair of such a failure first requires repair of the metal substrate.

One of the most common repair problems is that of cleaning and recoating old steel structures, tanks, ships, or offshore drilling or production platforms, where the coating has broken down on the edges of structural steel shapes or over welds, or where rust scale is forming under the plane areas of the coatings. This is a typical undercutting type of failure, where the corrosion begins at an edge or a break and gradually works its way under the coating, forming a hard black rust scale that can be as much as 6 mm (¼ in) or more in thickness.

Figure 15.9 shows typical edge undercutting of a coating in a marine atmosphere. This type of corrosion can be quite severe, completely eating away the steel under the coating. Figure 15.10 shows an edge where the steel has been completely corroded away, leaving only the coating intact.

Rust scale is primarily sub-oxides of FeO—OH, with some red Fe_2O_3 on the surface and in the fractures. The extent of the undercutting of an organic coating depends on the strength of the adhesion of the coating. The stronger the adhesion, the less undercutting, and the easier the repair. Where the adhesion is marginal, the surface preparation necessary to clean the corroded area free of rust may damage the apparently good coating to the point where no repair other than complete renewal of the coating is practical. Where the coating adhesion is good, the repair procedures should be as described earlier, followed by mechanically working a highly penetrating primer into the cleaned and feathered area, building the topcoats to the required thickness and, if the repair areas are extensive, applying a topcoat overall.

Galvanized Steel

Galvanized surfaces that have been coated, while usually not severely corroded, often require repair because the coating has started to chip and scale from the galvanized surface. The primary reason for this is the use of oil-based, alkyd, or similar coatings on the original galvanized surface without a zinc-compatible primer. When such a condition exists, the best procedure is to remove all of the previous coating from the surface. This usually can best be done by chipping, scraping, or water jetting, since once the coating reaches this condition, it can be easily popped from the surface. Abrasive blasting or similar procedures are not recommended for removal of such a coating because of the damage to the zinc surface by the blasting process. Baking soda blasting and polyurethane foam pellet blasting are effective cleaning methods that do minimal damage to galvanizing.

Where galvanizing remains uncoated for a considerable period of time and has begun to fail, the galvanizing usually fails by pinpoint rusting, with the rusting progressing over a period of time until it covers the entire surface. For practical repair, the galvanized surface should be coated prior to the time that the pinpoint rusting reaches the continuous stage. In this case, the repair procedure is to lightly blast the surface, removing all pinpoint rusting, and, if possible, touching up the previously corroded areas, using an IOZ coating as a base coat. This renews the zinc in this area and allows the following organic coating adhesion to have a continuous corrosion-resistant base. The general procedure for making repairs to a galvanized surface is as follows.

1. Make certain that the zinc surface is free of all previous coating that has chipped and scaled. If corrosion has started in bare areas on uncoated galvanized surfaces, lightly blast or hand sand the surface free of corrosion.
2. Touch up the previously coated areas with an IOZ coating and allow it to cure as recommended in the instructions.
3. Select a primer for the surface that is compatible with the galvanizing and which will not react with it. Many such primers are available, usually based on inert resins such as acrylics and epoxies.
4. Brush the primer onto the surface to provide complete wetting and the best possible adhesion.
5. Following the primer, apply compatible topcoats of the type desired.

Cast Iron

Cast iron, being ferrous, has many of the properties of steel. However, since it has a large, cast crystal structure, it appears to be more porous than the conventional steel surface. Nevertheless, for repair purposes, the surface is quite similar to that of steel, with only one or two exceptions. Where there are breaks in the coating, the cast iron may be pitted, and the pits in cast iron are generally deeper than

those in steel. It is necessary to thoroughly remove the corrosion product from the pits and to abrade the pits down to the solid cast iron surface. The pits in cast iron are often filled with graphite that may appear reasonably solid. This is called the graphitic corrosion of cast iron. If it exists, the material needs to be removed by blasting down to the solid cast iron surface.

The cast iron surface may also absorb moisture and other volatile materials into the surface to the point where, if a coating is applied over such contamination, it will fail again quite rapidly. In this case, it is recommended that the cast iron surface be heated with a blowtorch or acetylene torch in the manner previously recommended for steel.

The general procedure for coating cast iron is as follows:

1. Remove all of the corrosion products from any breaks in the coating, feathering the coating as recommended for steel.
2. Warm or heat the surface to the point where it is hot to the touch.
3. Once the surface is heated the primer should be applied by brush to the warm surface. The primer should be applied in a full wet coat for maximum penetration to be obtained.
4. The selected topcoats can follow as soon as the primer has properly dried.

Aluminum

Coated aluminum is often covered with a factory-applied coating that has been applied under controlled conditions and usually baked to obtain maximum adhesion. However, they are primarily an acrylic or vinyl acrylic, which has excellent weathering resistance. Aluminum hulled boats and yachts, however, usually are coated with epoxy primers and aliphatic urethane topcoats. For the most part, such coated aluminum surfaces are primarily recoated or repaired where damage has occurred or where the coating has weather to the point where general recoating of the surface is necessary. For the most part, there is little or no corrosion of the aluminum on such surfaces. Thus maintenance and repair usually only involves the application of an additional coat or coats of a compatible topcoat over the previous coating. In this case, the required surface preparation primarily involves a thorough washing to remove any chalk, dirt, grease, or other impurity, followed by the recoating procedure. The aliphatic polyurethanes on boats and yachts, however, require sanding or light abrasive blasting to dull the glossy finish prior to coating.

Occasionally, coated aluminum surfaces are corroded. The corrosion product is usually a white aluminum oxide that may form in small pinpoints in and around the break in the coating. On aluminum surfaces such as those on the aluminum deckhouses on ships, particularly where such structures are joined to a steel hull, aluminum corrosion can be quite extensive with undercutting and considerable pitting of the aluminum surface. Where aluminum is corroded, the surface should be abraded free of the corrosion product and the abrasion should be light. If blasted, the blasting abrasive should be very fine and the nozzle held a considerable distance away from the surface. Aluminum is a soft metal that both cuts and warps readily.

The general procedure for coating coated aluminum surfaces is as follows.

1. Thoroughly wash the surface of the coating with clean water to remove dirt and contamination. Oils and greases should be removed by a detergent-solvent-water combination prior to washing with clean water.
2. Lightly abrade any corroded areas to remove the entire white corrosion product. This can be done using a light sweep blast and fine abrasive. Hand sanding or a fine power disc may also be used on small areas.
3. Apply aluminum-compatible primer over any corroded areas of the surface.
4. Apply the proper compatible topcoats.

Other Metals

The coating of other metals (e.g., copper, magnesium, SS, and similar alloys) is usually an exception, so therefore the repair of coatings over these surfaces is likewise uncommon. Any repair procedure that may be required would be similar to that used for zinc or aluminum.

Wood

Coated wood surfaces, particularly around industrial plants, marine areas, and similar atmospheres, seem to be in constant need of repair. Wood is substantially different from the metals described earlier, as it is not a uniform or consistent surface. Coatings that are applied over wood fail primarily due to checking and cracking or chipping and blistering.

It should also be noted that coatings that are entirely satisfactory for metal surfaces may not be and generally are not practical for wood. Metal coatings initially may have good adhesion and appearance over wooden surfaces. However, because they are generally of high molecular weight, they do not penetrate the wood surface well. With the continual expansion and contraction of the wood, the coating tends to crack because of the different rate of expansion of the summer and winter grains.

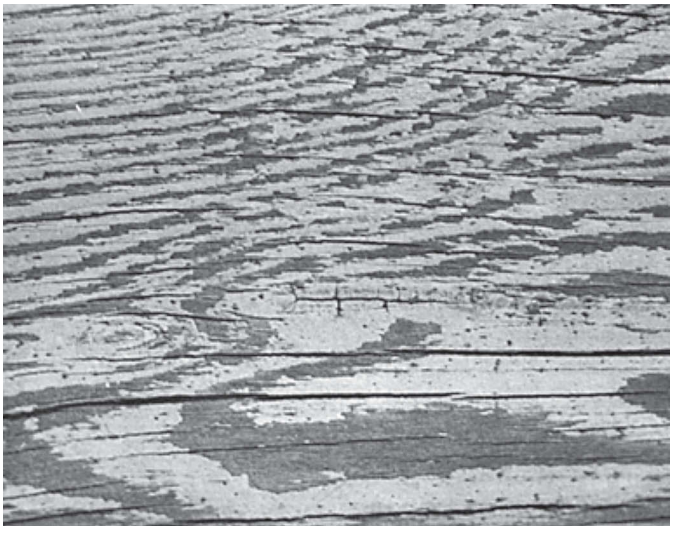


FIGURE 15.11: Coating failure over a flat grain wooden surface.

The coatings that prove the most satisfactory, as previously discussed, penetrate the wood, cure within the wood pores, and therefore tend to have strong adhesion to the wood and are thus able to move with the wood surface to a much greater degree than coatings that merely lie on the surface. There are many water-based coatings on the market that are recommended for wooden surfaces, many of which work well over a previously coated surface that has no cracking, peeling, or scaling on the bare wood. However, these materials do not penetrate. Thus, it is recommended that where such materials are used, a penetrating primer should be applied to the bare wooden surface prior to the application of

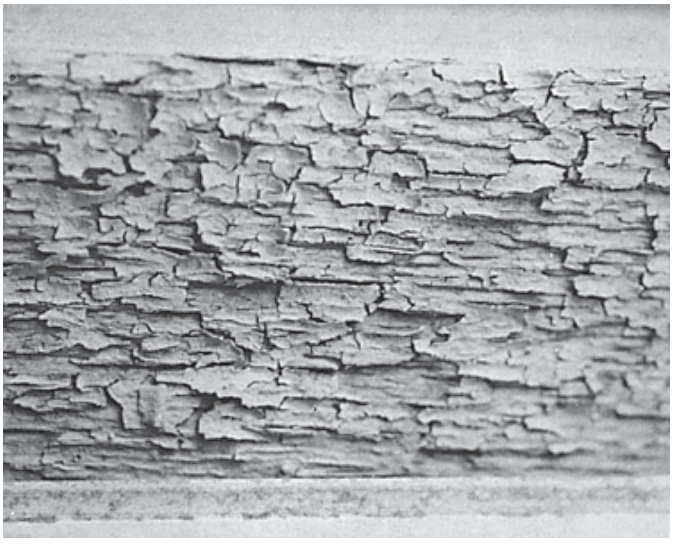


FIGURE 15.12: Coating failure over an edge grain wooden surface.

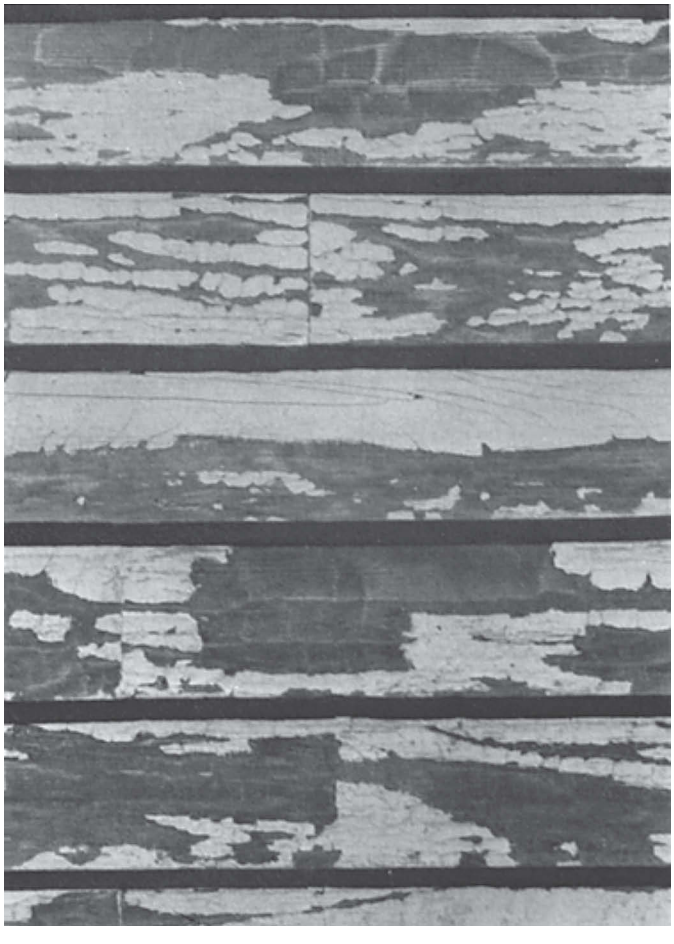


FIGURE 15.13: Chipped and scraped wooden surface prior to recoating.

water-based topcoats.

With wood surfaces, it is always beneficial to apply relatively thin coats and to maintain and repair the coating before cracking, peeling, blistering, or scaling damages the surface. The maintenance program should be scheduled so those surfaces are inspected at regular intervals, in order to renew the coating with an additional relatively thin coat prior to the exposure of any of the wood. This procedure is preferable to one that allows the wood to reach a cracking or scaling state, when it is difficult to properly prepare the surface.

Wooden surfaces (Figures 15.11 and 15.12) are extremely difficult to repair and recoat because of the problem of properly preparing the surface. It is not possible to abrasive blast such surfaces without damaging the soft grain area of the wood. Chipping and scraping is only partially successful, and even heating the painted surface in order to scrape the worn paint from the wood is a long, difficult, and costly job. Figure 15.13 shows a chipped and scaled wooden surface. While the chipping and scaling was done as thoroughly as possible, it can be readily seen that the life of any coating applied over such a surface is in jeopardy. Low pressure blasting with baking soda abrasive, either with or without water injection, is a very effective method of preparing painted wood surfaces for repainting.

Wooden surfaces are difficult to maintain. Where wood is exposed, the following general repair procedures are suggested.

1. Chip and scrape and hand or power-sand the areas where the coating is failing and the wood is exposed. It is essential to make certain that all loose coating has been removed. On the other hand, the surface should not be over sanded, as it is easy to cut deeply into the wood in the areas where the coating is removed. This is particularly true when using a power sander.
2. The unbroken surface of any remaining coating should be lightly sanded and all dirt and chalk removed. Low pressure baking soda blasting is effective at removing both failed coatings and oxidation residues from sound coatings.
3. Apply a proper penetrating primer to the surface, working it well into the wooden surface by brush.
4. Once the primer has thoroughly dried, apply a compatible topcoat over the surface. It is not recommended that heavy coats be applied, but that thin coats are used, and that these are applied at closer intervals for proper maintenance.

Concrete

The repair of concrete surfaces requires one of the most difficult coating repair procedures to be followed. The problems are those inherent in the coating of concrete, as described in Chapter 11. In addition, however, the repair of concrete coatings usually involves a number of contaminants that may react with or penetrate into the concrete surface. The problem is complicated because of the vast number of areas where concrete is used in the coated condition. Examples of such areas are floors (which are undoubtedly the most difficult areas for coating repair), walls, ceilings, concrete pump bases, drainage ditches, sumps, sewers, and other structures.

That the coating and maintenance of concrete surfaces is difficult is evidenced by the many different and complicated methods of treating concrete, particularly where corrosion and wear is a problem. Treatments consist of procedures ranging from relatively thin coatings to heavy mastics and resinous cements. The ultimate in concrete floor protection is the use of acid-proof brick and cements. Quarry tile and brick floors are common in most areas where concrete is most affected by the service (e.g., kitchens, food plants, areas of acid exposure, pump bases, etc.).

With all of the variables, including the normal variables of a concrete surface, it is little wonder that repair of coatings on concrete surfaces is such a chore. The repair of coatings on overhead areas and concrete walls is much less complicated and less difficult than the repair of coatings on floors. In overhead areas and sidewalls, there is much less chance of damage to the coating and therefore, a much greater possibility of an intact coated surface with only limited damaged areas.

Where the coating is intact, any surface contamination can be washed from the surface without penetration into the concrete itself.

In fact, the primary reason for coating concrete walls and similar surfaces is to prevent splash and spillage of chemicals or other contaminants from penetrating into the concrete. This is particularly true in nuclear power and chemical plants where any penetration of radioactive material would cause substantial problems. In sewer and wastewater treatment facilities, the primary purpose of the coating system is to prevent penetration of reactive acids into the underlying concrete.

The primary cause of coating failure on walls is dampness from an outside source; for example, a roof or a drain, or because the concrete is below ground level. Where the concrete is damp from an outside source and the coating is porous, the dampness within the concrete will dissolve cementitious salts, which will then be transferred to the surface as a white crystalline material. In so doing, the coating is pushed from the surface and damaged, usually to the point of requiring repair.

One of the first steps in the repair is to determine the source of moisture and to remove that source, if possible. If the source of moisture can be removed by waterproofing the opposite surface of the concrete, the damp concrete should then be allowed to dry prior to making the coating repair. In areas such as this, the efflorescence and the damaged coating must be thoroughly removed. This can be done by light abrasive blasting, power sanding, power washing, or by the use of other power tools to remove any soft concrete down to the hard, dark gray concrete base.

If the area is damaged sufficiently so that coating alone will not be practical, a resinous concrete surfacer is recommended for the area. This is usually preceded by a highly penetrating concrete primer to obtain the maximum penetration into the concrete surface and to bind the resinous surfacer strongly to the basic concrete. If the area can merely be recoated, a highly penetrating primer is also recommended to bind the coating to the surface as tightly as possible. With either of these procedures, concrete topcoats can then be applied.

Floors, as previously mentioned, are extremely difficult to repair. They are subject to water, chemicals, oils, and greases of all types. Not only are these materials spilled on the concrete surface, but also the surfaces are subject to wear by motorized equipment and foot traffic. The worn and damaged areas in the coating accumulate contamination, which is usually worn into the surface. Contaminants can consist of pure water, which tends to etch the concrete surface; carbonated water, which will also etch concrete; other acids, such as acetic acid; acid salts; alkalies; various dry chemicals, such as those used in the fertilizer industry; and oils and greases. Vegetable and animal oils and greases are particularly difficult in the food industry where these materials are commonly encountered.

On walls and ceilings, where the coating is intact and tightly adhering to the surface, and on other areas that are not subject to damage, there is little problem of repair since the contaminating materials can be washed from the coated surface. It is only in the damaged areas where repair problems exist.

The first step in any repair procedure is to thoroughly inspect the area, and determine the type of coating damage and the extent of the damage to the substrate. Sources and types of contamination should be identified, if possible. Following the inspection to determine the condition of the coating and substrate, it may be well to test the substrate areas to determine suitable surface preparation methods. A four-step procedure was developed by NACE Technical Committee T-6G-21. The testing of substrate areas is outlined as follows.

Testing of Substrate Areas

The following four-step procedure can be used to determine a suitable preparation method:

Step 1. Treat a small area [0.09–0.9 m2 ft2 (1–10 square feet)] with a 1:1 solution of 36% concentration of commercial muriatic acid in water. If acid bubbles and leaves a clean surface, this treatment may be used for cleaning. If there is no reaction, try Step 2.

Step 2. Scrub a similar small area with a 20% concentration of lye solution, rinse, and then treat as in Step 1. If the area bubbles and leaves a clean surface, this method may be used. If there is no reaction, try Step 3.

Safety Precaution: Workmen handling the lye solution, acid mixing, spreading and other operations must wear safety goggles, protective clothing, and rubber gloves and boots.

Step 3. Scrub a similar small area with a chlorinated solvent (trichlorethylene) to which has been added a strong compatible solvent. Do not let surface dry. As soon as thoroughly scrubbed, wash with clean water. This will remove both the solvent and the dissolved grease. Treat as in Step 1. If the area bubbles and leaves a clean surface, a high flash point solvent with low volatility [anything over 39 °C (100 °F) flash point] can be used for cleaning. If there is no reaction, try Step 4.

Safety Precaution: The high boiling solvents such as trichlorethylene and perchloroethylene should not be heated or evaporated with an open flame torch, but should be removed by the use of a high velocity circulating fan, or in the winter, with a salamander that has an outside fresh air inlet duct to prevent recirculation of the perchloroethylene fumes through the combustion chambers. Although perchloroethylene is not flammable, the fumes from the chlorinated solvents can decompose when heated to high temperature and emit toxic fumes of chlorides.

Perchloroethylene or trichlorethane to extract fats and oils from concrete is good from a fire safety standpoint. It is very important to remember when using perchloroethylene or a chlorinated solvent of this type that an abundance of air circulation (fresh air) is required. The threshold limit value of per chloroethylene is 100 ppm. Materials such as benzene or toluene should never be used to remove fats and oils because they are extremely volatile.

Step 4. Remove at least 1.6 mm (1/16 in) of surface using a chipping hammer, chisel or bush hammer. Treat as in Step 1. If acid bubbles, the entire surface may be prepared by mechanical means with acid etching. If there is no acid reaction, remove more concrete and repeat acid test to determine depth of contamination. Suggested methods of removal include: power tool grinding, scabbling or scarifying, dry abrasive blasting, water jetting and centrifugal blasting.

As a general rule, monolithic organic corrosion resistant floor surfacings and tank linings used to protect heavy-duty maintenance or immersion service require a stronger base than thin coatings. Weak concrete at the surface in contact with the topping or lining could result in failure of the bond by the following:

1. Shrinkage stresses formed during the hardening and curing of the resin corrosion-proof overlay.
2. Excessive stresses, generated by the differences in thermal contraction of the concrete and corrosion-proof overlay.[15]

Concrete Preparation. The shrinkage stresses mentioned earlier are common, and epoxy toppings and even simple epoxy coatings will often develop stresses sufficient to pull up sizable pieces of the surface concrete. This emphasizes the fact that the concrete over which concrete toppings and coatings are applied must be solid, hard, and with as high a tensile strength as possible. In many cases, where concrete surfaces have been exposed to chemicals of a number of types found in industry, or where concrete has been subject to sewage conditions, the concrete can have very poor or marginal strength.

Where sewage corrosion is a problem, concrete may have to be removed to a depth of 1.5 or 2 in (38 to 51 mm) to reach the solid gray concrete underneath the corrosion product. The same is true of a number of other chemicals, particularly sulfuric acid (H2SO4) or sulfates. Where conditions such as this exist, the concrete is usually sufficiently rough so that tensile testing is not practical and the concrete must be removed by blasting or by using concrete scarifying tools. Blasting of such concrete surfaces is the most practical way of getting down to solid gray concrete. The color gray must be emphasized since sulfates develop a yellowish-white corrosion product and, unless the concrete is removed below the color zone, the topping or cement used to build up the surface will not adhere properly. There is usually an obvious line of color demarcation between the corroded concrete and the solid gray concrete.

If the concrete has been saturated with oils and fats or petroleum products (and this is more common with floors than with other areas of concrete), the use of Elcometer, Hate, or Dyna Adhesion Testers is an aid in indicating the type of surface preparation necessary and whether or not it is necessary to completely remove the surface from the concrete floor. The adhesion test will usually identify inadequate cleaning of the surface, or whether or not the surface is sufficiently impregnated so that cleaning is impossible.

A practical method for determining the adhesion of a coating or the tensile strength of the concrete surface is shown in Appendix 15A. Any time that the floor is completely and deeply saturated with oil and grease, complete replacement of the top ¼ to 1 in of concrete may be less expensive than applying the floor surfacing or coating and having it blister or peel from the surface after a short period of use.

In places where the concrete has been severely eroded due to chemical attack or physical abuse, the use of organic floor toppings and surfacers is recommended as the best method of repair. Where concrete is seriously corroded and an inch or more must be replaced, concrete may be used to build up such areas. The floor toppings and surfacings can then be applied over this new surface. Generally, however, where a damaged area is 1/8 to ¼ or even 1.2 in (30 mm) in depth, the organic (epoxy) floor toppings provide excellent adhesion to the tight concrete and provide a good abrasion and chemical resistant surface.

Blasting. Abrasive blasting is a good method of preparing concrete surfaces. It will not only remove the old coating which may be loose on the surface, but it will also, if properly used, provide a good surface for the repair coating. However, there are some precautions to use in connection with abrasive blasting of concrete. Concrete is relatively soft, so that, if heavily blasted, the surface can be etched away for a considerable depth before the operator is aware of it. Thus, the blast nozzle must be kept at a distance from the concrete surface and a brushoff blast procedure used. It is also recommended that a fine abrasive be used to prevent too great an etch of the surface.

Floors that have a sidewalk finish (i.e., where a dense cement sand topping is applied over the basic concrete floor surface) are much easier to prepare by blasting than where the concrete has been surfaced without the topping. In the latter case, once the smooth-troweled surface has been broken, an abrasive blast will etch into the underlying area quite rapidly, causing pits, which then have to be filled with a surfacer rather than with the coating alone.

Wet abrasive blasting may also be used and is helpful in removing dust and other contamination. However, the same problem exists with wet abrasive blasting as with dry abrasive blasting. Fine abrasive should be used and attention paid to the blasting process so that the concrete etch is not too deep. High-pressure water jetting without abrasive can also be used. This is particularly effective where the concrete has not been badly corroded or where there are considerable areas of loose coating to be removed. Newer water jetting equipment, which include spinning heads, resonating chambers, and other tools, can blast down through concrete corrosion to the solid gray concrete surface in the same manner as where an abrasive is used. A secondary advantage of water jetting is the removal of soluble contaminants, which is impossible with dry abrasive blasting.

Acid Etching. Acid etching can be used in connection with repair of coatings on concrete. It will help remove a number of chemical contaminants and will also provide a mild etch to the surface where the coating is broken or removed. Excessive etching should not be used, as it may react to some depth, causing loose aggregate on the concrete surface. This would then have to be removed before a coating or a topping could be applied. Certain acids can also damage galvanized ductwork so it is important to use the proper acid. The procedure for acid etching and the precautions for its use are outlined in Chapter 9 on "Surface Preparation."

Power Tools. Power tools for cleaning the surface of concrete should be used with caution, unless the surface of the concrete is to be scarified and removed to some depth. Power wire brushing or power sanding can cut the surface of the concrete sufficiently so that usual concrete coatings will not provide a smooth surface. Heavily etched or cut surfaces would then require troweled concrete topping of the epoxy type to provide a smooth surface for coating.

Repair of Coatings on Concrete. The coating of concrete surfaces will never be eliminated because of the various types of service to which the concrete surface is subjected, and the many variables inherent in the concrete surface. Because concrete is not a uniform material and because of its various uses, each repair situation is unique and must be carefully studied in order to reach a satisfactory and long-lasting solution. In spite of this, there are some general recommendations, as follows, that can be made for the repair of coatings on concrete.

1. Remove all of the damaged coating, or coating with loose adhesion, back to a point where the adhesion is consistent and satisfactory. Feather the edge of the remaining solid coating.
2. Remove the entire concrete corrosion products, such as the white carbonate deposit on the surface, the whitish or yellow corrosion product of sulfates, or any loose or projecting aggregate from the surface. If chemical action has occurred on the concrete, remove all of the softened surface back to clean, gray concrete. This may require chipping, scraping, water jetting, or abrasive blasting the surface. If the surface is saturated with oil or grease, use a strong solvent combined with an emulsifying agent. Remove all contamination. Wash and dry.
3. If the coating has failed because of water in the concrete, the surface should be thoroughly dried. This can be done by a blast from an air fan moving across the surface, or the concrete can actually be heated using a warm air source. Confined spaces can be dried very efficiently with dehumidification equipment. At this point, it should be determined whether or not it is possible to eliminate the source of moisture or water within the concrete. If this can be done, it makes the repair of the coating much more permanent and satisfactory.
4. If the source of moisture cannot be removed, the surface of the concrete should be dried and a highly penetrating, highly alkali-resistant primer applied. There are several of these products on the market. The primer should be applied by brush or roller and

should be applied rather heavily for penetration. However, any excess should be removed from the surface so that no heavy areas or puddles are formed. Penetrating primers of the type described are generally based on liquid epoxy resins of a low viscosity. They are internally reacted and may be either amine or polyamide-cured.

5. If the concrete is subject to severe abrasion or chemical use, even though it may not contain moisture, the above penetrating primer is also recommended.
6. If the concrete has contained contaminants and the surface is clean and dry, use the penetrating epoxy primer to prime and seal the surface.
7. Should the concrete be deeply eroded or corroded, leaving a rough surface, the application of a heavy surfacer over the penetrating primer is recommended. The surfacer must be compatible with the primer in every way and generally will be an epoxy-type product.
8. Once the concrete surface has been primed and is smooth, compatible topcoats may be applied overall.

Plaster Repair. Plaster or stucco is generally quite similar to concrete, particularly where the plaster is a cement plaster. Where such surfaces have been damaged or corroded, a procedure similar to that recommended for concrete is suggested. If, however, these surfaces are only for light service and have been coated with water-based or emulsion-type products (e.g., vinyl acetate or a vinyl acrylic), the following procedure is recommended.

1. Thoroughly wash the surface free of all dirt, grime, grease, or other contaminant. This can be done with clean water or a surfactant type cleaner, followed by clean water.
2. Once the surface is cleaned and dried, reapply the water or emulsion-type coatings.

Cracking. One of the serious problems concerning concrete is its tendency to crack. These cracks may be very fine surface shrinkage cracks or substantial working cracks. The fine cracks, since they are not working cracks, are usually covered in any repair by the repair coating. However, substantial working cracks of any type must be repaired prior to applying the repair coating. The general procedure recommended is to "V" out the crack using a chisel or similar tool. Once this has been done, the crack should then be filled with an epoxy or similar concrete surfacer and troweled smooth and level with the surface. Use of a bond breaker type patch is recommended in conjunction with the epoxy surfacer to prevent further cracking along the line of the patch. A penetrating primer is highly recommended prior to the application of the surfacer in order to penetrate the crack as deeply as possible.

Repair of Failures

Earlier in the chapter, several types of failure were listed, along with ASTM specifications for their evaluation. However, because of the importance of the proper repair of such failures, more detailed information is included in the following sections, both as to the cause of failure and the method of repair. This information has also been outlined in a paper entitled, "Practical Aspects of Coating Repair."[16]

Blistering

Blistering of an original coating can cause substantial difficulties in coating repair. There are three types of blisters.

1. The area underneath the blisters is dry and the blister itself is raised by gas. Such blisters can be caused by trapped solvents or, where immersed, by the formation of hydrogen gas in areas underneath the coating.
2. The blisters are filled with liquid, and there is usually little or no corrosion underneath the blister. While the surface of the steel is wet and the blister filled with a watery liquid, the steel remains bright and un-corroded. This is because water will pass through a semipermeable membrane such as the coating to a much greater and faster degree than oxygen. Until oxygen passes through the coating and into the water area, no corrosion can occur. Often, the primer for the coating is also inhibited, and the inhibiting agent in the coating tends to prevent corrosion under the wet blister.
3. There is both liquid and corrosion underneath the blisters. Usually, such blisters have been in place for some time and oxygen has gradually diffused through the coating into the liquid, creating the possibility of local corrosion cells underneath the blister.

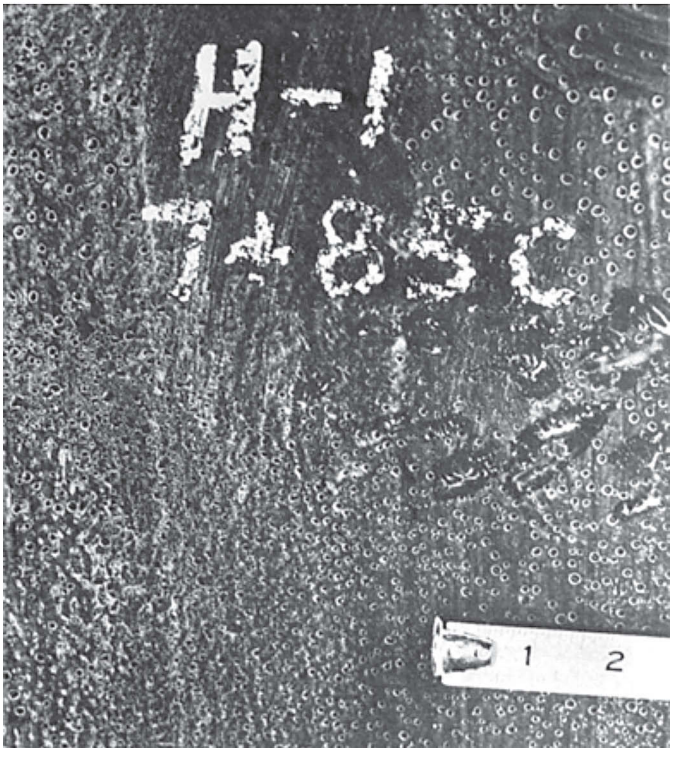


FIGURE 15.14: Fine blistering of epoxy coal tar coating after short exposure to potable water (ASTM Rating 6, Dense).

Regardless of the type of blister, the repair of these areas is difficult at best. If the blistering is widespread (Figure 15.14), as may be the case on the underwater hull area of ships, in ship ballast tanks, in water storage tanks, and in other similar areas, the repair of coatings is extremely difficult because of the numerous breaks in the coating extending over a large area.

Any repair on a blistered coating requires removal of the blisters. This can be done by scraping, in order to remove the raised areas of the coating as well as any coating around the blistered area that may be loose or have poor adhesion. Blisters often are removed by abrasive blasting, sweeping the surface to remove the blisters, and then feathering the edge of the coating around the blistered opening as previously described. Star cracks between the blister areas due to the use of heavy abrasive particles may be

new focal points for corrosion, even though the repair coating is applied overall.

It has often been observed that once a generally blistered surface, even with an ASTM rating of "few," is repaired and replaced in service, the blistering is rapidly renewed, usually starting at the edge of the old blisters and moving out onto the previous coating. This occurs even if the repair coating is tightly adherent to the steel in the area of the previous blisters. With the base coat having questionable adhesion, blistering will continue under the old film, even though the new coating may adhere tightly both to the steel and to the old coating. Thus, wherever there is general blistering of a coating, it is usually the best procedure to completely renew the coating (i.e., remove all of the old coating from the surface and begin fresh with a new primer and complete new body and topcoats) instead of trying to repair it.

Isolated blistering areas, even though they may be reasonably extensive, can be repaired. In this case, it is necessary to remove all of the blistered area by blasting or other mechanical means back to where the coating has strong adhesion. The edge of the coating should be feathered mechanically. Following this, a primer compatible with both the steel and the previous coating can be applied, preferably by brush in order to work it into both the steel and the feathered edge area. Topcoats can then be applied as indicated by the coating service. Topcoats usually would be applied over the entire surface, unless the blistered areas were entirely local and covered only a small percentage of the coated surface.

Recoating

The recoating of previously coated undamaged surfaces can also create problems. In the case of a coating where the resinous materials are permanently soluble in coating solvents (e.g., vinyls, chlorinated rubbers, and solvent-based acrylics), the solvents in the added coat will penetrate into the previous coatings, swelling them slightly. Even though no actual coating disruption occurs and the application of the topcoat looks smooth and adhesive, if the coating is then immersed or heated (such as by the sun), blistering may occur under the original coating. This is due to the softening of the original coating by the repair coat solvents, by the retention of these solvents in the old coating, or due to the moisture vapor transferring more easily through the coating and down into the previous coats when it retains solvents.

The combination of the swelling of the original coating, the absorption of the solvents, and the absorption of moisture vapor can cause a release of adhesion resulting in blistering. This type of coating difficulty is not as frequent where highly cross-linked and insoluble coatings (e.g., phenolics, epoxy phenolics, epoxy polyamides, and coal tar epoxies) are being used. However, even though these materials are generally insoluble in their previous solvents, some solvent penetration may occur with subsequent release of adhesion when immersion and absorption of water vapor also occur. The solution in any of these cases is to repair the coating as previously indicated, and then make certain that the repair coating is thoroughly dry or cured and that the undercoating is also thoroughly free of solvents prior to putting the coating in service. Use the maximum drying time possible whenever a repaired coating is to be immersed.

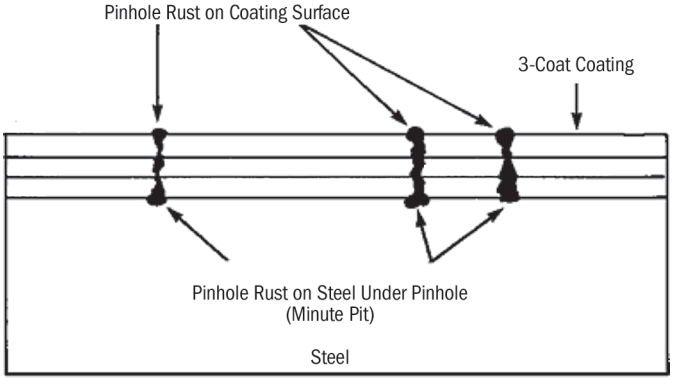


FIGURE 15.15: Pinpoint rusting of a coating.

Pinpoint Rusting

Pinpoint rusting of coatings is a common type of failure. It occurs where there are pinholes in the coating, where there are thin areas in the coating, or where the coating has eroded to the point where pinpoint rusting occurs. Pinholes are usually defects in the original coating. If repair is started soon enough, pinpoint rusting can be limited to isolated areas and therefore successfully and easily repaired.

Pinpoint rusting of coatings is caused by the penetration of moisture and oxygen into pinholes or minute cracks or checks in the coating, so that a minute spot of rust is started on the steel beneath the coating (Figure 15.15). The corrosion product in this area tends to expand; the coating being pushed up into a pinpoint at the point of corrosion. The expansion of the coating at this point causes cracking, and the rust comes through to the surface. Each of the pinpoints of rust is a true corrosion cell, and if left unrepaired or unattended, the coating will tend to undercut, with consequent general rusting of the surface in these areas. Thus, the best repair procedure is to remove all of the coating in the pinpoint rust areas and out beyond the area to sound coating. This procedure is similar to that recommended for isolated blistering, with the coating being blasted free from the surface and the edge feathered out to where the coating is sound.

Repair by mechanically sanding the surface and removing the rust pinpoints from the surface is only a stop-gap procedure. However, it can be reasonably successful in areas of light corrosion and where subsequent coats can be applied when the surface is warm and dry.

Under these conditions, it is necessary to apply a highly penetrating primer over the area; that is, one that will effectively wet the pinpoint rusted areas and penetrate down to the metal, followed by topcoats that have a low moisture vapor transfer rate and adequate thickness to thoroughly seal these areas away from both moisture and oxygen. This latter method should not be used where the coating is subject to severe service such as a marine environment, a chemical environment, or an environment where there is consistent high humidity or condensation.

Delamination

Another type of coating failure that poses problems from a repair standpoint is coating delamination between coats. A problem exists because the coating may look perfectly smooth and appear to have good adhesion; however, once the interface between the coats is penetrated by moisture or moisture vapor, the topcoat releases from the undercoat and the entire topcoat may be released in large areas. Inter-coat blistering is one indication of this type of delamination.

Delamination most often occurs in coatings that are highly cross-linked and where the cure reaction is either from a catalyst or a reac-

tive curing agent, or where the coating may react with moisture or oxygen from the air in order to become insoluble. It is less prevalent where the coatings are permanently soluble in their own solvents (e.g., vinyls or chlorinated rubbers). In the case of the insoluble types (e.g., epoxies, phenolics, coal tar epoxies, etc.), inter-coat delamination can occur from the condensation of moisture on the surface, rain, or, in the case of coal tar epoxies (Figure 15.16), the coating having been subject to sunlight for more than short periods of time between coats. The difficulty occurs where the coating that has delaminated comes off from the previous surface, leaving the original coating thin in that area and therefore, subject to much more rapid corrosion than would have been the case with a full-thickness coating.

Repair consists of the removal of all of the delaminated coats back to a point where there is sound adhesion between all coats. If corrosion has started in the thin coating area, the best procedure is to remove all of the thin coating down to bright metal and carry the surface preparation out to where the full-thickness coating is tightly adherent to the steel. If an overall coat is to be applied, the surface of the epoxy or other insoluble coating must be roughened by brush blasting. Care to prevent any star cracking in the coating is essential for a proper repair job. Once the surface preparation is complete, the repair coating may be applied as previously described under "Blistering," or under "Film Corrosion."

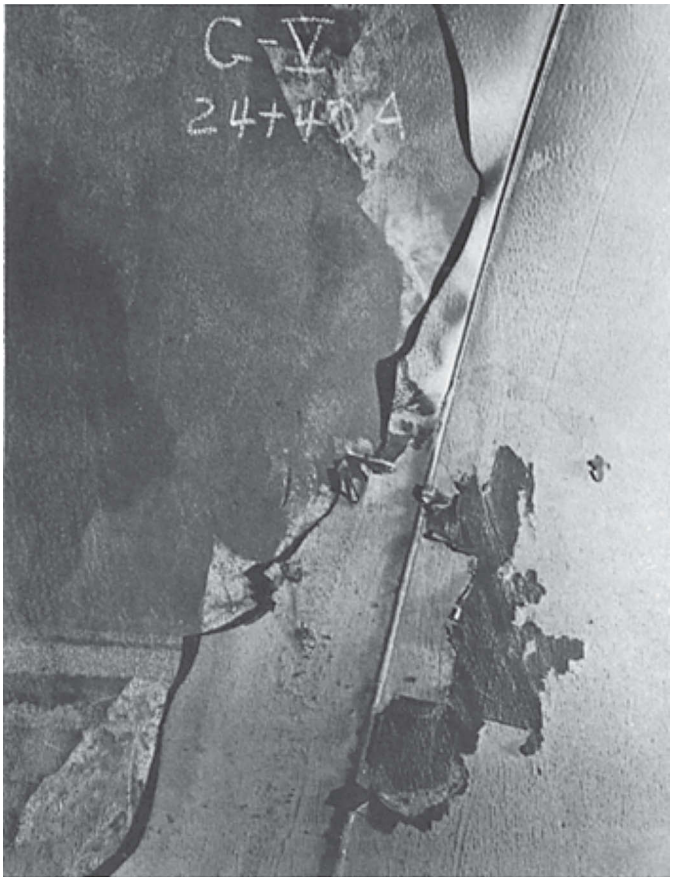


FIGURE 15.16: Delamination of a coal tar epoxy coating.

Chalking

It has often been said that chalking is the most preferable type of coating failure since it results in the coating gradually decreasing in thickness to a point where the primer may show through or where pinpoint rusting may begin. Nevertheless, there are problems in the recoating of chalked surfaces, particularly when dealing with epoxies, coal tar epoxies, and similar insoluble coatings where chalking has been general yet substantial.

A chalked surface is one where the resins in the coating have been disintegrated by the actinic rays of the sun and other weather phenomena, releasing the pigment to remain on the surface as a chalk or soft powdery substance that, of course, must be removed. In the case of epoxies and other insoluble materials, the solid surface must also be abraded for proper adhesion of the repair coats. Removal of the chalk can be done by brush blasting the surface using extremely fine abrasive and holding the gun some distance from and at an oblique angle to the surface. This not only removes the chalk, but also will lightly abrade the surface for adhesion of the repair coat. Chalk can also be removed by high-pressure water, preferably accompanied by light abrasion or scrubbing.

Care in surface preparation is essential so as not to star crack the original coating and cause areas of incipient future failure. It is preferable where a surface is simply chalked to apply the first repair coat by brush. If this is not possible, as is ordinarily the case due to the magnitude of the surface area, the coating to be applied over the chalked area should be strongly penetrating and have a high wetting potential for the chalked surface. If this is not the case, any area where the chalk is not removed will be an area where the repair coat delaminates from the original coating, since it merely lies on top of the previous chalk without penetrating.

Epoxies and coal tar epoxies are undoubtedly the most difficult to recoat where the surface is chalked. Vinyls and chlorinated rubbers are somewhat less susceptible to delamination problems because of the penetrating character of the solvents used. Water-based coatings, being highly thixotropic, wet chalked surfaces poorly, and all chalk must be removed before recoating.

Repair of Coatings

Coal Tar Epoxies

It must be assumed that any coal tar epoxies that have been in use for a period of time will have an insoluble and impenetrable surface, and that any additional coating applied without careful surface preparation will tend to delaminate. This is particularly true where the coal tar epoxy is used for immersion. The surface of a coal tar epoxy must be roughened sufficiently, preferably by brush blast cleaning (NACE No. 4/SSPC-SP 7/ISO Sa 1) to give some mechanical adhesion to the following repair coat. For best results, especially for immersion, it is suggested that a thoroughly compatible epoxy primer be used over the previous coal tar epoxy surface to provide a better bond for the coal tar epoxy repair materials. The epoxy primer is good insurance for a sound coal tar epoxy repair.

Inorganic Coatings

Repair procedures for inorganic coatings are different from those previously outlined for organic coatings. When repairing inorganic coatings, only a single coat 50 to 100 µm, or 2 to 4 mils in thickness, is involved. The failure of inorganic coatings is primarily by pinpoint rust forming after a long period of life or use (Figure 15.17). The same type of failure is true of all zinc coatings, including galvanizing (Figure 15.18).

The failure continues slowly, over a long period of time, until the entire surface is covered with pinpoint rust. With IOZ coatings, this type of failure occurs in thin areas. It has been observed a number of times that with a single coat of IOZ, the failure takes place in between the spray passes. In other words, where the spray is overlapped, the coating is slightly thicker. These areas will remain good,

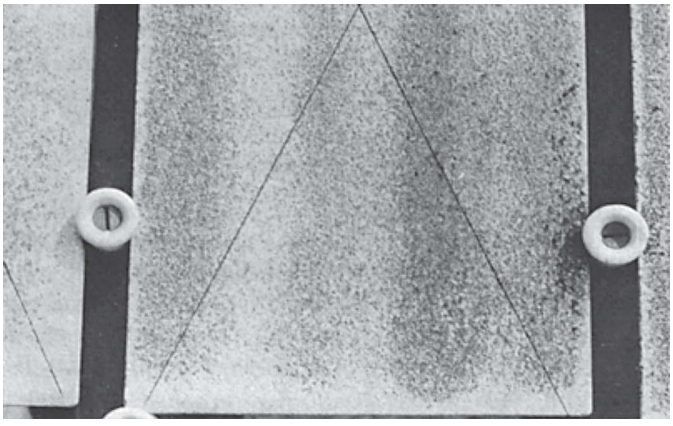


FIGURE 15.17: Pinpoint rusting of an IOZ coating.

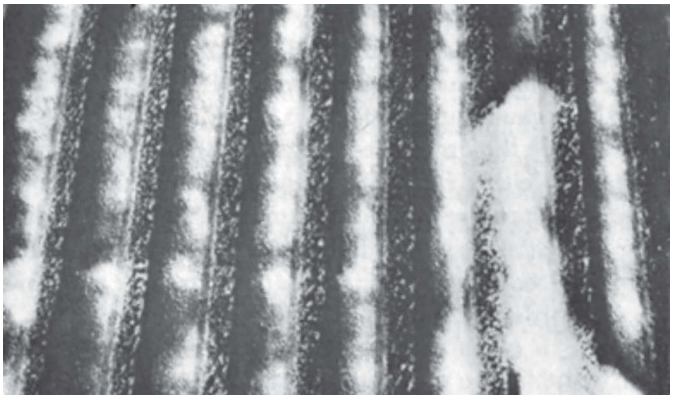


FIGURE 15.18: Rusting and failure of a corrugated galvanized surface.

while the thinner areas between the overlaps will show pinpoint rusting.

During the aging of the IOZ, there does not appear to be any loss in coating thickness. Usually, there is considerable zinc left in the coatings even though pinpoint rust is starting. Again, this is true for a pure zinc surface like galvanizing. Organic zinc coatings also tend to fail in a similar way when they are not topcoated. From the appearance of the failure pattern, the zinc reaction products that continue to form over many years tend to become denser and seal the inorganic surface. This causes it to become inert and surrounds the zinc particles with the zinc oxide and carbonate reaction products to such an extent that they no longer tend to ionize and provide zinc ions in the area. The inert reaction products and the dense surface do not allow the repair coat of IOZ to adhere satisfactorily to an old IOZ or zinc surface. In order to obtain satisfactory adhesion, it is necessary to break up the surface of the original zinc coating, opening up and exposing the zinc that is present, to allow the repair coating to react with the zinc in the existing coating in the same way it reacts with the zinc particles in the new inorganic vehicle.

Sweep blasting is the preferred method of preparing the surface. Using this method, the rust stain is removed, any major failure area can be removed during the blasting process, and the sweep blasting will break up the surface of the existing IOZ or galvanizing and allow the adhesion of the following coat. The sweep blasting also provides tooth (profile) for the repair coating, in addition to opening up the zinc for reaction with a new vehicle.

For small areas of failure, needle gunning of the IOZ surface can also be done. A sharp set of needles should be used that will cut the surface, but will not gouge or polish it. Once the surface of the IOZ has been prepared, the repair coat of IOZ, either water- or solvent-based, can be applied in a normal fashion. It is important to remember that IOZs require a 1 to 3-mil anchor profile for proper adhesion.

Overcoated Inorganic Zinc

The repair of IOZ or galvanized surfaces that have been overcoated poses another problem. Most of the failure is due to impact or abrasion, and such areas are usually relatively small in relation to the overall surface. Ship hulls, barges, or similar transportation equipment have the most extensive areas that might require this kind of repair.

The major problem is the two different types of surface over which the repair coating must be applied (i.e., the inorganic base coat where the abrasion may have gone down to steel and the organic topcoat). The primary problem is the incompatibility of the inorganic coating with the organic topcoat. Satisfactory adhesion is not obtained when IOZ is applied over an organic surface.

The general surface preparation for repair of overcoated IOZ surfaces is similar to that already described for the organic coatings, that is, abrading the corroded area (either by brush blasting or power sanding), feathering the edge of the organic coating, and lightly roughening the surface of the solid organic coating to obtain a good bond of the repair coating. In this case, however, in order to maintain the zinc undercoat, it is necessary to use a compatible organic zinc-rich coating, which is applied to the corroded area, the feathered area, and to some extent out over the solid organic coating. The organic zinc-rich repair coating is required to obtain adequate adhesion to all surfaces—steel, IOZ coating, and the organic topcoat. Once this is applied, the organic topcoats can be applied to complete the repair. While this type of repair may not be as effective as the original IOZ base coat topcoated with the organic, it has been used in many instances, particularly in the marine field, with very good results.

There is one type of failure of overcoated zinc coatings that is as dramatic as it is catastrophic. It occurs in damp areas of high humidity and condensation and has been noted in chemical plants, paper mills, and particularly, in marine areas. In this case, voluminous white zinc salts are formed under the topcoat, pushing them away from the surface with the appearance of blistering. In some cases, the white zinc salts will penetrate the topcoat and form on the surface. This type of failure occurs where a thin or very porous topcoat is applied over the zinc coating. Moisture penetrates to the zinc coating and accumulates there as a result of the dampness and high humidity. Zinc hydroxide [$Zn(OH)_2$] and ZnO are formed (zinc oxychloride [$ZnCl_2$] may be formed in a marine atmosphere), creating a strong physical pressure under the topcoat and forcing it off from the surface. The problem is that the topcoat allows the moisture to penetrate and accumulate in the zinc coating. Once the zinc salts are formed, they tend to form at an ever-increasing rate, thus making for rapid coating failure.

Repair of such a failure is difficult. All of the topcoat in the affected area must be removed, as well as all of the underlying zinc coating. If the failure is general, full coating renewal is required. If the failure is localized, these areas can be removed and repaired as previously indicated.

The solution to this problem is to make sure that the IOZ coating is thoroughly cured and to apply topcoats that have a very low moisture vapor transfer rate. It is essential that the topcoats be applied in full thickness. Little failure of this type has ever been experienced where full-thickness, resistant topcoats have been applied.

Linings

The repair of lining materials is much more critical than the repair of exterior coatings. In order to be effective, the repair work must be the equivalent of the original lining material to both protect the substrate and minimize the contamination of the contained liquid. While thin coatings are also used as lining materials, such as linings for water tanks, the majority of lining materials is usually somewhat heavier than exterior coatings.

The original application of a lining material is usually more carefully done than that of an exterior coating, and failure of reparable linings is usually in relatively small, isolated areas. Failed areas may be due to physical damage or because of an isolated spot of poor adhesion causing blisters. An overall general failure of a lining in any container indicates that there is a basic problem with the coating material or its original application, and that the entire lining material should be removed. In this case, the repair actually consists of a completely new lining application. Only isolated spots can really be repaired.

The whole concept of repairing a lining is to duplicate the original lining work and to obtain equivalent resistance from the repaired material. The actual repair procedure should be to remove all of the corrosion products from the repair area, removing also any damaged lining out to where the original lining material has proper adhesion to the substrate. The edge surrounding the repair area should then be feathered to a thin film having an approximately 2-in feathered edge, while thicker coatings may be feathered to a width of from 4 to 6 in (102 to 152 mm). The surface profile must be sufficient to allow proper adhesion.

All of the difficulties that have been previously described for the repair of coatings are inherent in any lining repair. Star cracking of the original coating must be prevented. If blasting is used to make the surface preparation repair, fine abrasive should be used and every care should be taken to protect the surrounding lining from any abrasion by whatever abrasive may be used. Care must also be taken in the bottom of the container to prevent penetration of the lining by persons walking on any loose abrasive that might be on the surface.

In repairing tank linings, vacuum blast equipment provides a satisfactory method of surface preparation. The reclamation of the abrasive by the vacuum ensures that damage to the surrounding lining is kept to a minimum. Power sanders and grinders may also be used to repair small breaks in the coating. Where this type of power equipment is used, care must be taken to prevent damage to the surrounding lining, and yet the corroded or damaged area must be ground sufficiently to remove all corrosion products. Power sanders or grinders may also be used to feather the edge of the coating around any breaks where repair is necessary.

In the repair of linings, the original number of coats should be applied during the repair procedure. In small areas, brushing of the coating may be practical. In more extensive areas, spraying is suggested, with the exception that the primer should be applied by brush, if possible, in order to make sure that the coating properly wets the repaired surface. The repair material should be applied at the same thickness as the original coating, and it should be carried from the steel surface or substrate out over the feathered edge of the coating and on to a lightly abraded area beyond the feathered edge. It is usually not necessary or advisable to carry the topcoats out over the original coating if the remainder of the original coating is undamaged.

Once all coats have been applied to the proper thickness, curing of lining materials, particularly repaired areas, is extremely critical, and in almost all cases it is recommended that force drying or force curing is used. This essentially is the heating of the newly coated surface in order to thoroughly cross-link the coating to the same degree as the original coating or, in the case of thermoplastic lining, to remove the solvents from the newly repaired area so that there is not more solvent remaining in the repair than in the original coating. This cannot be overemphasized, since the majority of failures after repair in a lining are due to poor curing or poor drying of the repair coating.

The equipment that may be used for force drying or curing internal linings has been outlined in NACE RP018417 as follows.

2.3.1 Hot Air Heaters

2.3.1.1 Direct fired heaters using LPG or natural gas produce 700°F (370°C) air temperature and metal temperatures up to 400°F (200°C).

2.3.1.2 Indirect fired heaters using LPG, natural gas or other liquid fuels will produce approximately 110°F (60°C) air temperature rise and metal temperatures up to 175°F (80°C) when outside temperatures are 70°F (20°C) or above.

2.3.1.3 Heaters using electrical heated elements in the form of "heat guns" will produce air temperatures to 1,000 °F (540°C) and are most suitable for small repairs.

2.3.1.4 Do not use air heaters such as direct-fired oil heaters that produce gases or particles that contaminate. Properly designed and adjusted natural gas or LPG heaters do not contaminate other than by condensation, discussed in Paragraph 2.3.1.5.

2.3.1.5 LPG or natural gas direct-fired heaters may cause contamination in the form of condensation; however, a quick blush of con densation that evaporates is not necessarily damaging. The gases from direct-fired gas heaters have a dew point of approxi mately 180°F (80°C), and a cold substrate may cause condensation. Any observation of red rust during or after a preheating period will require repeat of surface preparation.

2.3.2 Infrared source of heat lamps may be used for curing small areas. These heater units only provide enough heat to cure baked type coatings on small spots.

2.3.3 Ultraviolet source may be a sun lamp or suitable UV source that may be purchased for curing coatings which are formulated for ultraviolet cure.

2.3.4 Dehumidification equipment may be used by itself or in conjunction with heating equipment to keep the air in a space at a dew point of at least 5°F (3°C) below the substrate temperature to prevent condensation.[9]

Tank Cleaning

Any lining that is installed on the interior of a container will need some type of general cleaning prior to any repair procedures. Many contained materials will leave little contamination on the surface, as is the case with volatile petroleum products, solvents, and similar materials. On the other hand, a tank for the storage of vegetable oil will leave an oily, greasy surface. Food oil tanks leave a heavy oily de- posit on the surface. Wine, beer, and similar food products often leave a precipitated deposit on the lining that is also quite difficult to remove.

Thus, the cleaning procedure for every type of contained product is somewhat different, and it must be varied by the type of lining that is in the container. There are some linings that can be cleaned by the use of steam; others require ambient temperature cleaning in order to not damage the lining. In any event, the cleaning solution and the procedure for cleaning the tank must be such that it will not damage the lining or the substrate where it might be exposed. It must also have the capability of removing

all of the contaminants from the surface of the coating. Special attention, of course, should be given to those areas where the coating has been broken, damaged, or has failed in order to ensure that these areas are as clean as possible prior to attempting any repair procedure.

While repairing a lining, it must be remembered that the lining is a valuable part of the tank itself, and any additional damage to the lining can be extremely costly. The cleaning solution used in the tank should not have any effect on the substrate. For instance, it would be disastrous if a highly alkaline cleaning solution were used on the material. Neither should SS be subject to chloride-bearing cleaning compounds. Detergents and similar materials may be used, as long as it is possible to thoroughly remove them from the surface and they do not have any effect on the substrate. Solvents may be used as long as they have no effect on the lining, and as long as the proper safety precautions are used to eliminate the possibility of physical harm to the workers from toxic exposure or fire.

It also must be remembered as a general rule of thumb, that 1% solvent vapor in air is a maximum, from the lower explosive limit standpoint. While most solvents have a somewhat higher lower explosive limit, there are a few that are borderline. The air within the tank should be kept below the 1% limit under all conditions. Reference to Chapter 16 is suggested wherever solvents are involved. Any en- closed area is dangerous and all safety precautions should be used.

The general surface preparation requirements for various surfaces have been previously covered. However, it is important to mention that where linings are concerned and where immersion is a condition of service, the very best possible surface preparation must be used for all lining materials. There is no substitute for a perfectly clean surface over which to apply a lining material. In fact, it is essential if future failure is to be avoided. This applies whether the substrate is SS, cast iron, aluminum, zinc, or concrete.

Lining Thickness

As outlined by NACE RP0184, there are three types of lining materials in terms of thickness:

(1) Thin—those with less than 10 mils of thickness
(2) Thick—those which range from 10 to 29 mils in thickness
(3) Thick film—those that are over 29 mils in thickness.[17]

These categories reflect the linings that are commonly used on the interior of all types of containers. The thin linings (i.e., less than 10 mils) can be composed of almost any type of coating previously described. IOZ coatings with a thickness of 3 to 4 mils are commonly used as a lining for many solvent, lube oil, and petroleum storage tanks. Vinyl linings in this thickness range have commonly been used for water and brine tanks. Epoxy coatings in this range are used as linings for various mild chemical tanks where they are resistant to the contained product. Baked phenolic linings and baked epoxy phenolic linings are used for any number of food tanks including beer, wine, and liquid sugar.

Intermediate thickness lining materials (i.e., those from 10 to 29 mils) are often used to upgrade the thinner lining materials by providing additional thickness. These materials are usually the higher solids, reactive type of vehicles, such as epoxies, coal tar epoxies, some urethanes, and some thinner, rubber type coatings. Many are used for lining water tanks and pipe, as well as for lining water process and wastewater processing equipment. They may be used for the lining of tanks, tank cars, or ships for specific products.

The heavy thick film linings (i.e., those from 30 mils up) are the heavy-duty lining materials used in many areas of the chemical and mining industries, refining and chemical processing, marine and water reclamation plants, and piping systems.

Types of Linings

Sheet Linings. One of the lining materials that is not included in the NACE RP0184 on linings is the vinyl sheet lining material used to line concrete pipe structures in sewage treatment plants and outfall piping. It is also used as a lining for many chemical tanks, such as ferric chloride tanks, as well as chemical leaching tanks in the mining industry. These areas are subject to severe corrosion, and the lining may be applied to either steel or concrete structures.

Repair of the lining for any of these services is much the same. Small damaged areas may be repaired by using a patch of the original vinyl lining material over the break in the lining. This is attached to the previous lining with adhesive, followed by heat welding a weld strip over all edges of the patch. For larger areas, the damaged lining is removed, usually in a rectangular pattern. The repair sheet lining is then cut to fit the rectangular area, and the new material held in place with adhesive, or, under certain circumstances, SS pins and washers have been used to mechanically hold the lining in place. These are driven into the surface using explosive charges. (This procedure is only applicable to concrete repair.)

Once the new lining is in place in the repair area, the joint between the new and the old lining is heat welded, using a welding strip over the joint between the two surfaces. The welding strip is usually ¾ to 1 in in width and is actually heat welded to the two surfaces. In this case, hot air guns are used to soften the two surfaces (i.e., the sheet lining, and the weld strip) to a semiliquid state where they fuse together. Hot air welding and sheet lining repairs are not simple tasks. New mastic epoxy and epoxy/polyurethane adhesives now allow for repair of vinyl and polyethylene sheet linings directly to concrete without the heat welding process. Lining manufacturer instructions should be carefully followed if a satisfactory repair is to be made. Such repair, if properly done, can be considered permanent.

Rubber Linings. Rubber linings are used in tanks, pipe, and various production or process vessels and special structures such as flue gas scrubbers. Like the sheet vinyl lining, they are used for difficult chemicals such as acid solutions or where abrasion and corrosion are combined. If a problem is going to occur with a rubber lining, generally it will happen within the first two or three months after being put into service, regardless of whether the problem is due to poor work methods or misapplication of the rubber lining of choice.

Repair of rubber linings is a very critical process and is dealt with in detail in Chapter 20, “Elastomeric (Rubber Linings).”

Glass-Reinforced Linings

It is frequently necessary to repair glass-reinforced epoxy, polyester, or vinyl ester linings. The need usually arises from physical damage, although in the past there have been a number of adhesion problems resulting from continued polymerization, where these ma-

terials have actually pulled themselves away from either concrete or steel surfaces. These were often on concave or cylindrical surfaces where the shrinkage of the materials during cure pulled the lining away from the surface. This has also occurred on flat tank bottoms, particularly around the circumference of the tank.

In these cases, repair can usually be made by removing the damaged lining and reapplying the same or a similar material over the broken area, applying the same number of layers of glass matte and glass cloth and resin. In any case, the adhesion of the original material should be thoroughly tested to make certain that the repair is carried back to a solid coating with good adhesion to the substrate.

Glass Linings. There are many glass-lined tanks in service, as well as glass-lined pipe and equipment. Every care is ordinarily used to prevent damage to such linings, since they are difficult, if not impossible, to repair. Glass-lined equipment does chip on occasion and, if the contained material is corrosive, rapid damage can occur. Some repair is done with resinous linings if the exposure is satisfactory and the temperature sufficiently low. Epoxy phenolic lining materials are often used, heating the repair area to thoroughly cure the resin.

Most glass-lining repair is made to small breaks in the lining. Some are sufficiently small so that gold or other inert metals have been used for repair. Large damaged areas usually require the vessel to be permanently taken out of service. The original manufacturer's recommendation should be followed for any glass-lining repair.

Summary of Lining Repair

The repair of lining materials is a critical job, and every repair is a unique operation. Generalized procedures are ordinarily not practical. Nevertheless, in order to provide a quick overview, the following is a limited summary of lining repair procedures.

1. Clean the tank or lined surfaces free of all dirt or residue by the appropriate method.
2. Remove damaged or disintegrated coating back to an area of good adhesion to the substrate.
3. Prepare the metal substrate in the best possible manner—white metal abrasive blasting is recommended (NACE No. 1/SSPC SP-5/ISO Sa 3.0[18]). Small repairs may be made with power grinders or sanders. Use particular care to protect the existing lining during surface preparation.
4. Prepare concrete substrates by removing all soft and damaged concrete back to solid gray concrete. Rebuild to original surface level with cement plaster or resinous surfacer (epoxy surfacer, if applicable).
5. Feather edge existing coating 1 to 2 in for thin linings, 2 to 3 in for medium thickness linings, and 4 to 6 in for thick linings (over 30 mils). Lightly abrade original lining a short distance beyond the feathered area.
6. Apply appropriate primer or first coat to substrate and over feathered area. Extend a short distance out over the original lining.
7. Apply original number of intermediate or topcoats over the repair area. Use spray application for large areas, if practical; use brush for small areas.
8. An overall finish coat is usually not recommended or necessary. This is particularly true of epoxy, urethane, and phenolic linings, because of adhesion problems between coats.
9. Cure repaired area thoroughly. This step is vitally important. Use heat to force-dry or cure, if necessary, to obtain original coating resistance.
10. Specific suggestions for specific linings include:
    a. Urethane linings usually require an epoxy primer for adequate adhesion to the substrate and original coating. Some of the new hybrid versions are recommended direct-to-metal. However, the adhesive properties of an epoxy primer is well worth the extra cost versus a potential failure of the urethane lining.
    b. Where IOZ is used as a repair base coat, remove the IOZ from topcoat and feathered organic area by rubbing with screen wire or other mechanical means. This is essential for proper adhesion of the topcoats.
    c. Extra care must be used with coal tar epoxy linings to thoroughly roughen the original coating surface to obtain adequate adhesion. Where possible, use a polyamide epoxy primer over the substrate and original coating for best adhesion.
    d. High-baked lining materials (phenolic and epoxy phenolics and epoxy novolacs) must be cured to the same degree as the original lining. Lack of full cure means certain failure for any repair.
    e. Thick rubber-type linings, where damaged or blistered, must be cut away back to an area of good adhesion, the edges of the rubber skived, and the original rubber system replaced and cured. Use the manufacturer's recommended procedures.
    f. Thermoplastic sheet linings (usually vinyl) are repaired by cutting sheet away from the substrate. The area is usually cut in a rectangle. A similar sized rectangle of lining is replaced in the repair area using an adhesive. The joint between the old and new lining is then heat welded using a weld strip. This makes a very effective repair. Use the manufacturer's recommended materials and procedures for making repairs of this type.
    g. Glass linings are difficult to repair. Damage is usually in the form of small mechanical breaks. Glass cannot be replaced. Obtain the manufacturer's recommendation for repair.
    h. Glass-reinforced epoxy or polyester linings can usually be repaired by using glass matte or glass cloth with the original resin-catalyst combination.

These general recommendations provide a guide to the reconditioning of a coated surface. Coating or lining maintenance, however, includes much more than simply following rules for the repair of a surface. It is, as previously stated, the protective management of the surface, which is not limited to periodically touching up a few rust spots. As defined previously, it means management of the coating process from the beginning of the original application to its present and future states. It therefore includes such activities as material studies, specifications, inspection, record keeping, observation of the coating condition, and establishment of the limits of failure beyond which repair and recoating automatically take place.

Of all of these activities, the most important are writing proper specifications and following up the specifications with thorough inspection. Good specifications and inspection procedures can ensure a satisfactory and long-lasting repair job, just as good specifications and inspection procedures can ensure a long life and effective service from the initial coating.

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18. NACE No. 1/SSPC-SP 7/ISO Sa 3.0, "White Metal Blast Cleaning" (Houston, TX: NACE).

APPENDIX 15A[1]

Procedures for Adhesion Test[2]

Scope

This test method is intended to determine the surface strength of concrete and to evaluate or measure the bond of applied coating, and other corrosion protection materials, to concrete surfaces cleaned and prepared in accordance with the guidelines provided in this report.

Significance

The test can be used to evaluate the tensile bond strength of applied coatings, polymer lining (filled and unfilled), and flooring systems to concrete.

The surface integrity of concrete can be evaluated by this method. Concrete surfaces that have been exposed to chemical and other conditions may have poor or marginal tensile strength for application of corrosion protection materials. It is essential to measure the tensile strength of concrete surfaces before applying heavy duty floor toppings or linings. Many topping or lining products are considerably stronger than the concrete, and the adhesion of products to concrete also exceeds the tensile strength of the concrete. A tensile strength of 1.0 MPa (200 psi) for indoor exposure, or 1.4 MPa (250 psi) for exterior are the generally accepted minimum required values for heavy duty resin floor toppings or linings. At values lower than these, the concrete surface is too weak to accept a heavy-duty floor topping.

Apparatus and Materials

Elcometer Adhesion Tester Model 106:

Scale No. 1 (0–35 kg/cm2; 0.500 lbs/in.2)
Scale No. 2 (0–70 kg/cm2; 1–1,000 lbs/in,2)
Scale No. 3 (0–140 kg/cm2; 0–2,000 lbs/in.2)
Scale No. 4 (0–280 kg/cm2; 0–4,000 lbs/in.2)

Aluminum dollies (adhesive contact area 3.24 cm2; 0.502 in.2)

Epoxy Adhesive

For testing the surface integrity and strength of concrete, fast set commercial adhesives can be found in hardware stores, but care should be taken to ensure that the strength of these adhesives is greater than that of the system being tested. For testing the bond of applied coatings and materials to concrete, it is best to use an adhesive based on the resin or polymer of the coating, topping, or lining being evaluated.

Hole saw (inner diameter 21 mm; 0.84 in.)

A nominal 2.5 cm (1 in) OD hole saw with HSS Starret edge will produce this inner diameter.

Magnetic dolly clamps for vertical surface adhesion to steel substrates

Coarse sandpaper (grade 60)

Strong solvent (methylene chloride or equivalent)

Procedure

Drill 21 mm (0.84 in.) diameter circular cut in the concrete and abrade the surface of aluminum dolly with the coarse sandpaper. Make sure the surface is clean and free of contaminants by wiping with a strong solvent. For greater bond strength, the dolly may be brush-blasted prior to adhesion.

On drilling large substrates, the use of plywood or other device template has been found essential to controlling the hand-held drilling operation.

Bond the high tensile strength aluminum dolly to the test surface using a suitable adhesive. Any excess around the base of the dolly should be removed and the adhesive left the appropriate time to cure.

When the adhesive curing time has elapsed, the adhesion tester is placed in position by lowering the claw at the bottom of the unit so that it slides over the dolly. Make sure that the three swivel pads are positioned so as to transfer the force evenly; this will ensure that the claw will pull perpendicular to the substrate.

Tightening the hand wheel or nut applies a pulling force to the dolly. At the point of break, the scale will rise a little, and the reading will be retained by the dragging indicator on the barrel. Estimate readings to the nearest half scale division.

Discussion

Three general types of data can be obtained from this test.

Tensile Strength/Bond Strength

An approximation of the mean tensile strength and/or bond strength can be evaluated from the readings taken from the barrel.

Mode of Failure Analysis.

One of the most important diagnostic pieces of information in a bond test is the location of a failure in a composite system. Weak points may readily be defined by examining the fracture surfaces. In most cases the coating will fully adhere to the dolly and the test can be claimed as 100% valid. This can be determined by examination of the dolly after completion of the test. In certain instances a portion of the coating will be removed and partial adhesion to dolly may occur. Allowances for this must be made when finally evaluating the results of test.

In instances where the concrete surface is weak, floor topping or lining failures are usually concrete failures, since 0.3 to 0.6 cm

(⅛ to ¼ in) layer of concrete adheres to the corrosion protection products when they separate from the concrete base.

Improper cleaning of concrete saturated with oils or fats or other contaminants is usually easy to identify, since the topping or bonding adhesive used in test usually separates cleanly, taking no cement with it.

The "Go-No-Go" Test

This method of evaluation is of primary importance to field inspection work where minimum bond strengths have been written into the specifications of a system. If unusual application conditions are present during the installation of a product, its performance can be estimated from the mechanical efficiency displayed by bond testing.

Sources of Error. It is important to calibrate the adhesion tester from time to time to ensure that the spring constant for the Belleville[3] washers has not fatigued. This can be done by applying a known force to the tester and recording the difference in readings over the scale range.

It should be remembered that this is a method for estimating the average tensile strength and should not be confused with the actual tensile strength.

Sample preparation is important from the standpoint that the dolly must be parallel to the substrate surface to prevent shearing.

The available bonding surface on the dolly should be matched as closely as possible to the drilled hole. The hole saw recommended under the Apparatus and Materials Section will produce a surface matching error of 3%.

The choice of adhesive is important for consistency and significance in readings. If the adhesive is the weakest zone relative to the product, the product is not being evaluated.

Care should be taken to choose adhesives with tensile strength well above that of the product under test. In circumstances where finding a reliable adhesive becomes a problem, one might consider using the product itself as the adhesive, provided its bond to the dolly is sufficient.

Selecting the proper adhesion tester is also important. As listed in the Apparatus and Materials Section, there are four scales available in the Elcometer Model 106. The differences between these scales involve their capacities and accuracies; one would not choose a model with a capacity to 30 MPa (4,000 psi) to evaluate a bond with a typical value of 0.7 MPa (100 psi).

When operating the 14 and 28 MPa (2,000 and 4,000 psi) capacity models, it is important to crank the wrench in a plane parallel to the plane of the substrate. Failure to do so, again, would result in the generation of a shearing force that would produce inconsistent readings.

If the coupon as pulled does not have concrete attached to the whole surface, the test in invalid and must be repeated.

[1]"Surface Preparation of Contaminated Concrete for Corrosion Control," NACE Technical Committee Report T-6G-21 (draft) (Houston, TX: NACE, 1981).

[2]This is not a standard test method, but rather a practical field test derived from a review of current technology.

[3]Trademark of Universal Products, Inc., 224 North Montello, Brockton, MA 02401.

16 Safety

Safety requires a continuing level of consciousness, which attempts to foresee and thus forestall problems before they occur. It is a process that attempts to overcome the commonly held theory that if it is possible for something to happen, it will. Safety involves taking the precautions necessary to ensure that the possible does not happen and should be a primary consideration when dealing with high-performance coatings, because of the many potential hazards related to both the material and its application.

Every coating assignment exposes maintenance personnel to conditions and situations that represent actual or potential danger to themselves and to others in the area. The frequent use of toxic and flammable materials, pressurized equipment, ladders, scaffolding, and rigging always presents potential hazards. Hazards may also be inherent in the environment, or they may be brought about by the ignorance or carelessness of the operator. Therefore, it is extremely important to be aware of all potential hazards, since continuous and automatic precautionary measures will minimize problems and improve both the efficiency and morale of the coating crew.

These potential hazards that are a part of all coating operations make a continuing and enforced safety program absolutely essential. Adequate safety procedures will provide protection against the major types of hazards; namely, physical accidents, fire, explosion, and health problems. All personnel should be responsible for adhering to all established precautionary programs for their individual protection as well as that of others. Disregarding safety measures will significantly increase the potential dangers and the odds that an accident will occur.

Accidents can occur for a variety of reasons. The most common causes are outlined in the Department of Defense *Manual of Paints and Protective Coatings,*[1] as follows.

> Accidents during painting operations are caused by unsafe working equipment, unsafe working conditions, and careless personnel. Any or several of the following can cause accidents:
>
> a. Lack of knowledge, experience and training in the use of painting materials and equipment.
> b. Improper maintenance and storage of equipment.
> c. Failure to pre-check equipment for mechanical and structural flaws.
> d. Improper use of equipment.
> e. Failure to consider environmental conditions and existing hazards in work areas before, during, and after painting operations.
> f. Personal carelessness.

Accidents most frequently involve commonly used equipment. The most common and serious accidents, by far, are falls either from a height or on the ground because of a loss of footing. Falling or moving objects are the next most serious hazard.[1]

In recent years, the Safety Profession has recognized supervisory planning, business decisions or the lack thereof can bring about situations where employees choose to not follow their training because of management pressure or perceived pressure. Overconfidence in one's own skills or in management's expectations resulting in personal carelessness is probably the greatest cause of all accidents. There are no good or practical safeguards against ignorance or carelessness. All personnel must be advised of all potential hazards and the precautions to take against them. "Short cuts" usually involve poor safety procedures and therefore, must be avoided.

This chapter will emphasize the safety requirements inherent with the coating material rather than concentrating on the ordinary physical hazards involved with scaffolding, bosun's chairs, ladders, swinging stages, rolling towers, ropes, and similar equipment that is common to most construction jobs and to the coating process in general. There are literally hundreds of safety rules and regulations that are published and are requirements of various governmental agencies. These include city and county codes, state regulations, and, overall, the rules and regulations established by national government agencies such as the Occupational Safety and Health Administration (OSHA), Environmental Protection Agency (EPA), Department of Labor, and by the Toxic Substances Control Act (TSCA). Appendix 16A contains a number of references where additional information on safety rules and regulations may be obtained.

Introduction

One of the most comprehensive outlines for painter safety is NACE's *A Manual for Painter Safety* prepared by NACE Task Group T-6D-5 on Painter Safety. The entire manual is included here as Appendix 16B. Keep in mind that this manual was written before OSHA rewrote the book on safety. The principles are still accurate, but the regulations have changed. By following this manual and the various governmental codes that may apply, the application of paint and coatings should be reasonably safe.

There are definite hazards associated with the application of coatings, particularly high-performance coatings. The greatest hazards

exist while coating the interior of closed spaces such as tanks, processing equipment, or small rooms or chambers. These areas exist in almost all industries and can include the interior of water tanks; the interior of refined oil and crude tanks aboard ships; the interior of food vessels such as beer tanks; or the interior of tank cars or other transportation equipment. The existence of hazards involved in coating the interior or closed spaces is evidenced by the occurrence of numerous fatal accidents since the advent of high-performance coatings. However, the economic need for the product justifies the safety materials, methods, and procedures required to reduce the hazards involved in their use.

Many excellent examples of safety programs exist throughout industry. Two of the most outstanding are the programs established by the explosives industry and those employed in the development and use of nuclear energy. In both of these areas, safety precautions have been developed to drastically reduce the danger in working with these hazardous materials. The marine industry is also involved with many hazardous products in both the transportation and handling of such materials. The use of high-performance coatings also depends on the procedures and methods that are developed to ensure their safe handling.

Since each coating job is unique, the hazards involved are highly variable. A coating applied to the exterior of structural steel, the outside of an offshore structure, or the exterior of a tank, certainly poses different hazards than one applied on the interior of a tank car, barge, or tank. As mentioned earlier, the most dangerous areas are those that are enclosed. Although in many large, enclosed areas, the hazards do not seem to be very real, a number of accidents have resulted, primarily from an attitude of nonchalance or carelessness. For example, a coating was being applied on the interior of a refined oil vessel, which involved several men working in the tank. At lunch time when all the men left the tank, the ventilation was turned off, supposedly to save power. When they returned and entered the tank after lunch, the tank blew up, killing all of the workers. After the accident, a half-smoked cigar was found at the bottom of the ladder, indicating the type of carelessness that compromises safety.

Another example involved coating the interior of a floating roof tank, where the floating roof was held on legs or supports approximately six feet (1,8 m) above the bottom. After an explosion occurred, it was found that the workers had been using a string of unprotected light bulbs in the tank. Undoubtedly, one of these dropped or was hit, causing the spark that set off the explosion. In both of these examples, the work was being done on overtime so that no superintendent was present. Unfortunately, overtime jobs where supervision is less adequate are often the jobs that incur safety problems. Unfortunately, once an incidence occurs, the obvious lack of understanding as to the importance of safety procedures is inconsequential.

Changes in the Coating Industry

Some major changes in the coating industry are resulting in changes in the composition of coatings, basically from those based on solvents to those that use no solvent at all or a reduced amount of solvent. These changes will have a marked effect on the necessary safety precautions. A look at some of these changes is given in *Applied Polymer Science*[2] in a chapter on the chemistry and technology of solvents, as follows.

> Government regulations regarding solvents and coatings will have a profound effect upon future products and practices. The regulations are concerned with the following topics:
>
> A. Air pollution: federal activities under the Environmental Protection Agency (EPA) as well as state and local regulations.
>
> B. Health: Occupational Safety and Health Administration (OSHA) as well as separate and overlapping laws from other agencies.
>
> C. Safety: Department of Transportation (DOT) and other agencies concerned with flash point, labeling and related matters.
>
> D Energy conservation.
>
> In virtually all cases, the regulations will tend to restrict solvent usage. As one consequence of restrictions, the introduction of new solvents will be inhibited in continuation of a trend already in existence. Indeed, the production of some existing solvents will be discontinued as has already happened in the case of some solvents where small volumes simply could not be sold profitably. Some producers of hydrocarbon products have eliminated many solvents from their lines.
>
> Although normal growth of paint products approximates 3% per year, total solvent usage for paint will not grow commensurately. Trade sales coating for architectural use are already largely water-based and industrial coatings are now experiencing a strong impetus toward water-based types. Other types of coatings will grow but at a lesser rate than water-based; these include high solids coatings (at least 70-80% solids), powders, and 100% convertible coatings where the reactive solvent becomes part of the solid final cured coating. Switching from solvents is difficult, costly, and fraught with uncertainties. Replacing solvent paints by low solvent or non-solvent types may not be sound economically or environmentally in many cases. Because of long experience and some inherent advantages (wetting, adhesion, color-matching, durability) of solvent paints as a class, the need for less frequent or no repainting can often make up for greater initial cost or emission of solvents from solvent paints.
>
> In product finishing, because of increased fuel costs, incineration of solvent fumes is becoming less popular, but solvent recovery is becoming of greater interest. Single-solvent systems or those with few components are more easily recovered than the usual multi-component solvent systems and will be favored where solvent recovery is concerned.
>
> The product mix will be altered because of the impact of composition limitations of solvent blends under air pollution laws such as Rule 66.1. Aromatic hydrocarbons are quite vulnerable under air pollution laws; acceptable substitutes usually can be made from a mixture of about 20-50% oxygenated solvent and 80-50% of an aliphatic hydrocarbon. There is some pressure, only partially supported by technical data, to eliminate distinctions among solvents as to their oxidant or smog-producing capacity. Overall, most regulations have the two-fold effect of reducing total solvent usage and altering the product mix.
>
> Since total solvent production will undoubtedly grow in the future because of increasing use of solvents as chemical intermediates, solvents will always be available for the conventional uses, which make use of the solubilizing and viscosity-reducing characteristics.[2]

This last point (i.e., the availability of solvents) is extremely important since many high-performance coatings cannot be modified materially and still retain their effective anticorrosion properties. As previously discussed, both water-based and high-solids or 100% solids coatings present many difficulties in field application. Also, water-based materials made primarily from emulsions and dispersions do not form the same continuous impervious type of film that is developed through solution techniques. It is the opinion of many persons in the high-performance chemical and corrosion-resistant coating field that it is going to require many years of development and research to eliminate solvent-based coatings from the high-performance field. Thus, from the standpoint of the corrosion engineer, solvents are still going to be involved in highly corrosion-resistant applications and, because of this, safety procedures for the use of solvent-based coatings will remain necessary.

Primary Hazards

There are essentially four primary hazards involved in the use of high-performance protective coatings. These are characterized as fire, explosion, reactivity, and health. Each one of these should be carefully considered. In addition, a new hazard has presented itself from the evolution of protective coatings—physical hazards from pressure.

Fire

All coatings that contain solvents are flammable. In many cases, the coating's binder resins are also flammable. This is particularly true when the coating is in the liquid stage. Any time that a solvent-based coating is liquid, whether in a container or applied to a surface, there is the possibility of fire. Thus, every safety precaution should be taken to prevent a flame or spark from contacting the paint while it is in the liquid stage. Coatings in the liquid stage generally are not explosive. This means that if the surface of the liquid coating in a container is on fire, it will not explode from the flame on the surface. This does not mean that a closed coating container will not blow its lid in a simulated explosion as a result of the vapor pressure of the solvents developed by the external heat. Such an exploding container materially adds to the fire by spreading the flammable material over a wider area.

None of this information should be interpreted to mean that fire is not a major hazard. For example, in the internal lining of a pipeline, where a workman was making repairs using a solvent-base material, the container caught fire, and in the excitement that followed, was tipped over. The ensuing fire was sufficient to start the repaired coating area aflame, and before the workman could get out of the pipe, the entire pipe lining was aflame.

Enclosed areas are particularly dangerous where solvent-containing coatings systems are being applied Therefore, every precaution must be taken to eliminate any possible source of flames or sparks that could ignite the coating.

Explosion

Explosion is differentiated from fire because it basically involves a different type of reaction. In the case of explosion, there is sufficient solvent evaporated into the air so that, if there is a source of spark or flame, the entire air-vapor volume will react at one time, creating an explosion. Explosions can occur without fire, although they are often combined, with the explosion igniting the liquid coating. Explosion is probably the greatest risk from the standpoint of catastrophic loss of life and property, and there are a number of phenomena that are important in preventing explosion.

Lower Explosive Limit

The lower explosive limit (LEL) of any solvent or combination of solvents can be defined as the percentage of solvent vapor in air that is the point at which an explosion will occur if the air and solvent mixture is ignited with a spark. The lower explosive limit of a solvent or solvent mixture is extremely important to the whole safety program in the application of coatings due to the fact that if the lower explosive limit is never reached, no explosion can occur. This means that every effort should be made to prevent the solvent-air mixture from reaching the lower explosive limit. There is also the upper explosive limit, above which the percentage of solvent vapor in air is sufficient to inhibit the explosive reaction. At this point, no explosion can occur, even though a spark may be available within the solvent vapor-air mixture. This is what prevents an automobile from starting when it is over choked and the carburetor is said to be "flooded." The upper explosive limit is much less important from a safety standpoint than the lower explosive limit. Information on the lower explosive limits of individual solvents has been published in various sources for many years.

Information on mixed solvent explosion limits has not been as well documented. Battelle Memorial Institute has done some work along these lines for private interest. In this research, they developed apparatus for accurately measuring the solvent volume in an air mixture and then determining the percentage of solvent vapor and air that would cause an explosion when set off by a spark. They checked both individual solvents and solvent mixtures used in high-performance coatings.

Table 16.1 shows the test explosive limit for individual solvents, and Table 16.2 shows the test limits for mixed solvents as they would be found in protective coatings. It is interesting to note in these tests that the lower explosive limit of the mixed solvents was less than the lower explosive limit of the individual solvents with the highest LEL, and the lower explosive limit of the mixture was above that of the solvent with the lowest LEL.

It should be noted that one should not be complacent about respiratory issues while focusing on fire and explosion. Earlier threshold limit values for protection from toxic vapors were set at 1/10th of the LEL for the same chemical. Research has only more strictly adjusted these values. Workers could be overcome by the vapor levels long before fire or explosion would be possible in confined areas.

Flash Point

Flash point is another term that is commonly associated with solvent-type coatings. The flash point is commonly defined as the temperature of the solvent at which it releases sufficient vapor to ignite in the presence of a flame. The higher the value; the safer the solvent (with respect to the flash point).

There are two ways of determining a flash point: (1) the closed-cup method, which evaporates the solvent in a closed vessel, measuring the temperature of the liquid solvent, and determining the temperature at which the solvent flashes in the presence of a flame; and (2) the open-cup method, where the solvent is placed in an open cup, again with the temperature of the liquid solvent being determined, and the flash point, in this case, being the temperature at which the solvent in an open container flashes in the presence of a flame. The open-cup flash points are usually considerably higher than the closed-cup flash points. For this reason, the closed-cup procedure is used more often in determining this property.

Evaporation Rate

Evaporation rate, or the relative evaporation time of a solvent, is based on an arbitrary value of 1 for ethyl ether. In this case, the higher the evaporation time, the longer it will take for the solvent to evaporate and form solvent vapor in air. This is both good and bad. A solvent with a relatively slow evaporation rate will be slower in buildup to the lower explosive limit. On the other hand, by staying wet longer, the flammability is more of a hazard.

TABLE 16.1: Test Explosive Limit Data for Individual Solvents

Solvent	Spark-Explosion Limit, Percent Vapor By Volume in Air	Pressure, mm Hg	Temperature °F	Temperature °C
Ethyl Alcohol	3.31	760	77	25
Isopropanol	2.59	760	77	25
n-Butyl Alcohol	No limit found	665	122	50
Tetrahydrofurfural Alcohol	No limit found	743	122	50
Acetone	2.88	760	77	25
Methyl Ethyl Ketone	2.15	760	77	25
Methyl Isobutyl Ketone	1.80	760	77	25
Cyclohexanone	1.49	760	122	50
n-Butyl Acetate	1.57	760	122	50
1-Nitropropane	2.32	760	122	50
Xylol	2.24	760	122	50
Aromatic Petroleum (toluol range)	1.19	760	122	50
Aromatic Petroleum (xylol range)	1.29	760	122	50
Petroleum, Naphthenic fraction	No limit found	626	122	50
Mineral Spirits	1.10	760	109	43

Source: C.G. Munger, "Safe Application of Protective Coatings—Identifying the Hazards," *Plant Engineering* (Feb. 7, 1974).

TABLE 16.2: Test Explosive Limit Data for Mixed Solvents

Solvent	Spark-Explosion Limit, Percent Vapor By Volume in Air	Pressure, mm Hg	Temperature °F	Temperature °C
Ketone Aromatic Thinner	1.13	760	82	28
Ketone Aromatic Cleaner	1.66	760	86	30
Wash Prime Solvents	1.98	760	86	30
Vinyl Tank Lining Solvents	1.40	760	86	30
Vinyl Exterior Coatings and Solvents	1.35	760	77	25
Asphalt Gilsonite Solvents	No limit found	760	122	50
Epoxy Ester Solvents	No limit found	760	122	50
Tank Lining Epoxy Solvents	1.48	760	95	35
Phenolic Tank Lining Solvents	2.49	760	88	31

Source: C.G. Munger, "Safe Application of Protective Coatings—Identifying the Hazards," *Plant Engineering* (Feb. 7, 1974).

Evaporation rates are important from a coating safety standpoint because the solvents in a coating continue to evaporate over a period of time and not just during the application process. This means that once a coating is applied, the solvents are evaporating during the drying period in accordance with their respective evaporation rates. These can build up solvent concentration, particularly in a closed space, to the point where the lower explosive limit of the solvent is reached.

This was vividly demonstrated in one instance when a coating was being applied to the interior of a tank. When the coating was completed, the ventilation fans were removed. After an hour or so, a welder who was doing some work nearby needed a place to cut a piece of steel. He placed it across the manhole of the tank and proceeded to cut the steel with a torch over the manhole opening. The solvent in the bottom of the tank had built up to a lower explosive limit, and as the hot metal from the cutting torch dropped down to the lower portion of the tank, the solvent-air mixture exploded. While no one was hurt in this particular instance, there was a very surprised and frightened welder who will never again use a manhole as a convenient place to cut a piece of steel.

Solvent Vapor Density

Solvent vapor density is another safety factor to be seriously considered. Nearly all solvent vapors are heavier than air, and therefore will concentrate in the lower portion of an enclosed space, which is what happened in the previous example. The solvents in the tank had accumulated in the lower area in sufficient volume to create a zone of solvent vapor in air that was above the lower explosive limit in the bottom of the tank. This is often a cause for an explosion in a garage or home (e.g., a water heater) where there is a source of escaping gasoline or natural gas. The concentration of the vapor of gasoline or natural gas residues spreads across a level floor to a point where the explosive limit of the air mixture is reasonably close to the flame. This is the point at which an explosion occurs.

It must be recognized then, that since solvent evaporation from a coating is governed by time, safety precautions must be taken in any closed area where solvent-based coatings are being applied. Even though there may not be sufficient solvent left in the coating to create an explosive condition within the total space of the enclosed area, for a considerable period following the coating application,

the solvents (being heavier than air) accumulate in a low spot in the tank to the point of reaching the lower explosive limit in that area. This often occurs on the interior of complex tanks, such as aboard ship, in complex closed areas in nuclear power plants, or in complex vessels where there may be one or more baffles in the container being lined.

Boiling Point

The boiling point of a solvent is relatively easy to determine. However, it has little to do with the actual hazards involved in working with the solvent. The boiling point of a solvent is the temperature at which the solvent rapidly changes from a liquid to a gas or vapor. Another way of determining this is to consider the temperature of condensation, where the solvent vapor condenses and forms into a liquid. This property, however, is not widely used in safety considerations.

Table 16.3 shows the properties of various solvents used in coatings, including the relative evaporation rate, flash point, explosive limits (both upper and lower), vapor density, and boiling point. These, of course, are all for individual solvents, and none of the figures would be necessarily representative of the solvent mixture in a corrosion-resistant coating. These figures do indicate that the boiling point has little to do with the lower explosive limit of a coating.

Some similar properties are given for several of the more common corrosion-resistant coatings in Table 16.4. This table shows that the percent of solvent vapor in air (lower explosive limit) for the various coatings (with the exception of oil-based coatings that might contain turpentine) is above a solvent vapor percentage of 1. This is important since it gives a relatively easy rule of thumb for the measure of safety using these various coatings. If the percentage of solvent vapor in air is kept below 1% at all times, then no explosion can occur. This concept is the key in the reduction of explosion possibilities to the barest minimum.

Calculation of Solvent Vapor Concentration

It has been calculated that a normal (i.e., not high solids) vinyl coating, when sprayed into a closed space, would produce approximately 25 ft^3 (0.71 m^3) of solvent vapor per gal. Vinyl coatings have relatively low solids, so they have a relatively high solvent percentage in the vehicle. Therefore, it is a reasonably safe assumption to use 25 ft^3 of solvent vapor for every gallon of coating as a measure for the calculation of the lower explosive limit in any given enclosed space. For example, if a tank has a capacity of 37,500 gal, it would have a volume of 5,000 ft^3 (142 m^3); 1% of this volume is 50 ft^3 (1.4 m^3). This would allow the spraying of 2 gal of coating into the tank before the lower explosive limit is reached. However, this assumes that the solvent vapor is uniformly distributed throughout the tank and not concentrated in any one particular area. Keeping the percent of solvent vapor in air well below the 1% figure is one of the best safety precautions that can be taken.

Reactivity

Reactivity is not ordinarily a major problem from a safety standpoint. However, it should be realized that many of the new coatings, especially those with 100% solids, are internally reactive and can generate a substantial amount of heat if allowed to remain in a container in any significant volume after the catalyst is added. Epoxy coatings mixed with a fast curing agent, for instance, can develop sufficient heat so that the coating within the container will smoke and possibly catch fire. This is an internal reaction throughout the mixture, and the center of the mass of liquid is the hottest area since it has the most insulation. In fact, one painter was mixing coatings of this type, and, before he could get from the mixing area to where he wished to apply the coating, the epoxy coating was expanding out of the can, smoking, and, once the painter got away from the container, it actually caught fire. While it was thoroughly doused with water, the reaction continued unabated since the cooling capability of the water on the outside of the container was not sufficient to cool down the internal mass of the coating.

Reactions such as this are primarily important when someone mixes the catalyst and the resin and then allows them to sit for some period of time (even overnight, if they are forgotten). Under these conditions, the exothermic reaction can build up to a flammable level. Fully polymerized coatings, such as vinyl resins, acrylics, chlorinated rubbers, and materials of this type do not have any internal reactivity so that they do not suffer from this type of hazard. Epoxies, polyurethanes, and similar reactive materials such as polyesters, however, can develop a substantial amount of heat, so that whenever they are being used, the mixed catalyst and resin should not be stored in any volume, even one gallon, without being used immediately.

Additional issues may arise such as with oxidizers and acids. Oxidizers can speed the reaction of some plural-component systems; they also change the reactivity of potential fuel sources. Generally, oxidizers should not be stored on wood, on any combustible material, or in an area that a spilled or breeched container could allow contact. Acids in contact with ferrous metals and some non-ferrous metals can release hydrogen. If this happens in an enclosed container, a BLEVE, or pressure explosion, may occur. If a source of ignition is nearby, a fireball could erupt. It is important to read all storage information on product data sheets and MSDS (Substance Data Sheets under the new Global Harmonized System [GHS]). With recent changes in the GHS, workers need to be trained not only on the separate SDS for each component, but also on the SDS that must be supplied on the hazards of the mixed paint.

Health Hazards

Health hazards are last on the list of major difficulties involved in the use of high-performance coatings. This does not mean, however, that they are any less serious than the hazards described earlier. In fact, in many circumstances they may be more serious.

Any substance can be safely utilized industrially if the precautions and protective equipment that are necessary for the safe handling of the product by personnel are economically justified. Some hazards may be sufficiently dangerous because of the amount and character of the toxic material, so that even with maximum safeguards, they should be avoided. However, this is not the case with most protective coatings. Most are not so toxic that the proper equipment and protective clothing cannot provide full protection.

Physiologic Action of Solvents

In order to provide some understanding of the physiologic action of solvents, the following are some excerpts from a book by A.K. Doolittle, *The Technology of Solvents and Plasticizers,*[3] which examines the physical effects of solvents.

> Foreign chemicals must reach susceptible cells in order to injure the body. To injure internally they must enter the body fluids, and their

TABLE 16.3: Properties of Flammable Liquids Used in Coatings and Lacquers

Solvent	Evaporation Relative Rate (Ethyl Ether 1)	Closed Cup, Flash Point		Explosive Limits % by Volume in Air		Vapor Density (Air=1.00)	Boiling Point	
		°F	°C	LEL	UEL		°F	°C
Acetone	4	0	32	2.15	13.0	2.0	134	56
n-Amyl Acetate	50	76	25	1.10	–	4.49	300	149
n-Amyl Alcohol	100	91	32	1.20	–	3.04	280	138
Benzene	8	12	−9	1.40	8.0	2.77	176	80
Sec. Butyl Acetate	–	66	16	1.70	–	4.00	234	110
n-Butyl Acetate	30	72	22	1.70	15.0	0.88	260	127
n-Butyl Alcohol	70	84	29	1.70	–	2.55	243	118
Carbon Tetra Chloride	8	–	–	–	–	–	–	–
Cellosolve	100	104	40	2.60	15.7	3.10	275	135
Cellosolve Acetate	32	124	50	1.71	–	4.72	313	155
Cyclohexanone	–	147	85	–	–	3.38	313	155
Di Acetone Alcohol	200	145	84	1.8	6.0	–	–	–
Ethyl Acetate	8	24	−6	2.18	11.5	3.04	171	77
Ethyl Alcohol	20	55	14	3.23	19.0	1.59	173	78
Fuel Oil No. 1	–	100–165	38–75	–	–	–	–	–
Furfural Alcohol	–	167	76	1.8	16.3	3.37	340	170
Gasoline	–	−40	−40	1.3	6.0	3–4	100–400	38–204
n-Hexane	–	−7	−21	1.25	6.9	2.97	156	70
Isopropyl Alcohol	25	65	16	2.5	5.2	2.07	181	82
Kerosene	800	100–165	38–75	–	–	–	–	–
Methyl Alcohol	10	54	13	6.00	36.5	1.11	147	65
Methyl Amyl Ketone	–	120	50	–	–	–	303	150
Methyl n-Butyl Ketone	–	–	–	1.22	8.0	3.45	262	128
Methyl Isobutyl Ketone	20	73	22	1.34	8.0	3.45	2.44	118
Methyl Ethyl Ketone	8	30	−1	1.81	11.5	2.41	176	80
Methyl n-Propyl Ketone	–	–	–	1.55	8.1	1.96	216	202
Mineral Spirits	150	100–110	38–43	1.10	6.0	–	300–400	149–204
Naphtha, Coal Tar	105	100–110	38–43	–	–	–	300–400	149–204
Naphtha, Safety Solvent	–	100–110	38–43	1.10	6.0	–	300–400	149–204
Naphtha, V.M. & P.	20	20–45–7– +7	–	1.20	6.0	–	212–320	100–160
n-Propyl Alcohol	–	59	15	2.50	–	2.07	207	96
Stoddard Solvent	–	100–110	38–43	1.10	6.0	–	300–400	149–204
Toluene	15	40	4	1.27	7.0	3.14	232	111
Turpentine	100	40	35	0.80	–	–	300	149
Water	100	–	–	–	–	–	212	100
o-Xylene	35	63	16	1.00	–	3.66	291	145

Source: C.G Munger, "Safe Application of Protective Coatings—Identifying the Hazards," *Plant Engineering* (Feb. 7, 1974).

TABLE 16.4: Characteristics of Commonly Applied Coatings

			Flammability				
			Flash Point Open Cup		% Solvent Vapor in Air (LEL)	MAC Parts/Million Solvents	Toxicity
Type of Coating	Resin	Solvent	°F	°C			Resin
Oil-Based Paint	Linseed Oil—Flammable	Aliphatic hydrocarbon, may contain turpentine	100+	38	0.80 if contains turpentine, 1.1 if contains mineral spirits	If turpentine, 100; If only mineral spirits, 500	Nontoxic
Alkyds	Flammable	Aliphatic or aromatic petroleum	100	38	1.1	200 to 500	Nonirritating
Chlorinated Rubber	Chlorinated rubber and plasticizing, generally nonflammable.	Aromatics	40 to 60	4 to 16	1 to 1.3	100	Chlorinated rubber is nontoxic. Possible skin irritation due to aromatic solvent.
Vinyls	High molecular weight chlorinated hydrocarbons, self-extinguishing	Ketones and aromatics	30 to 100	–1 to –38	1.3 to 1.8	100	Nontoxic
Vinyl (water dispersed)	Vinyl acetate will support combustion	Water	None	None	None	None	Nontoxic
Epoxies (solvent based)	Epoxy-amide, epoxy polyamide will support combustion	Ketones and aromatics	30 to 95	–1 to –36	1.3 to 1.8	100	Some cause dermatitis in sensitive individuals
Epoxy-Coal Tar	Will cupport combustion	Ketones and aromatics	30 to 95	–1 to –36	1.3 to 1.8	100	Fumes very irritating. Skin irritation. Dermatitis
Epoxy (water dispersed)	Will support combustion	Water	None	None	None	None	Possible skin irritation
Polyurethane	Flammable	Ketones and aromatics	40 to 75	4 to 2.5	1 to 1.3	100	Contains isocyanates. Toxic fumes can cause irritation during application. Dermatitis possible
Asphalt—Gilsonite Cutback	Will support combustion	Aliphatic or aromatic petroleum	100+	38	1.1	200 to 500	Nontoxic
Coal Tar Cutback	Flammable	Aromatics	40 to 100	4 to 38	1.1 to 1.27	200	Severe skin irritation
Inorganic Zinc Silicate (water based)	Inorganic silicate, nonflammable	Water	None	None	None	None	Silicate mildly alkaline. Limited skin irritation.
Inorganic Zinc Silicate (solvent based)	Inorganic silicate, nonflammable	Ethyl Alcohol	55 to 60	15	3.2	1,000	Silicate—possible mild skin irritation

Source: Munger, C.G., Safe Application of Protective Coatings—Identifying the Hazards, *Plant Engineering*, Feb 7 (1974).

physical properties must allow transportation within the body. A compound in the digestive tract or in the lungs does no harm until it contacts susceptible cells. It may injure surface cells in the lining of these cavities by dissolving in the film of fluid upon them, and, if it is sufficiently irritating, it may kill these boundary cells. It may be absorbed into the circulating body fluids and contact susceptible cells at a distance. But, if it is not absorbed at all and if it is not sufficiently irritating to injure surface cells, it cannot harm the body, and eventually it will be eliminated from the cavity.

The most rapidly moving fluid circulation of the body is the bloodstream, but it bathes directly only the cells lining its vessels. From its ultimate branches the capillary network, the fluid components reach every cell in the body.

Chemicals soluble in fats are withdrawn from the blood fluid by tissues high in fat and can attain high concentrations and exert their action selectively upon particular organs such as the nervous system. Substances like ethyl alcohol and methyl alcohol will be found almost uniformly distributed throughout the body in the water of tissue and blood, but others, such as benzene, which are more fat-soluble, will be found in greater concentration in tissues high in fat.

When a material is absorbed from the digestive tract, much or all of it enters the bloodstream and passes first to the liver…Thus when a chemical is swallowed it reaches the liver promptly, if it is absorbed at all, where it may be so metabolized as to be harmless but where in the process it has an opportunity to exert serious injury.

> Contrasted with this, when a material is absorbed from the lungs or through the skin it enters first the peripheral circulation and passes through the body before the liver has an opportunity to act upon it. It is for this reason that some chemicals exert qualitatively and quantitatively different actions when swallowed and when inhaled. It appears that during the eons in which our bodies evolved there was relatively little chance of injury from gases and vapors, and evolution accordingly did not lead to efficient defense against inhaled chemicals. Today (particularly with the application of protective coatings), we find ourselves with many opportunities for inhaling dangerous vapors, but, because defenses are not adequate to exclude them from our bodies, external controls must be provided.
>
> The injury that a solvent can exert upon a cell is governed by the amount that is absorbed upon the cell wall or the concentration that can be built up within the cell. Either of these amounts depends upon the concentration of the chemical in the fluid surrounding the cell and hence upon the total amount that entered the body.
>
> Absorption of vapors and gases through the lungs is an equilibrium process. The concentration of vapor in the inhaled air almost instantaneously attains equilibrium with that part of the blood that is in the tremendous surface area of the lung capillaries. The concentration in the inhaled air and the distribution coefficient of the vapor between blood and air is, of course, also a function of the rate of elimination from the body in urine and by other routes, as well as of the rate of oxidation or other form of metabolism within the body.
>
> The maximum concentration that can be attained in the blood (and hence the maximum injury that can develop in a single exposure) is therefore governed only by the concentration in the air breathed. The blood concentration may never reach an injurious level when a man is breathing 500 ppm. of a vapor but may soon reach this level when he is breathing 1,000 ppm.
>
> The rate of attaining a particular blood level is dependent on the distribution coefficient of the vapor and the activity of the man as it affects his rate of respiration and circulation. Thus, 30 minutes' inhalation of a high concentration may not result in a dangerous blood level, whereas 60 minutes may give too much, as may 30 minutes during violent activity with the resulting rapid respiration and circulation.
>
> As soon as a man leaves contaminated air he starts to eliminate vapors from the blood to the exhaled air, and the same equilibrium is maintained as during absorption. His blood level drops, but usually more time is required to eliminate a given amount of vapor than was required to absorb it, because the concentration gradient is likely to be less during elimination, particularly when a fat-soluble vapor has reached fatty tissue. Thus, although a man may inhale a vapor for only 30 minutes, his blood may contain a significant concentration for an hour or more. It is not unusual to find in the morning that the blood still contains dissolved vapor from the day before and the peak blood concentration rises day by day until the end of the week because of slow elimination overnight.[3]

This has been experienced many times where solvents were readily noticeable on the breath and in the urine, even after an overnight rest from coating application. In these instances, the solvents were ketones and aromatics, both of which could be identified by their distinctive odor. This reaction is a common one where workers do not use proper protection. Doolittle continues:

> The body mechanisms operate in such a way that the internal environment remains nearly constant. As soon as any foreign chemical or excess of a native chemical is present in the body, various processes tend to eliminate it. Elimination through the lungs is the most important route for a volatile chemical. Elimination through the kidneys into the urine is the next most important path. If a compound does not easily pass into the urine, it may be converted to an ionized acid that facilitates filtration, or it may be oxidized, reduced, or coupled with products such as glucuronic acid, sulfate, or hippuric acid. These chemical changes take place largely in the liver, and liver cells may be injured in the operation. The process is often known as detoxification, but it may result in the formation of a more toxic compound, as when benzene is oxidized to phenol or aniline to p-aminophenol. Elimination through perspiration is much the same as the kidney function, but less important in amount. Some materials leave the liver in the bile, entering the intestine where they may or may not be reabsorbed.

Skin Injury

Contact of chemicals with the skin may result in three kinds of injury. Some compounds cause primary irritation upon the skin of almost every person. This action may be only a mild reddening (erythema) as that resulting from xylene or from traces of organic acid in esters, due to dilation of the capillaries and increased permeability of their walls. It may be a severe erythema and formation of blisters from prolonged contact with turpentine. In more serious cases it may appear as a destruction of the skin (necrosis) leaving an open sore as from dimethyl sulfate, in organic alkalies, or mineral acids.

Primary irritation is more severe when the solvent contacts the skin under clothing or gloves, because the covered skin is more moist, thus permitting easier penetration through the protective horny layer. Irritation from most compounds starts to subside shortly after contact ceases, and unless necrosis was produced, no scar or permanent injury is to be expected, although an irregular distribution of skin pigment may persist for months. Prevention requires avoidance of contact by care, or impervious garments, and prompt removal of any chemical that may reach the skin in spite of precautions.

Compounds that are good fat solvents may injure the skin mechanically by removing the natural protective and plasticizing fats. These substances are also removed by prolonged contact with water or mild alkalies such as soap and phosphate cleaning solutions. Washing the hands with solvents after work is a frequent cause of skin defatting. The epidermis is left harsh and stiff, prone to crack, and a ready prey to bacterial and fungus infection. It will return to normal after infection is conquered if no further exposure is allowed. Prevention requires avoidance of frequent or prolonged contact with objectionable fluids, and replacement of fat removed by the application of hydrated lanolin or another suitable ointment.

Allergic dermatitis is seldom a problem in the handling of the commonly used industrial solvents because these materials do not sensitize many individuals. But when dermatitis does occur it is much more troublesome than the two other forms of skin injury because its manifestations may persist for weeks after contact with the causative agent ceases, and a victim may relapse later after a new encounter with a minute amount of the offending solvent or a closely related molecule. It appears that any compound that is soluble to even a very small extent in body fluids is capable of sensitizing some portion of the population. A resin from cashew nut oil is a frequent industrial offender. About three weeks after a person capable of being sensitized has the first contact with a particular chemical or after some ill-understood change following years of contact, an antibody concentration exists over the entire body. The next encounter after this state is established results in the development of a skin eruption, scaling areas, or blisters from the liberation of histamine in a type of anaphylactic shock. The reaction starts in a restricted area where the skin was exposed to the chemical, but it may eventually involve the entire body surface. Dermatitis is seldom a menace to life, but it may incapacitate a person for weeks. Impervious garments and care will reduce the number of workers who become sensitized, but after a severe attack the victim should not handle the offending chemical again. Barrier creams offer some protection to those who contact solvent infrequently but they must be spread thoroughly over the skin to be of value. When not formulated to match the particular solvent to be excluded they may actually intensify injury by

dissolving the offending chemical and holding it in intimate contact with the skin.

Through a similar mechanism, sensitization reactions may also occur in the form of asthma and hay fever symptoms, although this phenomenon has been rarely caused by solvents. These result from contact of the mucous membranes of the respiratory tract with chemicals in the form of dust, droplets, or vapor.3

Dermatitis

Dermatitis can arise in an even more difficult form from some of the high-performance coating resins such as the epoxies and some of their curing agents. The liquid epoxies are particularly hazardous in this regard, and many people have been seriously incapacitated because of allergic reactions and dermatitis from the epoxy resins. This type of dermatitis is apparently cumulative in that, once the person is sensitized, even limited contact with the resin will cause the dermatitis to break out again all over the body. In one instance a person became so sensitized that even if he entered the same room with the epoxy coating that caused the problem, he would again break out with a severe case of dermatitis.

The effect is very similar to poison oak, with leaking skin blisters and open skin sores developing. Often, these areas are on the parts of the body that sweat most, causing even more discomfort. Not all persons are affected in this manner, and some can be in contact with the resins over a considerable period of time without any ill effect. Nevertheless, the problem is sufficiently serious so that every care should be taken to prevent contact of the epoxy resins with the skin.

The solvents in epoxy coatings can make the problem more severe because they dilute the epoxy resins and the curing agents and make them more penetrating from the standpoint of wetting the skin and the pores. While the solvents themselves might not contribute to the actual dermatitis problem, they do increase the danger from the epoxy resins several fold, because they thin the resins and make them more liquid and therefore more penetrating.

Injuries to skin can be permanent. In the case of aliphatic hydrocarbons, this can be true. Aliphatic solvents break down the fatty tissue in the skin; this is the connective tissue between the skin and muscle. The skin, without sufficient anchor, pulls itself apart, resulting in open, painful lesions. Some older diesel mechanics suffer from this fate because diesel is an aliphatic solvent. This greatly illustrates the use of proper polypropylene (PPE) made of the correct material for the hazard.

Inhalation of Solvents

Regarding inhalation injury, Doolittle states:

> The volatility of most industrial solvents is not great enough to permit a concentration to be reached sufficient to reduce the oxygen content below that necessary to support life, even though the atmosphere were to become saturated with the solvent vapor. Accordingly, injury to a person from entering storage tanks and confined spaces saturated with solvent vapors is not usually caused by oxygen deprivation but is a true toxic process.
>
> Injury from single exposures to the vapors of solvents is most likely to consist of partial or complete anesthesia, because most of them are narcotic agents. The earliest stages of narcosis are not infrequent. These consist of a sense of well-being (euphoria), impairment of judgment, and an increase in reaction time. It is this pleasant state which leads to addiction to some vapors, notably trichlorethylene, tetrachloroethylene, and ethylene. Vapors of the fluid hydrocarbons and the alcohols are too irritating when inhaled to allow frequent addiction to develop.[3]

Several cases are known where applicators have removed air masks and reacted as if they were in a happy state of drunkenness. In one instance, a worker was found sitting on the bottom of a tank, completely oblivious to where he was, singing at the top of his voice. If he had not been noticed by a fellow worker on the outside of the tank, he soon would have been in a much more serious state. In another situation, an applicator was finishing the coating of a tank and was standing so that he was half in and half out of the manhole. This reduced the ventilation to a minimum and he passed out hanging in the manhole. Again, a fellow worker saved him. This demonstrates that even a short exposure to strong solvent fumes can create serious physical problems.

Solvents of any sort in a closed area are a serious hazard. Doolittle continues:

> The odor of almost any solvent is sufficiently strong so that the critical workman should feel warned against inhaling sufficient to cause anesthesia. However, complete anesthesia from entering storage tanks inadequately purged of vapor or from major spills of solvent is quite possible. If anesthesia persists for more than a brief interval, death may ensue, due to arrest of respiration or circulation. If an anesthetized person is removed to clean air promptly enough to regain consciousness, he suffers no permanent injury from most solvents, but some chlorinated hydrocarbons and ethylene oxide derivatives may cause serious kidney injury which will result in death after several days. Anesthesia from almost any solvent will cause some degree of lung irritation, and rest under medical care is advisable to guard against a serious respiratory infection.
>
> Accumulation of solvent in the blood due to slow elimination overnight increases the tendency toward accidents. As blood concentrations increase day after day, the degree of narcosis rises until judgment and reaction time are impaired. However, this phenomenon is not what is meant by chronic injury. When enough vapor is inhaled each day to cause damage to liver cells, for instance, which is too great for natural processes to repair overnight, then each day increases the liver injury, and it is considered that chronic poisoning is taking place. Eventually the surplus of functioning tissue in the organ is eliminated and after months of daily inhalations the victim begins to perceive symptoms. At some earlier stage a clinical study might have revealed the injury, but unless careful periodic medical examinations are made the damage will be undetected until it has progressed far. In most cases adequate function will be restored if the workman is shifted at the earliest symptoms to a job where he does not inhale the vapors. A notable exception is benzene, which has been known to kill by its injury to the bone marrow months after the last inhalation. The odor of most solvents cannot be depended upon to protect workmen from inhaling enough to cause chronic injury. Dangerous concentrations may build up in a working environment without causing discomfort, because of olfactory fatigue. The same phenomenon explains the lack of perception by a workman of the gradual failure of a chemical cartridge respirator or leakage in an air hood.
>
> The commonest sites of chronic injury from solvents are kidney, liver, blood-forming organs, central nervous system, and peripheral nerves. The early symptoms of chronic injury are seldom sufficiently characteristic to lay the blame upon a particular solvent in a mixture. They are part digestive disturbances, a feeling of oppression in the chest, fatigue, insomnia, restlessness, nausea, shortness of breath, personality changes, anemia, and loss of weight. The diagnosis of the cause of such symptoms is difficult for the physician...In view of this lack of sensitivity in diagnosis it is desirable that every effort be made to control exposures so that no injury results.
>
> When workmen first handle a new solvent there is likely to be a wave of complaints of weakness, nausea, insomnia, and the like. These should never be ignored, because they may have a physiological basis. On the other hand, many times the complaints have only a psychological basis.

Usually after a few days or weeks no one feels the objectionable symptoms at all because the odor is now familiar. If processes and protective equipment had to be adjusted to the point where no one had any subjective complaint, vapor concentrations would have to be reduced to an extremely low level, far below the value at which the first physiological injury could develop. The above considerations show one of the difficulties encountered in trying to establish a fixed maximum allowable concentration for a particular material.

Injury by Skin Penetration

Skin penetration of solvents, and to a very minor extent of their vapors, occurs more frequently than is commonly supposed. Aniline and chlorohydrins are notorious offenders. Penetration through the skin leads to systemic injuries similar to those of in halation. The factors that influence the rate of skin penetration of a particular compound are not well defined. It is wise that unnecessary skin contact with any solvent should be avoided and that clothing wet with a chemical should be removed at once and laundered before being reworn.

Injury by Swallowing

It is probably correct that no industrial solvent except water can safely be swallowed, and that there is no excuse for drinking any of them, because the desirable effects one expects from a beverage will not result, or will be accompanied by such unpleasant side effects that the experiment will be unhappy or fatal. Nevertheless, almost every solvent has been drunk either by accident or by intent. Fortunately, a frequent result is the protective reflex of vomiting. When a solvent is swallowed it will produce all the effects that it would if inhaled in high concentration. Even lung irritation is to be expected because much of the dose will leave the body as vapor in the expired air.

Eye Injury

The entry of most solvents into the eye in the form of drops will cause corneal necrosis. Fluid should be flushed out of the eye at once with copious amounts of water. No other flushing solution will serve so well, even when the solvent is completely insoluble in water. If the eye is apparently damaged, expert medical aid should be sought.

High concentrations of vapors may result in similar damage to the cornea, and lower concentrations can cause chronic inflammation of the conjunctiva. There have occurred a few cases of very spectacular injury in which the cornea was so damaged as to be completely opaque; yet the only known exposure was to a moderate concentration of a usually inoffensive solvent vapor. One of these cases was traced to a vinyl or similar unsaturated impurity present in small concentration in the solvent. Happily there was no permanent loss of vision in any of these victims.[3]

The acute toxicity of a compound is the injurious effect that follows a single dose by mouth or on the skin or the inhalation of vapors for a single period up to one day. Chronic toxicity is the summation of small injuries acquired by many single doses or inhalation extending over a period of months or years. For the reasons stated above, the old rule of thumb to flush the eye with water for 15 minutes has been replaced with continuous flushing until medical help arrives.

Toxicity of Individual Solvents

Aliphatic hydrocarbons are so fat soluble or lipid soluble that they can attain a high concentration in the central nervous tissue. Their elimination from these areas is slow, primarily through the lungs. There is no significant metabolism of these materials within the body. The physiologic effect is simply one of narcosis, which reaches its peak at about eight carbon atoms. The longer carbon chain molecules are less of a problem. In several of the hydrocarbons, the anesthetic dose is very close to the fatal dose, so that even though straight chain hydrocarbons like kerosene appear innocuous, they can still cause difficulties. Multiple bonds in the molecule increase the narcotic effect, and a single exposure can lead to inebriation, nausea, headache, unconsciousness, convulsions, and even death.

Aromatic hydrocarbons or alicyclic hydrocarbons are more strongly narcotic than aliphatic ones and somewhat more readily metabolized. Turpines like turpentine injure the skin, lungs, and kidneys more than any of the others, with skin sensitization the most likely result. Aromatic hydrocarbons concentrated in tissues high in fats or lipids are, however, more readily metabolized than the aliphatic hydrocarbons, and the water soluble metabolic products can be eliminated through the kidneys. Benzene, because of its oxidation products, can cause changes in bone marrow and a marked reduction in white blood cells. Aromatics such as toluene or xylene cause less of a problem, even though their narcotic effect is greater. All aromatic hydrocarbon vapors are lung irritants. The very high fat solubility of chlorinated hydrocarbons causes them to concentrate in the fatty tissues and the brain. Elimination of these is through the lungs, but metabolism in this case is even greater than with hydrocarbons so that the metabolic products also are eliminated by the kidneys.

Chlorinated hydrocarbons are much more narcotic than corresponding hydrocarbons. In industrial applications, it is their chronic toxicity that is most important. Foods that are rich in protein and carbohydrates help to reduce the chance of injury by chlorinated hydrocarbons. The lower aliphatic alcohols are rapidly distributed in all of the body fluids and tissues because of their water solubility. The same factor delays elimination through the lungs. As the molecular weight is increased, water solubility drops and lung elimination rises, as does the narcotic power.

Primary alcohols are oxidized in the body to aldehydes and acids. When acids are easily oxidized, the reaction products are carbon dioxide (CO_2) and water. Primary alcohols are oxidized to ketones, while tertiary alcohols are narcotic agents with very little chronic toxicity. Unsaturated alcohols of only a few carbon atoms are much more toxic than the corresponding saturated compounds, and skin penetration is also possible. Esters are even more powerful narcotic agents than alcohols, but they are easily saponified by the body enzymes, and their physiologic effect is chiefly that of alcohol and acid. Few, if any, of the alcohols and carboxylic acids manifest chronic toxicity to any significant degree.

Ketones and aldehydes are largely devoid of chronic toxicity, although the introduction of the double bond between carbon atoms creates a tendency in that direction. Aldehydes are highly irritating to the skin, eyes, and respiratory tract, and the unsaturated representatives are outstanding in this respect. Ethers are little changed within the body, if at all. They react like narcotic agents, but their low water solubility leads to rapid elimination of the more volatile members through the lungs. Chronic toxicity is generally absent. Glycols and their derivatives, if sufficiently absorbed, injure the kidney to some extent and chronic poisoning is possible. All in all, chronic toxicity is expected of benzene and, to a limited extent, of the other aromatic hydrocarbons.

Chronic toxicity is also a characteristic of the saturated chlorinated hydrocarbons, many nitrogen compounds, glycol derivatives, and carbon disulfide. The other solvents, with a few exceptions, are harmful during industrial exposures absorbed during any one day. There can be some accumulation in the blood due to slow elimination of the solvent, but there is not the continuing day-after-day

TABLE 16.5: Threshold Limit Values of Common Solvents

	Threshold Limit Value Time Weighted Avg. TLV–TWA ppm in Air mc/cu m Air	Threshold Limit Value Short Term Exposure Limit TLV-STEL ppm in Air mg/cu m Air	Major Health Hazards
Acetone	500	1000	A4, CNS, URT, eye irritant and hematological effects
Benzene	.5	2.5	Leukemia
n-Butyl Acetate	150	200	Irritation to eyes and Upper Respiratory Tract (URT)
sec-Butyl Acetate	200	250	Irritation to eyes and Upper Respiratory Tract (URT)
Carbon Tectrachloride	5	10	A2 and liver damage
Chloroform	10	50	CNS, Liver damage; Embryo/Fetal damage
Cyclohexanone	20	50	Eye irritant and Upper Respiratory Tract (URT)
Diacetone Alcohol	50	7	Eye irritant and Upper Respiratory Tract (URT)
Diisobutyl Ketone	25	–	Eye irritant and Upper Respiratory Tract (URT)
Ethyl Acetate	400	–	Eye irritant and Upper Respiratory Tract (URT)
Ethyl Alcohol (Ethanol)	–	1000	A3, Eye irritant and Upper Respiratory Tract (URT)
Ethyl Ether	400	500	CNS, Eye irritant and Upper Respiratory Tract (URT)
Ethylene Dichloride	10	15	A4, Liver Damage and Nausea
Furfuryl Dichloride	10	15	Eye Irritant, Skin and Upper Respiratory Tract (URT)
Gasoline	300	500	A3 and Lower Respiratory Tract
Heptane	400	500	Central Nervous System, Upper Respiratory Tract
Hexahydrophenol (Cyclohexanol)	50	–	CNS, Skin, Upper Respiratory Tract
n-Hexane	50	–	Eye, CAN, Peripheral neuropathy
Kerosene	–	200	CNS, Skin, Upper Respiratory Tract (URT)
Methyl Acetate	200	250	Eye, Headache, Ocular nerve damage, URT
Methyl Alcohol (Methanol)	200	250	Dizziness, Eye, Headache, Nausea, Skin damage
Methyl Chloride	50	100	CNS, Liver, Kidney and Testicular Damage
Methyl Ethyl Ketone (Butanone)	200	300	CNS, Peripheral Nervous System, URT
Methyl Isobutyl Ketone (Hexone)	20	75	A3, Dizziness, Headache and URT
Nitroethane	100	–	CNS, Liver Damage, Upper Respiratory Tract (URT)
Nitromethane	20	150	A3, Lung Damage, Thyroid Effects, (URT)
1-Nitropropane	25	–	A4, Liver Damage, Upper Respiratory Tract (URT)
Propylene Oxide	2	–	A3, Eye, Upper Respiratory Tract (URT)
Stoddard solvent (Mineral Spirits)	100	200	Eye, Skin and Kidney Damage, Nausea, CNS
Toluol (Toluene)	20	150	A3, Female reproduction, Pregnancy loss
Toluene-2, 4-Diisocyanage (TDI)	.005	.02	A4, Respiratory, Sensitization
Trichloroethylene	10	25	A2, Cognitive Decrements, CNS, Renal toxicity
Turpentine	20	–	A4, CNS, Lung and skin damage, URT
Xylol (Xylene)	100	150	A4, eyes, CNS URT

Source: Threshold Limit Values for Chemical Substances and Physical Agents in the Workroom Environment with Intended Changes for 2013, American Conferences of Governmental Industrial Hygienists, Lansing, MI.

(1)Threshold Limit Value-Time Weighted Average (TLV-TWA)—the time-weighted average concentration for a normal 8-hour workday and a 40-hour work week, to which nearly all workers may be repeatedly exposed, day after day, without adverse effect

(2)Threshold Limit Value-Short Term Exposure Limit (TLV-STEL)—the maximal concentration to which workers can be exposed for a period up to 15 minutes continuously without suffering from (1) irritation, (2) chronic or irreversible tissue change, or (3) narcosis of sufficient degree to increase accidental proneness, impair self-rescue, or materially reduce work efficiency, provided that no more than four excursions per day are permitted, with at least 60 minutes between exposure periods, and provided that the daily TLV-TWA also is not exceeded. The STEL should be considered a maximum allowable concentrate, or ceiling, not to be exceeded at any time during the 15-minute excursion period.

Abbreviations:
A1: Confirmed Human Carcinogen
A2. Suspected Human Carcinogen
A3: Confirmed Animal Carcinogen with Unknown Relevance to Humans
A4: Not Classifiable as a Human Carcinogen
CNS: Central Nervous System
LRT: Lower Respiratory Tract
PNS: Peripheral Nervous System
URT: Upper Respiratory Tract

TABLE 16.6: Equivalent TLVs in mppcf and mg/m³ (Repirable Mass for Mineral Dusts)[1]

		Threshold Limit Value	
Substance	Count mppcf[4]	Respirable Mass mg/m³	Total Mass[2] mg/m³
Silica (iO_2)			
Amorphous	20	(3)[3]	(6)
Cristobalite	1.5	0.05	0.15
Fused Silica	3	0.1	0.3
Quartz	3	0.1	0.3
Tridymite	1.5	0.05	0.15
Coal Dust	(12)	2	(4)
Diatomaceous Earth (Natural)	–	1.5	–
Graphite (Natural)	15	(2.5)	(5)
Mica	20	(3)	(6)
Mineral Wool Fiber	–	(5)	10
Nuisance Particulates	30	(5)	10
Perlite	30	(5)	(10)
Portland Cement	30	(5)	(10)
Soapstone	20	(3)	(6)
Tripoli	(3)	0.1	(0.3)

Source: Threshold Limit Values for Chemical Substances and Physical Agents in the Workroom Environment with Intended Changes for 2013, American Conferences of Governmental Industrial Hygienists, Lansing, MI.

[1]Assuming that the massmedian diameter is 1.5μm and density is 2.5 g/cm³.

[2]Unless otherwise specified, respirable mass is presumed to equal approximately 50% of total mass.

[3]All values in parenthesis () represent newly calculated values based on equivalence of 6 mppcf = 1 mg/m³ respirable mass and respirable mass is 50% total mass.

[4]mppcf = millions of particles per cubic foot of air, based on impinger samples counted by light-field techniques.

injury, which is the criterion of chronic effect.

Table 16.5 lists a few of the more common solvents that may be encountered when high-performance coatings are used. The threshold limit value (TLV) is given and is listed in two ways: (1) threshold limit value-time weighted average (TLV-TWA); and (2) threshold limit value-short term exposure limit (TLVSTEL). The definition of these terms is given by the American Conference of Governmental Industrial Hygienists (ACGIH).

These limits should be used as guides in the control of health hazards and should not be used as fine lines between safe and dangerous concentrations. These limits were previously referred as maximum allowable concentrations or MAC. The National Institute of Occupational Safety and Health (NIOSH) list stricter levels for many of the same chemicals.4 The government authority for the area where the work will take place controls exposure levels.

Dusts

There are some dusts substances that may be involved in the application of high-performance coatings. These are materials such as quartz sand, flint grit, garnet, most beach or river sands, and a number of the synthetic abrasives such as copper slag. The ones containing silica are the most difficult from a health hazard standpoint. However, even copper slag has a TLV, as it would be in the class of Nuisance Dusts (particulates). These are described by the ACGIH in this way:

> Nuisance Particulates. In contrast to fibrogenic dusts, which cause scar tissue to be formed in lungs when inhaled in excessive amounts, so-called "nuisance" dusts have a long history of little adverse effects on lungs and do not produce significant organic disease or toxic effect when exposures are kept under reasonable control. The nuisance dusts have also been called (biologically) "inert" dusts, but the latter term is inappropriate to the extent that there is no dust that does not evoke some cellular response in the lung when inhaled in sufficient amount. However, the lung-tissue reaction caused by inhalation of nuisance dusts has the following characteristics: (1) The architecture of the air spaces remains intact; (2) collagen (scar tissue) is not formed to a significant extent; (3) the tissue reaction is potentially reversible.
>
> Excessive concentrations of nuisance dusts in the workroom air may seriously reduce visibility, may cause unpleasant deposits in the eyes, ears, and nasal passages (Portland Cement dust), or cause injury to the skin or mucous membranes by chemical or mechanical action per se or by the rigorous skin cleansing procedures necessary for their removal.[5]

Table 16.6 provides a list of materials that, as dusts, are considered hazardous.

Pigmentation

In addition to the hazards involved in solvents and resins, there are also some hazards that result from the pigmentation of high-performance coatings. Many of the toxic pigments are used in prime coats as corrosion inhibitors. The vinyl wash primer coating systems contain red lead in the vinyl intermediate coat, which follows the wash-prime coat. In this case, it is a very effective inhibitor and well worth the extra safety precautions that should be used during its application. The wash primer also contains active chromates as

inhibitors in addition to phosphoric acid, both of which can be a hazard if in contact with the skin or eyes.

Lead compounds, in addition to red lead, may be incorporated in many different binders (e.g., alkyds, epoxies, vinyls, acrylics, etc.). The types of lead compounds that may be found, in addition to red lead, are metallic lead, lead chromates, chrome yellow, chrome orange, chrome green, basic lead silica chromates, basic lead carbonate, basic lead silicate, blue lead, di-basic lead phosphite, and di- and tri- basic lead phosphosilicates. These are all good pigments. Unfortunately, all lead compounds are toxic to a greater or lesser extent. While lead has come into disuse in the United States, and many other countries, it is still used. Of course, its residue is that the same hazards of the dust in application are the same for removing the coating.

Of all the "soluble" types of inhibitive pigments, the best known and probably the most effective are the chromates. These materials ionize in water to provide a source of hexavalent chromium ions, the active inhibitor. Chromates are available in a wide range of solubilities, from completely soluble sodium chromate to relatively insoluble lead chromate. Among pigments, calcium chromate ($CaCrO_4$) is the most soluble, but when used alone, is too fugitive for long- term protection. The less soluble zinc-potassium complex ($4ZnO{\cdot}K_2O{\cdot}4CrO_3{\cdot}3H_2O$, known in the United States as zinc yellow and in Europe as basic zinc chromate) is one of the more widely used pigmentary inhibitors in the coatings industry.

Still less soluble is strontium chromate ($SrCrO_4$). This pigment is soluble enough, however, to provide effective primer compositions. It has been used to a greater extent in high-performance coatings than basic zinc chromates, because of its reduced solubility. Its lower solubility gives it better stability (compared with zinc yellow) in water-based coatings, which are highly sensitive to large amounts of hexavalent chromium ions and, consequently, are difficult to pigment. Unlike zinc yellow, strontium chromate is a noncomplex pigment, free of hydratable material and, therefore, quite heat stable up to 1,000 °F (538 °C).

Zinc tetroxy chromate ($5ZnO{\cdot}CrO_3{\cdot}4H_2O$, often called basic zinc chromate in the United States) is a lower solubility chromate with limited use in inhibitive primers, although it is the principal pigment of the WP-1 wash primer pretreatment [DOD-P-15328D (1978)]. Barium chromate ($BaCrO_4$) and lead chromate ($PbCrO_4$) have even lower solubility and show little promise as corrosion inhibitors for coatings, although lead chromate is the prime ingredient in the pigments known as chrome yellows and chrome oranges, which are used in finish coats because of their good color and opacity.[6]

Toxicity is an important consideration in the use of chromates. Hexavalent chromium has long been suspected of being a carcinogen, and is presently under investigation by several organizations around the world. Recent data from studies involving chromates indicate some connection with its use and the incidence of lung cancer.[6] Safety precautions should be used when applying or removing coatings that contain these pigments.

However, toxic pigments are felt to be less of a hazard than the danger of fire or explosion, since proper clothing and masks can effectively reduce any toxic hazard to a minimum. Also, pigments are incorporated into and coated by the coating resin and are reasonably well encapsulated. The danger from pigmentation is primarily due to physical contact of the coating on the skin, or inhalation of the resinous coated pigments due to dry spraying of the coating during application or during the removal of an existing coating. Hazards from pigmentation can usually be eliminated by the use of protective clothing and the proper respirator equipment. One can now consult USA OSHA rules as a best practice in this regard at 29 CFR 1910.1026. which can be found at www.osha.gov.

Some of the tin compounds used in antifouling coatings are not nearly as easy to handle. Some of these materials are in liquid form, others are solids. Nevertheless, they have strong toxic characteristics, and persons spraying antifouling coatings can inhale sufficient fumes or dust to cause nausea, dizziness, and similar symptoms. Antifouling coatings may also contain such materials as Paris Green (copper acetoarsenite), mercury compounds, organic biocides, and so on, as well as the common copper compounds (copper oxide, metallic copper). Again, protective clothing and the proper respirators are generally adequate to fully protect the applicator.

Other Chemical Compounds

There are also other chemicals that may be encountered during the coating of structures. Metal surface treatments for zinc and copper are commonly used. Usually these are acidic and may contain some organic liquid as well. Paint removers are often strongly alkaline and may contain strong and very penetrating organic materials, such as phenols. Proprietary metal cleaners of various types may be strongly acidic or alkaline. Brush cleaners often contain strong solvents, as well as other organic compounds such as phenols; and proprietary oil, grease, and sludge cleaners may contain aromatic solvents. All should be treated with caution, and proper protective clothing, masks, gloves, and goggles should be used when handling such compounds.

Urethane

Urethane coatings have, in addition to solvents and pigments that can cause safety hazards, isocyanate reaction products. These are toxic materials and add a special hazard to the use of urethane coatings.

Like several other substances used in coatings, isocyanates can irritate the skin, eyes, and respiratory tract of anyone coming into contact with the vapor or spray mist. Isocyanates may also cause an allergic sensitization or asthmatic response in some susceptible individuals. The distinction between irritation and sensitization-type (allergic type) reactions to isocyanate exposure is very important. Different measures should be taken to protect the individual for each case.

Irritation is a direct response resulting from the contact of isocyanates on the body surface (i.e., skin, mucous membranes of the nasal passages, throat and respiratory tract, eyes, etc.). Irritation will take place at airborne levels of about 400 parts per billion (ppb) in most individuals. Symptoms usually include watering of the eyes and a burning sensation in the nose and throat. The amount of irritation is dependent upon the dose, tissue exposed, and individual susceptibility, but it is generally independent of the individual's exposure history. These acute symptoms are generally reversible.

Sensitization, on the other hand, is a totally different type of response. Sensitization is believed to occur only in certain susceptible individuals as a result of numerous exposures and/or exposure at a high concentration. Exposures after this sensitization has taken place result in an allergic respiratory reaction similar to asthma. The response usually includes coughing, wheezing, shortness of breath, and tightness in the chest. The symptoms may be immediate or delayed. The airborne concentration of isocyanates necessary to cause a reaction in a sensitized individual is much lower than that which will cause an irritation response in most people, and may be as low as 5 ppb. Skin sensitization can also develop in some individuals as the result of direct contact with certain isocyanates. Once

sensitized, these individuals when exposed to isocyanate vapors at concentrations that have no effect whatsoever on most people, or when they come in direct contact with very small quantities of the liquid, may develop a rash, swelling of extremities, redness, and scaling of the skin.

If an individual experiences an irritation response while handling urethane coatings, it should be determined whether or not contact with the isocyanate has caused the irritation. If isocyanate contact was the cause of irritation, a careful evaluation of the handling and/or application procedures should be made. If irritation persists in spite of proper protective measures, ventilation, and personal protection equipment, the individual should be removed from areas where isocyanates are processed or used.

Note: Persons having a sensitization response to isocyanates must not be exposed further to vapors or spray mist containing isocyanates.[7]

The isocyanate effect from the contact of liquid coating can be increased because of the solvents used in the coating. These may be ketones or aromatic solvents, both of which aid in the wetting and penetration of the skin. Proper masks and protective clothing should be used during the application of the urethane coatings. The question then becomes what is a proper mask? NIOSH, the research arm of the Centers for Disease Control in the United States, recommends a level of .005 ppm for a TLV-TWA. At this level, an organic vapor cartridge stacked with a HEPA filter may give adequate protection. However, a break in the face seal while talking or moving could allow a concentration far above that level. For one Isocyanate compound (toluene-2,4-diisocyanate), NIOSH recommends supplied air full-face respirators at any detectable level. Isocyanates are the chemical group that was released from a Union Carbide facility in Bhopal, India in 1984. As of 2013, as many as 15,000 deaths have been confirmed from the release. Most industrial hygienists recommend only supplied air respirators when working with or around these coating systems.

Exterior Applications

There is no doubt that all of the previously described hazards exist during the application of protective coatings. However, if proper precautions are taken to eliminate the hazards, the actual risks involved can be quite low. The application of most protective coatings on the exterior of equipment, tanks, and structural steel generally provides rather low risks to the applicator. The reason is that there is free circulation of air surrounding the applicator, with a rapid dilution of any of the solvent or coating spray. With only a mild air movement, the solvent and any overspray from the resin coating are rapidly dispersed and moved away from the actual point of application. Unless the air movement is directly toward the applicator, he or she is in little danger of overexposure to the hazardous materials. There are, of course, areas in exterior applications where solvents might accumulate and not be dispersed as rapidly as indicated above. These areas should be considered the same as enclosed areas, and safety precautions taken in the same manner. Before undertaking any project with an unfamiliar coating system, consultation with an experienced safety professional or industrial hygienist is highly recommended. These persons are capable of calculating exposures during the planning stages. Professionals certified as Certified Industrial Hygienists (CIH), Certified Safety Professionals (CSP), or Chartered Members of the Institution of Occupational Safety & Health (CMIOSH) are the preferred professionals for this consultation.

Enclosed Areas

As discussed previously, the primary areas of exposure to solvents and other coating ingredients are those that are enclosed (e.g., the interior to tanks, vessels, and ships, even the interior of rooms, pump enclosures, manholes, wet wells, or similar areas). When the coating is applied on the interior of such areas, solvents evaporate from the coating and build up a concentration of solvent vapor in the air. The most effective way of preventing a hazardous condition is to dilute the solvent concentration by mixing it with additional air; that is, proper ventilation. If the solvent vapor concentration in air cannot reach the level of 1% in the enclosed area, then no explosion can occur. Air dilution is also applied to the maximum allowable concentration of solvent to which the applicators may be exposed. The greater the dilution of the solvent concentration in an enclosed area, the less physical contact that is possible. Physical exposure, as well as fire and explosion hazards, are reduced by proper ventilation.

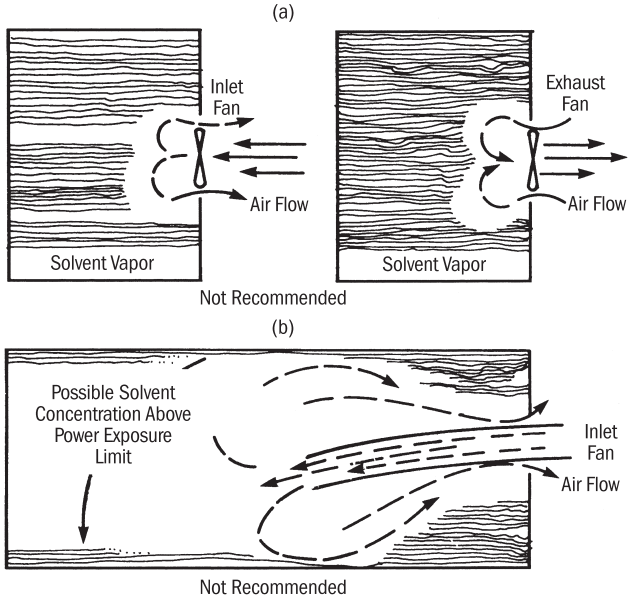


FIGURE 16.1 (a) Placing the blower in the tank opening is not recommended because air is circulated only at the opening. (b) Extending the short trunk from the blower may be unsatisfactory because air is not evenly circulated. Source: C.G. Munger, "Safe Application of Protective Coatings—Recommended Practices," *Plant Engineering* (March 21, 1974).

Ventilation

Proper ventilation is the key to safe application of coatings on the interior of closed areas. Its significance cannot be overemphasized from the standpoint of fire, explosion, or health. It is too often mistakenly assumed that proper ventilation is provided by placing a fan or blower in a manhole, doorway, window, or tank opening and blowing air into the area where the coating is being applied. Unfortunately, the dilution of the contaminated air occurs at the inlet, the pressure from the fan pushing air in and the internal pressure immediately pushing it out the same opening. The same is true with an exhaust fan under the same conditions. In this case, the exhaust fan pulls some of the contaminated air from the interior, but does it primarily at the opening. The suction pulls air from the outside around the fan and does not allow proper air dilution deeper in the interior of the closed area. Even if a short ventilation duct is used and air is blown in with a blower through the duct, it only changes the air in the area of the end of the

duct, forcing the incoming air out through the opening where the blower is located.

These types of ventilation and the path of air circulation are shown in Figure 16.1. It can be seen that most of the air in the enclosed space is static under these conditions and is not circulated or diluted. This allows the concentration of solvent and fumes to build up above the maximum allowable concentration or the lower explosive limit, both of which are hazardous conditions.

In order to provide proper ventilation to the interior of an enclosed area, air must be exhausted rather than blown into the area. Air blown into the area does not create the same degree of ventilation as does the exhaust of air from the same enclosure. When solvent vapors are heavier than air, as previously indicated, they tend to fall to the bottom of an enclosed space or tank and accumulate there. Thus, the exhaust system must draw the air from the lowest portion of the tank or enclosed space. This automatically draws air from the upper portion of the tank down across the bottom and into the duct. When this is done, clean air from the outside washes down from the upper portion of the tank, bringing the heavier-than-air solvents with it, and is immediately evacuated from the lowest portion of the enclosed area. This provides the most effective ventilation and the maximum removal of solvents.

The interior of a tank or container is often quite complicated, with a number of baffles or, in the case of a tank aboard ship, the area is filled with reinforcing members, stiffeners, and similar structural members. These can divide the lower portion of the interior of the tank into isolated spots where the air circulation is not good unless the duct system is designed to bring the solvent fumes and air from each one of these isolated areas. For example, in some of the liquid natural gas vessels, there are approximately 600 individual compartments that are joined only by small manholes. The evacuation of the solvents in a complicated structure such as this is both necessary and extremely difficult. In cases such as this, holes actually had to be made in the hull of the ship to provide the proper ventilation required when the interior of these compartments was coated.

Again it must be stressed that suction blowers in combination with forced air are the most satisfactory method of removing vapors from a closed area. Blowing air into a tank alone is not satisfactory since circulation of the air does not reach many portions of the tank without an exit for the mixed air. The ACGIH has published its extensive research into ventilation in *Industrial Ventilation: A Manual of Recommended Practice,* 25th Edition. This text has become the accepted manual for calculating ventilation.

Each individual tank is different. However, if the principle of pulling the air from the lowest portion of the tank is practiced, good air circulation and solvent removal should result. In addition, suction fans in combination with forced air tend to lower the air pressure to some degree within the enclosed area, making for more rapid solvent dispersion and solvent evaporation.

During World War II, there were many underground concrete storage tanks lined with vinyl and other coatings to resist the petroleum products that were to be stored in these tanks. They were quite large, approximately 100 ft (30.5 m) in diameter and 30 ft (9 m) deep, and for the most part, since they were underground, had only one or two manholes in the tanks and these were in the top. The manholes were large, and 3-ft (0.9-m) diameter suction trunks were dropped through the top manhole to the bottom of the tank with a large suction blower attached at the top. Even though the solvents for the vinyl coatings were extremely volatile and a large amount of coating was applied in any given period, air circulation in these tanks was sufficient so that there was no solvent problem in the interior of the tank. The 20,000-ft3 (566 m^3) suction blower changed the air in the tanks every 10 minutes. Air circulation was sufficiently good so that the solvent-air mixture was kept far below the level of either a health or explosion hazard.

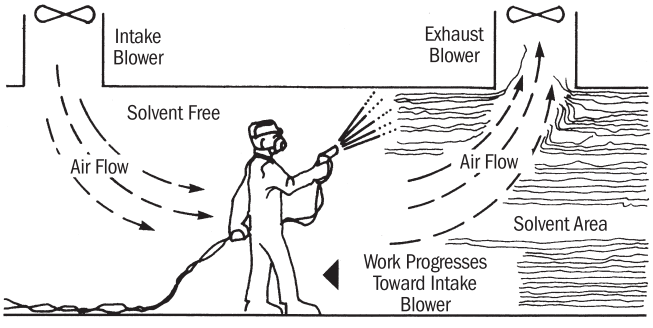


FIGURE 16.2: A suction blower at one manhole and a pressure blower at a second manhole provide a solvent-free work area in pipes and ducts. Source: C.G. Munger, "Safe Application of Protective Coatings—Recommended Practices," *Plant Engineering* (March 21, 1974).

The coating of large ducts, tunnels, or pipe also presents a ventilation problem, even though it is an easy one to correct, providing that the personnel working in the area understand how to cope with the ventilation. In this case, there should be two openings into the pipe or tunnel. An exhaust blower should be used at one of the openings and a pressure blower or intake fan should be placed at the other opening. The coating work should be started adjacent to the suction outlet, with the flow of air coming toward the worker, who then works toward the air inlet with his or her back toward the air flow. With this procedure, all of the solvent vapor and contaminated air are swept away from the point of application and the worker is constantly in a flow of fresh air. This type of operation is shown in Figure 16.2, which indicates the proper procedure for such work.

Buddy System

One mandatory safety procedure in the application of coatings in an enclosed area is the buddy system. Application of coatings by a single individual in such places not only increases the hazards involved, but should the unforeseen take place (e.g., solvents causing a worker to pass out), there is a much better chance of a warning and immediate remedial action by the second worker in the area. If the enclosed area is small, the second person should be watching through the manhole. If the area is large, more than one person usually will be working anyway. Two people working as a team should always be in reasonably close contact (by safety harness and rope if feasible) so one can provide immediate help to the other should any problem occur.

Solvent Retention

One of the items that must be kept in mind when applying solvent-containing coatings to the interior of a closed area is that the solvents are retained in a coating for a considerable period of time after it is applied to the surface. While it is true that a large amount of the solvent is evaporated in the first few minutes during and after application, solvents are retained in the coating film in sufficient volume so that the lower explosive limit can be reached, particularly in low areas of the enclosed space. Thus, it is necessary to continue the ventilation of the closed space for several hours following the last of the coating application on the interior. This is necessary

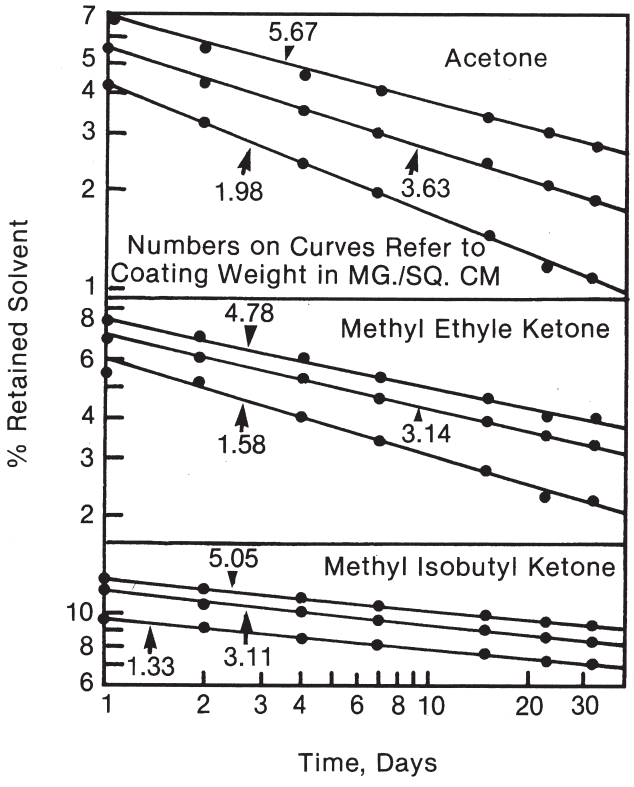


FIGURE 16.3: Percentages of solvent retained by a vinyl film. Source: A.K. Doolittle, Technology of Solvents and Plasticizers (New York, NY: John Wiley and Sons, 1954).

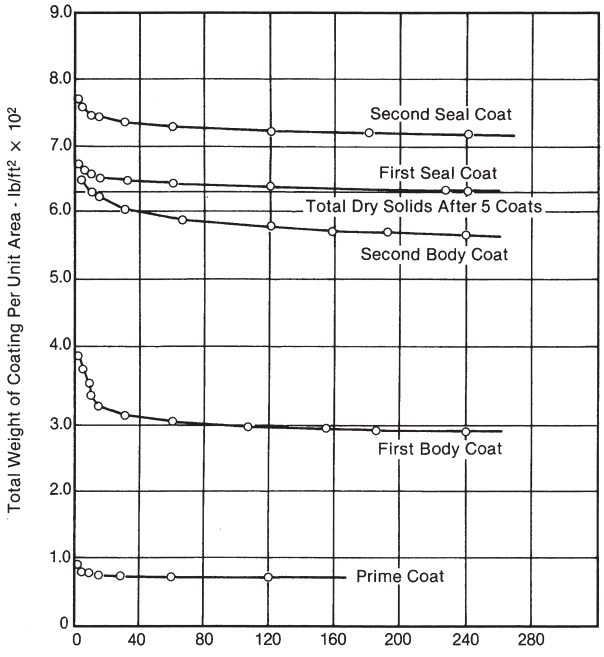


FIGURE 16.5: Evaporation rate from a five-coat epoxy tank lining. Source: C.G. Munger, "Coatings and Their Safe Application," Marine Section National Safety Congress, 1964.

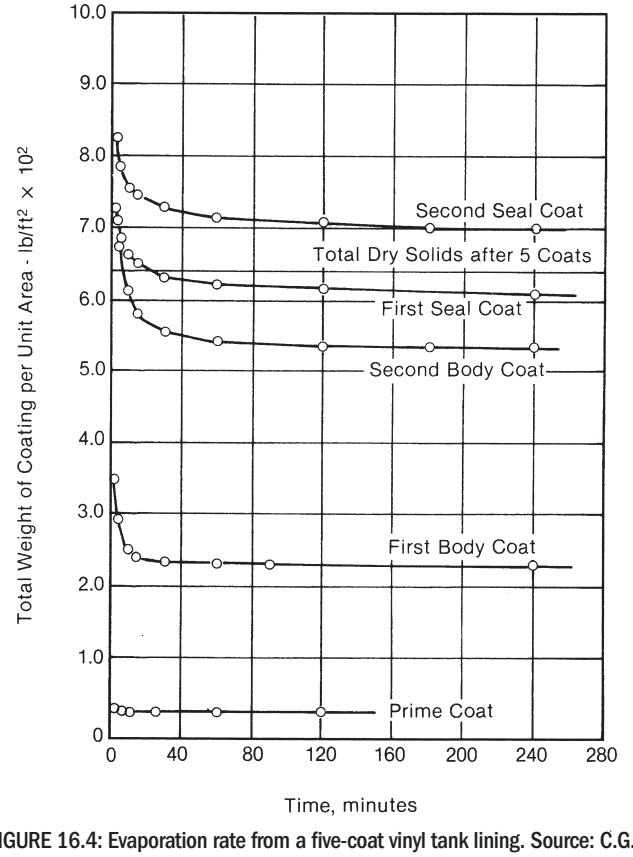


FIGURE 16.4: Evaporation rate from a five-coat vinyl tank lining. Source: C.G. Munger, C. G., "Coatings and Their Safe Application," Marine Section National Safety Congress, 1964.

to make sure that the solvent evaporating from the film does not build up to a lower explosive limit and created an explosion hazard (as was demonstrated by the welder mentioned earlier who used the manhole over a tank to cut a piece of steel).

Figure 16.3 shows the percent of retained solvent for different thicknesses of coating using different solvents. As this figure illustrates, higher boiling solvents are retained for a much longer period and in a greater concentration than the lower boiling ones. This same phenomenon is indicated in Figures 16.4 and 16.5, where two different coatings were applied and the solvent evaporation measured after each coat had been applied. Figure 16.4 shows the evaporation from the various coats of a five-coat vinyl system, and indicates that most of the solvent evaporated within a matter of minutes, but that the solvent continued to evaporate over a period of several hours. As each coat was applied, it took a greater period of time to evaporate the solvent from the coating, since the solvent from each individual coat penetrated the previous one. With the greater thickness of coating after each coat, a longer drying period was required.

Figure 16.5 shows the same information for a five-coat epoxy coating. In this instance, the epoxy was an amine-catalyzed coating. The drying of the solvents from the coating was somewhat slower than that for the vinyl, as indicated by the continuing slope of the solvent evaporation curve. This indicates that a considerable volume of solvent remained in the coating for a period of several hours, enough to create a hazard if the ventilation of the enclosed space is not continuous for several hours after the initial application of the coating. Even though this explosive limit in the tank probably would not be reached for the entire tank volume, there is sufficient solvent left in the coating for it to concentrate in the bottom of the enclosed space. If a spark of some type were to occur, a damaging explosion could take place with the solvent concentration in the lower areas of the structure. The primary safety precaution for enclosed spaces, then, is to continue the ventilation in a tank or enclosed area several hours after the application, not only to reduce the hazard from fire or explosion, but also to aid in the speed of the drying of the coating. Many countries have regulatory requirements on working in confined spaces. The United States has perhaps the most comprehensive procedure for reducing and/or eliminating hazards associated with

this type of work. This regulation, 29 CFR 1910.146, suggests using CIHs and CSPs to advise on acceptable entry conditions by the use of ventilation and/or gas monitoring.

Hearing Protection

The human ear is an extremely delicate mechanism. When a sound enters the ear and hits the eardrum, it vibrates and transfers the vibrations to a set of three bones in the ear. These bones carry the vibrations to a liquid filled spiral tube, called the chochlea, then onto nerves that communicate with the brain and interpret the vibrations into what we call sounds. Because moving parts are involved, wear will happen over the years. The wear can "deaden" the sound and make it more difficult for us to recognize the signals sent from our ears. But wear on these bones is a small fraction of hearing loss. Remember that liquid-filled spiral tube? Inside the lining of the tube are extremely fine hairs. The fluid conveys the vibrations from the bones to the hairs. As they bend over from the flow of fluid they convey the noise into a signal that the nerve can carry to the brain to be interpreted as sound. If the flow of fluid is violent enough (meaning if the sound is strong enough), it can cause permanent damage to these hairs, which are important parts of the structure needed to transmit sound. The more hairs that are damaged, the less sound that can be passed on to the brain.

One of the most commonly overlooked areas of safety on a coatings job site is the need for proper hearing protection in accordance with the actual noise levels on each individual job sight. The Occupational Safety and Health Administration (OSHA) in the United States set a limit of exposure to an average of 90 decibels (dB) over an 8-hour workday. Most workers do not realize what decibel levels of noise exist in the workplace or in the home environment. The following tables have been reproduced from the May 2013 *CoatingsPro* article, "Hearing Protection Pointers."[8]

TABLE 16.7: Sound Levels by Source

Decibels	Source
20 dB	Ticking watch
30 dB	Quiet whisper
40 dB	Refrigerator hum
50 dB	Rainfall
60 dB	Sewing machine
70 dB	Washing machine
80 dB	Alarm clock (two feet away)
85 dB	Average traffic
95 dB	MRI machine
100 dB	Blow dryer, Subway train
100 dB	Power mover, Chainsaw
110 dB	Screaming child
120 dB	Thunderclap
130 dB	Jackhammer, jet plant (100 feet away)

Source: P. Engelbert, "Hearing Protection Pointers," *CoatingsPro* (May 2013).

TABLE 16.8: Permissible Noise Exposure

Duration Per Day (Hours)	Sound Level dBA Slow Response
8	90
6	92
4	95
3	97
1	100
1.5	102
1	105
0.5	110
0.25 or less	115

TABLE 16.9: Typical Noise Levels Associated with Abrasive Blasting

Source	Decibels
Air discharge from blast nozzle	112 to 119 dBA
Supply air inside operator's helmet	94 to 102 dBA
Abrasive blast cabinets	90 to 101 dBA
Air Compressors	85 to 88 dBA

Unfortunately, on a coatings job site, you cannot always remove the source of the damaging noise. You cannot remove the air compressor or avoid a blast pot, for example. However, you may be able to re-set or relocate the equipment farther away. According to environmental, safety, and health experts, if you double the distance between you and the equipment, the sound level drops by 6 dB. It doesn't sound like much, but it can be the difference between natural hearing or wearing hearing aids after a career in abrasive blasting and coatings application.

A key element that must be taken into consideration in choosing and wearing the proper hearing protection is the time of exposure to those levels. Measuring how many decibels are present on the site can be helpful in determining what type of hearing protection you need to assume. Several scales and monitors are available to help with this in the field. For coatings contractors, the A scale, shown as dBA, should be used to measure the industrial noise and the possibility of hearing damage. The following tables are a good reference to calculating how many decibels of noise you are encountering on your workday.

Pressure

Pressure has always been an issue from compressed air hoses and the like. However, a higher level of pressure is now present on the job site. With the substitution of high volatile organic compound coatings by epoxies, we have developed newer spray pump technologies for airless spraying. These pumps use pressure of the paint alone to force the paint along the hose and out of the gun. These pressures generated by modern airless pumps can be thousands of psi. At high pressure, the paint and any solvent can be injected through skin. These are life-threatening injuries and require immediate medical attention.

The mixed paint, when injected, appears to have left only a small puncture mark on the skin. This is deceiving. Large volumes of paint do get into the flesh. There will be some mechanical damage, but the chemical damage is severe. Treatment usually involves cutting the flesh open and scarping out the pigment and binder. Any solvent will most likely have been absorbed into the surrounding tissue and the bloodstream. In many cases, partial amputation is a result. Airless spray guns come equipped with a safety tip, a plastic wing that acts as a spacer to keep body parts further away from the tip itself. Some operating pressures can be high enough to still inject skin further than the reach of the safety tip, thus airless spray guns must be handled with the same measure of safety as a firearm.

Airless hoses must be rated for the pressures at which the pump can operate. Many applicators use whip checks at the hose connection to prevent hoses from whipping and striking employees if the coupling fails. These hoses must be flushed at least daily and hung to dry. The manufacturer's recommendations should be followed as part of accident prevention. The same issues exist for plural-component pumps. Maintenance of this equipment is vital to a safe application.

Summary

Taking all of the above information into consideration, the application of protective coatings can be reasonably free from fire, explosion, or health hazards if a few simple rules of safety are practiced. The rules are good for the application of any protective coating applied in an enclosed area or where solvents are an essential part of the coating.

1. Good ventilation is by far the most important safety rule. With adequate ventilation, there is little chance that the lower explosive limit of the solvent will be reached, and, if the lower explosive limit is not reached, no explosion can occur. Adequate ventilation also reduces health hazards. This is true whether the solvents are aliphatic hydrocarbons or low-toxicity or aromatic hydrocarbons with considerably more dangerous physiologic properties. Good ventilation is the key to coating safety practice wherever coatings are applied in enclosed spaces.
2. When ventilating an enclosed space, always use suction blowers in combination with forced air. Solvent vapors are often heavier than air, so that solvent concentration can build up in the lower areas of the enclosed space. Suction blowers should be operated in such a way that no solvent concentration can build up in pockets within the tank, and free air movement is available from all isolated spots. Air should be sucked into the blower system from the lowest portion of the tank. In this way, the solvents are swept down through the upper area and removed from the lowest area.
3. Ventilation should be continued in the coated area until the coating is sufficiently dry so that with the ventilation removed, no area in the tank will build up to an explosive limit.
4. Intrinsically safe equipment must be standard wherever coatings are applied on the interior of a confined space. Electrical equipment and lights must be intrinsically safe. Tools and shoes must be spark-proof. Safety equipment must be readily available and considered an essential part of any safety program covering the application of coatings to enclosed areas.
5. Smoking, matches, fire, flames, torches, and welding must be prohibited within 50 ft (15 m) of an area where coatings are being applied. This means 50 ft from where they are applied to the exterior of tankage and equipment, as well as 50 ft from the access openings to enclosed spaces.
6. Visitors and workers in enclosed areas must wear compressed air-type masks at all times to ensure that everyone always has a supply of clean, uncontaminated air. This is a simple safety precaution to prevent inhalation of solvent vapor.
7. Where epoxies, coal tar epoxies, coal tar, phenolic coatings, or polyurethane coatings are being applied, protective clothing should be worn to eliminate contact with the liquid coating. In many cases, proper protective ointments and creams are good precautions wherever skin areas are exposed to such coatings.
8. The buddy system must be practiced wherever coatings are applied to enclosed areas.
9. Never assume you know all the answers. Up-to-date training is a must, followed by refresher training. Preferred trainers carry board certification as Certified Environmental, Safety, and Health Trainers (CETs).

These simple rules are easy to follow for any worker, supervisor, or superintendent. If followed, they reduce to a minimum any hazards that are inherent in the coating process itself. Maximum safety can result for all workers in an area only if such rules are established for every coating application.

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APPENDIX 16A

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APPENDIX 16B

This material is for reference only. The last revision date was prior to mandatory regulations in the United States. Many specifics may have been superseded by government regulation. Users are cautioned to research government regulations at the location of the work.

A Manual for Painter Safety[1]

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[1]Source: A Report of NACE Technical Unit Committee T-6D (C.W. Sisler, Monsanto Chemical Company, St. Louis, Missouri, chairman) on Application and Use of Coatings for Atmospheric Service. Prepared by Task Group T-6D-5 (Lowell S. Hartman-Walsh Painting Company, St. Louis, Missouri, chairman) on Painter Safety, 1963.

Introduction

The Cost of Accidents

Disabling work injuries in all industries totaled 1.9 million in 1959. Of these, 13,800 were fatal, and 85,000 resulted in some form of permanent disability. The other resulted in financial loss and physical suffering to the employee and loss production to the employer.

The average cost per case resulting in fatality or permanent total disability was $13,862 in 1959. The average cost per case resulting in permanent partial disability was $1,911 in 1959. The average cost per case resulting in temporary total disability was $296 in 1959. Thus, the total dollar cost of accidents is more than $2.5 billion each year! The cost in suffering can never be measured, of course.

The Causes of Accidents

Records of the National Safety Council, the Insurance Rating Bureau, painting contractors, and safety engineers in several chemical plants and refineries show that as many as 70% of the most serious injuries to painters are caused by falls. Falling or moving objects are the next most serious hazard, followed closely by harmful substances. Back injuries caused by lifting and handling equipment follow. Injuries resulting from improper use of hand tools are the least frequent.

Analysis of all types of injuries shows that several major factors are responsible:

1. **Unsafe Working Equipment**. Structural and mechanical failure because of broken, frayed, or chemically damaged rope and cables; towers that lose balance because of improper bracing, guying, or tying-in; stages of improper length for depth of side rails or stages that are not cabled: extension ladders and step ladders that are not rodded or that are light weight rather than heavy weight; outriggers and wood stages with knots and cracks and without straight grain required in stress areas.
2. **Unsafe Working Conditions**. Inadequate protection from falling objects; unguarded machinery: moving equipment; areas where heat is excessive or where chemical gases are prevalent; inadequate ventilation in enclosed spaces.
3. **Unsafe Personnel**. Inexperienced personnel who select improper scaffolding, attach stages and rigging to improper areas of buildings and structures, fail to provide protection against friction on ropes, improperly secure ladders and stages, tolerate surfaces slippery with wet paint and/or other products, over-reach, fail to look out for moving objects such as cranes, point spray or sandblasting guns at other workmen, and engage in horseplay and practical joking. Personnel subject to stress, illness, and overindulgence that result in lack of concentration, carelessness, forgetting to comply with safety regulations, physical reaction, eye strain, taking a wrong step, and losing grip.
4. **Personality Traits**. Personality traits of the employee are important. In one industry, a study of accidents showed that 48% of the primary causes of accidents were faulty attitude; impulsiveness; irresponsibility; failure to pay attention; nervousness; fear, worry, and depression. If these six basic items that cause accidents could be eliminated, accidents could be reduced by 48%.

Steps to Improve Painter Safety

Study of the causes and frequency of accidents shows that a number of steps can be taken to improve painter safety. Among the more important of these steps, discussed more fully in later portions of this mannual, are:

1. A thorough medical examination prior to employment and at intervals thereafter.
2. Elimination of faulty attitudes.
3. A reasonable set of personnel safety rules and rules for safe working conditions.
4. Rules for the use of working equipment.
5. Instruction in the toxicity, health hazard, and flam-ability of many coatings materials, and in how best to protect the painter from harmful effects during exposure.
6. Instruction in the use of protective devices and protective clothing.
7. A continuing program of painter education.

I. Personnel Safety Practices

1. Medical Examinations and Medical Records

Reasonably good health and freedom from physical debilities that might tend to make an employee "accident prone" or susceptible to chronic illness should be made the first requisite of employment. Even the best safety precautions cannot help men who are physically or psychologically unsuited to do the work required.

A thorough medical examination that includes chest X-ray, back X-ray, electrocardiogram, check for presence of hernia, and blood and urine analyses should be made prior to employment. Permission to enter results of the medical examination and replies to questions pertinent to past medical history in a permanent employment record should be made a condition of employment.

After the employee has passed a rigorous initial medical examination, he should be "checked out" under various on-the-job working conditions. Some men naturally are unsuited for work in confined spaces or at high levels, regardless of physical condition. These factors should be noted and made part of the employment record.

Follow-up medical examinations should be given at six-month or selected intervals, and results of these should be included in the employment record. Development of undesirable tendencies revealed by these medical examinations should be considered as an important factor in any decision to continue or to terminate employment.

Records of the employee's accidents should be kept up to date and should include accidents with former employers. Such a record will serve to determine whether or not the employee is "accident prone" and will help the employer decide whether or not the employ-

ee is suited to be an industrial painter under today's complex and demanding conditions.

Figures 1 and 2 illustrate typical medical history and medical examination forms that might be filled out and entered in the employee's record.

Figure 1: Typical Medical History Questionnaire

Please check each of the following items. If explanatory remarks are necessary, make them on an additional sheet and attach it to this form.

Have you ever experienced the following:

	Yes	No	Date
Frequent headaches	_____	_____	_____
Dizzy or fainting spells	_____	_____	_____
Fits, epilepsy, convulsions	_____	_____	_____
Loss of consciousness	_____	_____	_____
Blindness, color blindness	_____	_____	_____
Ear trouble, impaired hearing	_____	_____	_____
Stiff joints	_____	_____	_____
Deformities	_____	_____	_____
Tuberculosis	_____	_____	_____
Severe coughing, chest pains	_____	_____	_____
Heart trouble	_____	_____	_____
Shortness of breath	_____	_____	_____
High blood pressure	_____	_____	_____
Stroke or paralysis	_____	_____	_____
Rupture or hernia	_____	_____	_____
Hospitalization:			
For illness or injuries	_____	_____	_____
For operation	_____	_____	_____
Unusual weight gain or loss	_____	_____	_____
Received:			
Workmen's compensation	_____	_____	_____
Armed Forces disability	_____	_____	_____
Compensation	_____	_____	_____

Figure 2: Typical Items to be Recorded in Medical Examinations

Record results of the following examinations:

Eye Chart _____

Orthorater _____

Color Vision _____

Hearing _____

Urinalysis:

Sugar _____

Albumin _____

Reflexes _____

Electrocardiogram _____

Chest X-ray _____

Back X-ray _____

Blood Tests:

VDRL _____

Kahn _____

Examine and record under comments defects of the following:

Eyes _____

Tonsils _____

Skin _____

Abdomen _____

Arms _____

Legs _____

Ears _____

Throat _____

Lungs _____

Genitalia _____

Hands _____

Feet _____

Nose _____

Chest _____

Heart _____

Back _____

Fingers _____

Joints _____

Comments:

_____

_____

_____

_____

2. Faulty Attitudes

How many times have you said about a man, "He's a good worker, but... ."?

What about the "but"? What about the fellow who shows irrational anger, extreme irritability, or constant grouchiness? What about the fellow who is always talking sex, who is over-inquisitive, or who lies just for fun of lying? What about the fellow who is a queer duck and whom you just can't figure out, and who has all kinds of peculiarities and mannerisms which, although they may be too small to resent, nevertheless keep people under a strain? What about those fellows who will do things on impulse and then be sorry—and then repeat the same stunts some other time?

These are the unstable, impulsive, and irresponsible persons who are constantly in need of warning or discipline. They not only get themselves into messes, but, in keeping others on edge, they may cause others to get hurt, too. They are too costly to keep on the payroll because they may cause permanent injury to innocent bystanders.

Take any one of your employees and make a personality inventory. How does he affect the others in the crew? Is he liked by the rest of the men? Does he mix with the others, or does he keep to himself? Is he a good influence in a group, or is there argument and friction wherever he goes? Does he take criticism and correction in the right spirit? If his feelings are hurt, does he get over it quickly or does he brood? Does he gossip and say malicious things about people? Is he considerate of the feelings of others? Does he talk too much? Ask yourself these and other questions, and then ask yourself, "Why?" People don't quarrel or gossip or brood or talk too much just for the sake of doing such things. There is a deeper reason. They do it because it gives them an outlet for their feelings. They want to be happy, and people who quarrel and fight and gossip and brood are not happy. There is something behind these behaviors. They are only symptoms—signs that every one of these people needs help.

If safety depends on the elimination of faulty attitudes, ask yourself what you have done to create these attitudes, and then get together with your employees. If safety de- pends on the elimination of fear, nervousness, worry and depression, find out what is behind these things and try to remedy the situation.

All of them are distractors of attention. Nobody was ever hurt while paying strict attention to what he was doing. Things that distract attention, whether brooding about something or arguing, make people unsafe.

Figure 3: Typical Safety Check List

SAFETY CHECK LIST

- ☐ Eye protection
- ☐ Respiratory protection
- ☐ Safety Belts
- ☐ Warning tags and signs
- ☐ Toxic materials
  - ☐ Burns to skin
  - ☐ Falling objects
- ☐ Electrical hazards
- ☐ Footing
- ☐ Moving objects, cranes, traffic, etc.
- ☐ Safety showers and eye baths
- ☐ Fire alarm station
- ☐ Fire extinguishers, fire blankets
- ☐ Nearest telephone
- ☐ Barricades
- ☐ Equipment grounded
- ☐ Sparkproof tools
- ☐ Safety or fire permits
- ☐ Flammability or flash point

3. A Safe Working Environment

Before painters are sent to work in any plant area, the working environment should be studied to detect hazards such as concentrations of noxious fumes, presence of splash or spillage of harmful liquids, conditions of excessive heat, or areas where oxygen content of the air may be dangerously low. Where these conditions exist, they must be corrected before the painter is permitted to enter the area, or the painter must be protected by materials or devices that will allow him to work without fear of injury or illness that might otherwise result from exposure. In most plants, the safety engineer knows where the hazardous areas are located and what measures are necessary to counteract the hazard. The project superintendent and the painter foreman should always consult with the safety engineer before starting each project, and his recommendations should be followed. Safety control measures stipulated by safety engineers should be developed in cooperation with the plant industrial hygiene engineer if available, with the plant chemist who knows the composition of compounds and groups of compounds being used, and with the plant industrial physician with his knowledge of toxicology and preventive medicine.

It is an excellent idea to prepare and use daily a safety check-list of items that must be seen to before work commences. A safety check list might be a 3" × 5" card that provides blocks for checking the items shown in Figure 3. The project superintendent and the painter foreman should consult with the safety engineer to see that all pertinent items have been checked and that the painters have been informed of the relevancy of the items to his work during the day.

3.1 Threshold Limit Values for Solvents, Fumes, Mists, and Dusts

Table I lists threshold limit values, taken from the most recent list published by the American Conference of Governmental Industrial Hygienists, have been modified to suit industrial safety experience. These values should be observed when work is done in confined areas.

3.2 Ventilation

3.2.1 General Ventilation and Temperature Requirements.

Safe working conditions require that outside air be provided to all workrooms at the minimum rate of 15 cubic feet per minute per person, or one-and-one-half (1-1/2) changes of air per hour, whichever is greater. (In most instances, leakage through walls, doors, and windows will produce at least one-and-one-half air changes per hour).

A minimum air temperature of 60°F is recommended in all workrooms where work of a strenuous nature is performed. A minimum air temperature of 65 °F is recommended in all other workrooms unless prohibited by process requirements.

3.2.2 Local Exhaust Ventilation.

Local exhaust ventilation systems should produce and maintain a movement of air toward the discharge opening sufficient to prevent escape of contaminant into the breathing zone beyond the limits shown in Tables I and II during working hours.

- Velocity of airflow through branch and main ducts should be sufficient to transport the contaminant through the system without permitting it to settle.
- Exhaust ventilation piping should be located so as to be accessible for inspection and maintenance.
- Airflow equipment including hoods, pipes, fans, motors, and collectors must be adequately grounded.
- Operations involving more than one contaminant must never be connected to the same exhaust system when combination of

TABLE I: Threshold Limit Values for Commonly Used Solvents

Solvent	MAC[1]	Flash Point °F[2]
Acetone	1000	0
Benzene	25	12
n—Butanol	100	84
Butyl Cellosolve	50	141
Carbon Tetrachloride[3]	10	None
Cyclohexane	400	1
Ethylene Dichloride	100	56
Ethanol	1000	55
Gasoline	500	−45
Methanol	200	52
Naptha, Coal Tar	200	100–110
Naptha, Petroleum	500	<0
Perchloroethylene	200	None
Isopropanol	400	53
Stoddard Solvent	500	100–110
Toluene	200	40
Trichloethylene	100	None
Turpentine	100	95
Xylene	200	63

[1]Maximum allowance concentration of vapor in air (or hygienic standard) in parts per million by volume for breathing during continuing eight hour working day. These figures should be used as guides for evaluating exposures, and are subject to change when better information is available.

[2]TAG closed-cup tester: From "Flammable Liquids and Gases," National Fire Codes, Vol. 1.

[3]Because of cumulative health hazard, use of this cleaning solvent is not recommended.

the contaminants can create a fire hazard, explosion hazard, or otherwise dangerous mixture.

- It is imperative that the exhaust system takes suction from some point at the bottom of the room or tank in which work is being done.
- Processes or operations using or generating flammable dusts, gases, fumes, vapors, mists, fibers, or other impurities must be completely protected from all sources of ignition.
- The capacity of an exhaust system shall be designed so that all hoods, booths, and enclosures connected to the system are fully open, except where the system is so interlocked that only a portion of it can be operated at a given time. In this case, the capacity shall be calculated on the basis that all hoods in the group requiring the greatest rate of exhaust are open.

TABLE II: Threshold Limit Values for Fumes, Mists, Dusts

Hazard	MAC[4]
Lead	0.2
Dust (no free Silica)	50.0
Silica:	
High, above 50% free SiO_2	5.0
Medium, 5–50% free SiO_2	20.0
Low, below 5% free SiO_2	50.0
Total Dusts below 5% free SiO_2	50.0
Chromic Acids and Chromates as CrO_3	0.1

[4]Maximum allowable concentration (or hygienic standards), milligrams per cubic meter of air for breathing during continuing eight hour working day.

- Suitable air inlets must be sufficient to provide for re-placement of exhausted air. Fresh air shall be furnished from a protected area, free of all contaminants. The intake pipe shall never be downwind from the compressor engines, truck, automobile, or other internal combustion engine. Exhaust systems handling dusts and discharging to the outer air shall be provided with suitable air-cleaning devices to remove air contaminants prior to discharge to the outer air, except under unusual conditions.
- The discharge from any exhaust system shall be arranged so that no air contamination will enter any work space, window, door, or other opening in quantities sufficient to create a health hazard or a nuisance in surrounding areas.
- Collected materials shall be removed from the exhaust system at frequent intervals.

4. Personnel Safety Rules

The project superintendent, foreman, and workmen should learn and follow all plant safety rules and regulations. Where such rules are absent or are not specific, the following requirements should be met:

1. Before painting work is begun in an operating area, the operating supervisor shall be asked to inform painters of all conditions that might cause injury. The supervisor shall also be asked to explain the area's safety rules.
2. Provide and use adequate protective clothing, safety shoes, helmets, gloves, safety glasses or goggles, respiratory protection, ventilation equipment, and skin protection as recommended by the safety engineer.
3. Obtain necessary fire permits, tank entering permits, elevated work permits, and other procedural safeguards.
4. In confined spaces, check for explosion hazard with a gas tester recommended by the safety engineer. Since safe limits for

breathing flammable vapors are far below the minimum explosive range, use proper ventilation to prevent vapors from accumulating or provide masks, respirators, etc.

5. When machinery, including agitated tanks, is to be painted, have fuses pulled and switches thrown and locked out. Attach "DO NOT OPERATE" warning tags.
6. Do not paint moving machinery.
7. Locate and know the use of department safety showers, fire alarm stations, fire extinguishers, stretchers, fire blankets, etc.
8. Keep aisles, fire and safety equipment, and exits free of obstructions.
9. Do not point spray guns or abrasive blast nozzles at anyone.
10. Dispose of all oily rags and waste at the end of each day. If disposal is not feasible, store oily rags and waste in metal containers with a tight fitting lid.

4.1 Control of Surface Preparation Hazards

- Surface preparation requires the use of goggles, air helmets, neck scarves, and sometimes protective clothing, depending on the method of surface preparation employed.
- Provide and use adequate eye protection in all instances. For hand cleaning, power tool cleaning, and water blasting methods of surface preparation, approved safety goggles will be adequate. For sand or grit blasting methods of surface preparation, full-face protection is required. The most suitable equipment is safety goggles worn beneath a pressurized air helmet. Workmen in acid areas or areas in which corrosive liquids may be encountered are required to wear acid proof goggles rather than the conventional type.
- Provide and use appropriate respiratory protection when abrasive blasting. Provide and use creams on exposed skin areas. Encourage careful washing of the hands and face before eating.

5. Rules for Safe Working Conditions

The project superintendent and the painter foreman, with advice by the safety engineer, should be alert to see that the following rules are obeyed:

1. Check tank or other enclosed space interiors for explosion hazard, toxic materials, and adequate oxygen content for breathing. Before tank entry, provide life-lines and harness with an extra man stationed outside the tank. Ascertain if the tank opening is large enough to remove an injured man. Before entering a tank, check with operating personnel to ensure that all process lines entering the tank are blanked off.
2. Provide proper and sufficient lighting in interior of tanks and other dark areas. Be sure that lighting does not create shadows or glare. All wiring must be so constructed that there is no danger of electric shock. In many instances electric head-lamps such as are used in mines may be used.
3. When airline masks or hose masks are used, locate the intake air source or the blower in an area free from air contaminants. Check the output air for proper pressure and carbon monoxide content. Protect hose from damage and do not allow them to become tripping hazards.
4. Rope off or barricade work areas as required to protect passers-by.
5. Provide an adequate number of portable fire extinguishers.
6. Post warning signs which may include "WET PAINT," "NO SMOKING," and "MEN WORKING ABOVE."
7. Provide a safe storage cabinet for materials and equipment. Use ventilated metallic cabinets for overnight storage of paint brushes suspended in oil or solvents.
8. Protect machinery, equipment, and materials with fireproof tarpaulins.
9. Be sure that pressurized containers are fitted with perfectly functioning pressure gages and safety valves. Test safety valves daily before use.
10. Read the label and learn the properties of the materials that are being applied. If they are toxic, flammable, or harmful to any degree, find out what protective measures are necessary to prevent harm from exposure.
11. Follow the safety rules for working equipment that are given in following portions of this manual.

II. Safety Rules For Working Equipment

The safety of personnel depends to a large degree on the condition of equipment which must be used, and on the familiarity of personnel with safety procedures that must be followed when using the equipment. The following rules should be learned and enforced.

1. Rules for Safety With Ladders

1. See that all ladders conform to ASA A14.1 "Safety Code for Wood Ladders," and ASA A14.2 "Safety Code for Metal Ladders."
2. Inspect ladders frequently. Look for loose steps or rungs; loose screws, bolts, metal braces, and rods; split or broken side rails or rungs; and loose or bent hinge spreaders.
3. When ladders are found to be lacking in any safety device or to be defective in any manner, they shall not be used. Ladders found to be too defective for repairs must be destroyed.
4. Protect ladders with clear protective coatings so that cracks, splinters, or breaks will be readily visible.
5. Store ladders in a warm, dry place protected from the weather and from contact with the ground.
6. Equip all straight and extension ladders with safety shoes, unless special conditions prohibit their use.
7. Do not use portable ladders greatly than 60 ft in height. If greater heights are to be reached, provide intermediate landing platforms and use separate ladders.
8. Single ladders not constructed for use as sectional ladders shall not be spliced together to form a longer lad- der.
9. Extension ladders must not be taken apart in order to use either section separately.
10. Extension ladders shall have a minimum of 15% overlapping of each section.
11. Ladders made by fastening cleats across a single rail shall not be used.
12. Do not use stepladders over 20 ft in height.

13. Never use a stepladder as a straight ladder.
14. Never use the platform of a stepladder as a top step on which to stand.
15. In placing portable ladders, be sure that the horizontal distance from the top support to the foot of the ladder is one-quarter of the working length of the ladder.
16. Straight and extension ladders must be tied at the top when in use. A helper must hold the ladder while it is being tied or untied at the top.
17. When it is necessary to place a ladder over a doorway, the doorway must be roped off and signs must be erected to warn users of the door of the ladder's presence.
18. Ladders must never be used as skids, braces, scaffold members, or for any other purpose than that for which they are intended.
19. DO NOT USE METAL LADDERS OR STAGES IN AREAS WHERE CONTACT WITH ELECTRIC POWER LINES IS POSSIBLE.
20. Use hand lines, not ladders, to raise or lower materials and tools.
21. Do not reach too far in any direction while working from a ladder. Frequent changes in a ladder's position will forestall accidents from this source.
22. Always face the ladder when ascending or descending.

2. Rules for Safety With Metal Scaffolding

1. Provide adequate sills or underpinnings on all scaffolds to be erected on filled or otherwise soft ground.
2. Compensate for unevenness of ground by using adjusting screws where blocking is not practical.
3. Be sure that scaffolds are plumb and level at all times.
4. Anchor running scaffolds to wall approximately every 28 ft of length and 18 ft of height. Use additional care when using pulley arms.
5. Do not force braces to fit. Adjust level of scaffolding until the proper fit can be made with ease.
6. Horizontal diagonal bracing must be used to pre- vent racking of all scaffolds at bottom and intermediate levels of 30 ft.
7. Hand railing must be provided on all scaffolds regardless of height.
8. Use ladders when climbing the scaffold rather than the cross braces.
9. Erect the scaffold in such a manner that a ladder is accessible and is lined up from top to bottom.
10. Inspect all scaffolding parts before using. Never use parts that are damaged or deteriorated. Remember that the strength of rusted materials is not known.

3. Rules for Safety With Wood Scaffolding

1. Lumber used in the construction of wood scaffolding shall be of good quality and reasonably straight grained. It shall be free from injurious ring shakes, checks, splits, cross grains, unsound knots, knots in groups, decay, and growth characteristics that materially decrease the strength of the lumber.
2. All nails used in scaffolding construction shall be driven full length. No nail smaller than 8d shall be used in scaffold construction, and a sufficient number of nails must be driven to support the design loading. Design of the scaffold must be such that no nail is subjected to a direct pull.
3. Follow the applicable rules given for METAL SCAFFOLDS, above.

4. Rules for Safety With Planking

1. All planking used on a scaffold shall be of sound quality lumber that is straight grained and free from knots. All planking shall have at least 24 in. overlap. Secure all planks to wood scaffolding.
2. Planking overhang shall be 3 5.8" on stackup scaffolds. Wood cleats (1" × 4") shall be nailed across the top of planking at each frame and at outside end frames.
3. Planks used for platforms shall be of uniform thick- ness, laid close together. These planks must be overlapped at the bearers. An overlap of at least two feet must be al- lowed with the bearer in the center of the overlap. Planks should be fastened securely to the bearer at the opposite end to prevent tipping.
4. Platforms must be kept clear of slippery substances. They must be equipped also with handrails and ladders.
5. Planking must never be painted over; paint will conceal defects. Scaffolding boards shall be identified by painting each end. All scaffold boards shall be used exclusively for that purpose.
6. The nominal size of planking shall be determined from Table III. Values given are for planks with the wide face up, with loads concentrated in the center. Loads given in the Table are net. Allowance was made for weight of the planking. Loads in the Table may be increased 45% if select structural coast region Douglas Fir or merchantable structural

5. Rules for Safety With Rolling Towers

1. Towers of a height greater than 5 times the minimum base dimension must be guyed or tied-off when in use.
2. Apply all caster brakes when the tower is not in motion.
3. DO NOT RIDE TOWERS!
4. Look where you are going when moving a rolling tower. Do not attempt to move a rolling tower without sufficient help.
5. Provide unit lock arms on all towers.
6. Do not extend adjusting screws more than 12 in.
7. Do not use asters smaller than 6 in. in diameter, regardless of tower height.
8. The five-foot by seven-foot rolling tower now in general use is unstable at heights over 25 ft. while iin motion; stability must be maintained wither with outriggers or with handling lines.
9. Use horizontal diagonal bracing at the bottom and at intermediate levels of 30 ft.

TABLE III: Safe Center Loads for Scaffold Plank, in Pounds

	Size of plank			
Span in Ft	2 x 10 Dressed to $1\frac{5}{8}$ x $9\frac{1}{2}$	2 x 12 Dressed to $1\frac{5}{8}$ x $11\frac{1}{2}$	3 x 10 Dressed to $2\frac{5}{8}$ x $9\frac{1}{2}$	3 x 12 Dressed to $2\frac{5}{8}$ x $11\frac{1}{2}$
6	256	309	667	807
8	192	232	500	605
10	153	186	400	484
12	128	155	333	404
14	110	133	286	346
16		116	250	303

10. Guy or tie-off all fixed topers every 18 ft. of elevation.
11. Do not use brackets on rolling towers.
12. Do not attempt to use scaffold as material hoist towers or for mounting derricks without first determining the loads and stresses involved.
13. Inspect all tower parts before using. Do not use parts that are damaged or deteriorated. Remember that the strength of rusted materials is not known.

6. Rules for Safety With Swing Stages

1. Be sure to read the manufacturer's instructions on the proper use and maintenance of the equipment.
2. Never overload equipment. Follow manufacturer's prescribed load capacities.
3. Always use a guard rail of sound lumber. Never substitute with rope.
4. Replace cables immediately that show 5% of the wires per lay broken or that show evidence of excessive wear on corrosion.
5. Cables must be replaced only by experienced personnel, and then with the utmost care.
6. Allow none but careful, experienced men to erect or operate the suspended stage.
7. When locating cables on the job site, **CHECK NEARBY POWER LINES OR ELECTRIC SERVICE WIRING TO PREVENT ELECTROCUTION**. When in doubt, consult the power service company for advice.
8. Wood stages shall be 20 in. minimum width, rated by Underwriters Laboratories for center load of 500 pounds with safety factor of 4. Wood stages over 24 ft. in length shall be cabled.
9. Metal stages shall be not less than 20 in. wide, rated by Underwriters Laboratories for center load of 500 pounds with safety factor of 4. Stages over 24 ft in length shall be cabled, with no cracks in side rails.
10. Ropes and blocks of the stage shall be tested by suspending one foot off ground and loading at least four times the estimated work load.
11. Power stages shall have free fall safety devices with hand controls in case of power failures. Cables must be inspected regularly. Safety factor of cables must be four to one.

7. Rules for Safety With Ropes and Lines

1. See that ropes are of the proper size: Not less than ¾" manila for stages, 1/2" manila for safety hoists.
2. Discard ropes that have been exposed to acid or excessive heat. Twist strand open and check for dry rot, brittleness, and abrasions. Do not use frozen rope under any circumstances.
3. Inspect all wire ropes or cables frequently. Discard when 5% of the wires per lay are broken, when cable clamp damage is evident, or where there is evidence of corrosion.
4. Provide dry, empty drums for coiling.

8. Rules for Safety With Pressurized Equipment

The following safety rules apply to conventional and airless spray equipment, abrasive blasting equipment, and water blasting equipment that operate under pressure.

1. Use only pressure equipment that has been constructed as specified by the National Board Code and the ASME Code for Unfired Pressure Vessels. Make certain that this equipment carries a label certifying that such construction has been made. On equipment of this type, the manufacturer certifies that it has been built to rigid standards, that certain types and grades of steel have been used, that welding has been done by certified welders, that the machine has been tested to twice the expected working pressure, and that it has been inspected by state or insurance company inspectors.
   If a coded vessel is not used, the job may be shut down in certain states that specify code requirements; the user is subject to an unrestricted judgment by a jury should an accident occur (if a coded vessel is used, liability usually is restricted to the amount set forth in the workmens' compensation laws of the state).
2. Conduct a hydrostatic test of pressure equipment at least once, preferably twice, each year.
3. Test safety relief valves used on pressure equipment daily.
4. Use remote control deadman valves with pressure equipment. With valves of this type, the pressure equipment will be shut off instantly when the operator releases his grip on the nozzle. Be sure that the deadman valves are pneumatic type that use the same air for activation that is used for blasting or spraying.

5. Be sure that the nozzle, tank, and pressure equipment are grounded as illustrated in Figures 4 and 5. Have an electrician check the grounding periodically with an ammeter to see that it is operative. (Ground electric or pneumatic power tool equipment used for cleaning operations as illustrated in Figure 5 also.)

9. Rules for Safety With Abrasive Blasting Equipment

1. Use abrasive blast hose constructed with activated carbon to prevent electrical shock to the operator.
2. Be sure that abrasive blast hose is kept in dry areas when stored. When using the hose, be sure that it is running in as straight a line as possible, avoiding all 90 degree sharp bends. If a hose must be curved around an object, make a long radius curve; sharp curves will create rapid wear on the tube of the hose, causing a blow out at the bend.
3. NEVER point a sandblast nozzle at any part of the human body—your own or another's.
4. Use a completely contained safety helmet wherein a separate supply of air is fed to the operator to make certain that no dust can enter his respiratory tract. The helmet should be Bureau of Mines approved to make sure that danger of silicosis to the operator is minimized. It is important to note that air-fed helmets will not provide protection against fumes unless a separate air purifier or a special ring-free compressor is used to assure respirable air.

10. Rules for Safety With Waterblast Equipment

1. It is absolutely essential to have an automatic deadman safety control at the nozzle.
2. Water hose must be properly sized to suit the equipment and must be tested to withstand four times the maximum working pressure.
3. Fittings must be tested to withstand four times the maximum working pressure.
4. By-pass valves must be equipped with safety relief valves.
5. Nozzles must not be pointed at any person or any object that will break at working pressure, such as glass, scaffold supports, loose pipes, fittings, gages, lights, etc.
6. High pressure hose must be firmly secured at a distance not more than ten feet from the operator.
7. The operator must be protected with safety rubber gloves and a safety rubber suit that protects the head, face, neck, arms, legs, feet, and other parts of the body.
8. Face shields of heavy plastic shall be used in high-pressure operations. Safety goggles may be worn when cleaning is done at low pressure.

11. Rules for Safety With Airless Spraying Equipment

Airless spraying equipment consists of a high ratio fluid pump equipped with an air regulator that may generate fluid pressures to 3000 psig, specially-designed fluid hose and fittings that will safely withstand such pressures, and an airless spray gun that sprays at a rate of 80 ounces per minute through small orifices from 0.007 in. to 0.036 in. in size. Material to be sprayed is finely atomized by low boil- ing solvents under pressure, seeking release through these very small orifices. It is obvious that a jet of material being released at such high pressures will pierce the human body if the operator reaches close proximity to the spray cap on the gun head; the material does not become atomized sufficiently to form a spray pattern until it has traveled from 12 to 14 in. It is equally dangerous to pull the trigger on an airless gun when the cap has been removed. A large volume of material is then released at the same high pressure, and great bodily harm can result from contact with this stream. The following safety precautions should be observed and rigidly enforced:

1. Check all hose connections and fittings to be certain that they are tight and not leaking. Be sure that only components de signed for high pressures are used.
2. Check the fluid hose to be sure that there are no weak or worn spots created by kinking, abrasion, contact with moving parts of machinery, friction from sharp edges and corners, deterioration due to exposure to chemicals, or ordinary wear.
3. When handling or carrying the gun but not actually spraying, hold the gun by the grip and remove the fingers from the trigger. This will prevent the gun from being activated if the operator should inadvertently tighten his hold when stumbling or slipping.
4. NEVER point an airless gun at any part of the human body—your own or another's.
5. Do not disconnect the gun from the fluid hose, or the hose from the pump until the pressure has been released from the hose. This is accomplished by first closing off the main line air pressure to the pump and then bleeding off the pressure on the fluid hose by triggering the gun before disconnecting it.
6. If spraying with flammable materials, it is necessary to have the object being sprayed as well as the spray gun grounded to prevent a spark from static electricity. Be sure that all other sources of ignition are eliminated as well.

III. Safety With Materials

1. Handling and Applying Coatings Materials

Coatings materials should be stored in safe, well-ventilated areas where sparks, flames, and the direct rays of the sun can be avoided. Containers should be kept tightly sealed until ready for use. Warning tags should be placed on toxic materials.

Mixing presents many problems. Recommended safety rules for mixing operations include the following:

1. Use protective gloves.
2. Keep the face and head away from the mixing container.
3. Use protective face cream.
4. Avoid splash and spillage, and inhalation of vapors.
5. Use eye-protection goggles.
6. Mix all materials in well-ventilated areas away from sparks and flames.
7. Use low speed mechanical mixers whenever possible.

8. Clean up spillage immediately.
9. Check the temperature limitations of materials being mixed. Many materials are dangerous at high temperatures.

Protective devices and equipment required for application of coatings materials are determined by the type of coating as well as by the environment. The coatings manufacturers should provide complete mixing and application instructions, including definite references to safety requirements. Unless definite information regarding explosion and toxicity hazards inherent in the material are provided by the manufacturer, a written request for such data should be made before starting the coatings application. Records of previous applications using similar materials should be examined also.

Protective face cream is recommended for all spraying operations. Goggles should be worn wherever possible.

2. Health Hazards of Materials

A coatings material may be considered a health hazard when its properties are such that it can either directly or indirectly cause injury or incapacitation, either temporary or permanent, from exposure by contact, inhalation, or ingestion.

Degrees of health hazard are ranked according to the probable severity of injury or incapacitation, as follows:

1. Materials that on very short exposure could cause death or major residual injury even though prompt medical treatment were given. Types of these materials are:
   a. Materials which can penetrate ordinary rubber protective clothing.
   b. Materials which under normal conditions or under fire conditions give off gases which are extremely toxic or corrosive through inhalation or through contact with or absorption through the skin.
2. Materials that on short exposure could cause serious temporary or residual injury even though prompt medical treatment were given. Types of these materials are:
   a. Materials giving off highly toxic combustion products.
   b. Materials corrosive to living tissue or toxic by skin absorption.
3. Materials that on intense or continued exposure could cause temporary incapacitation or possible residual injury unless prompt medical attention is given. Types of these materials are:
   a. Materials giving off toxic combustion products.
   b. Materials giving off highly irritating combustion products.
   c. Materials that under either normal conditions or fire conditions give off toxic vapors lacking warning properties.
4. Materials that on exposure can cause irritation, but only minor residual injury even if no treatment is given. Types of these materials are:
5. a. Materials that under fire conditions give off irritating combustion products.
   a. Materials that cause irritation to the skin without destruction of tissue.
   6. Materials that on exposure to fire conditions offer no hazard beyond that of ordinary combustible material.

3. Flammability Hazards of Materials

A coatings material may be considered a flammability hazard when it will burn under normal conditions.

Degrees of hazard are ranked according to the susceptibility of materials to burning, as follows:

1. Materials which will rapidly or completely vaporize at atmospheric pressure and normal ambient temperature; which are readily dispersed in air; and which will burn. Types of these materials are:
   a. Any liquid which is liquid under pressure and having a vapor pressure greater than 14.7 psia at 100 °F.
   b. Materials which may form explosive mixtures with air and which are readily dispersed in air, such as mists of flammable or combustible liquid droplets.
2. Materials that can be ignited under almost all ambient temperature conditions. These materials produce hazardous atmospheres with air under all ambient temperatures and are readily ignited. Types of these materials are:
   a. Materials having a flash point of 100 °F or below and having a vapor pressure not greater than 14.7 psia at 100 °F.
   b. Materials which ignite spontaneously when exposed to air.
3. Materials that must be moderately heated or ex- posed to relatively high ambient temperature before ignition can occur. Materials of this type are those having a flash point above 100 °F but not greater than 200 °F.
4. Materials that must be preheated before ignition can occur. These materials are those that will support combustion for five minutes or less at 1,500 °F.
5. Incombustible materials.

4. Toxicity of Materials

Virtually all solvent solution coatings are highly flammable in liquid form, and vapors released in the process of application are explosive in nature if concentrated in sufficient volume in closed or restricted areas. Even vapors from ordinary enamels and oil paints may be accumulated in such density as to result in explosive reaction if a source of ignition is present. Generally speaking, however, solvents used in solvent solution coatings are more volatile and dangerous than those used in conventional paints or coatings.

A wide variety of solvents are used in the formulation of many coatings now available. These include, but are not limited to, the ketone group which includes such solvents as acetone, methyl ethyl ketone (MEK), methyl isobutyl ketone (MIBK), ethyl amyl ketone (EAK), cyclohexane, and others; the hydrocarbons group of toluol, toluene, xylol, xylene, and others. In many instances, particularly in vinyl resin base coatings, the ketones act as the solvents that hold the resins in solution; the hydrocarbons are used primarily as diluents to control the viscosity or flow qualities of the coating. Most coatings have a combination of solvents from each group. The epoxy and synthetic rubber coatings use mostly solvents of the hydrocarbons group although ketones may be used in limited quantities.

All of these solvents are highly flammable and should be handled with the greatest of care.

Solvents, as well as other components of many modern solution coatings, present other hazards which must be guarded against at all times. Solvents of all groups are toxic to varying degrees and may cause serious effects to those working with them unless appropriate

precautions are taken. Excessive breathing of concentrated solvent vapors may cause dizziness or nausea, excessive drying or irritation of the mucous membranes, and, in rare cases, allergic reactions on the skin.

The epoxides used in epoxy coatings and compounds are particularly irritating to the skin, and some persons are seriously affected by allergic reactions if proper hygiene is not practiced while these materials are in use. Common reactions include swelling around the eyes or lips, rashes of the skin, etc. Some epoxy coatings have polyamides as curing agents that react much like a mild acid on tender mucous membranes.

Mist and spray of lead based paints may be dangerous if these vapors are inhaled. These minute particles of lead may cause lead poisoning if exposure is not avoided. Good personal hygiene is necessary to control ingestion of lead from contamination by cigarettes or food.

The following basic safety precautions should govern the use of ALL coatings:

1. Always provide adequate ventilation.
2. Guard against fire, flames, and sparks, and do not smoke while working.
3. Avoid breathing of vapors or spray mist.
4. Use protective skin cream and other protective equipment.
5. Practice good personal hygiene.

5. Materials Requiring Special Handling

5.1 Styrene Monomer (Rubber or Polymer Grade). Styrene monomer is a volatile material. Adhere strictly to the manufacturer's specifications for mixing and application. Avoid contact with skin or eyes. Wash affected areas with soap and water. If irritation persists, see a physician.

5.2 60% Solution of Methyl Ethyl Ketone Peroxide in Dimethyl Pthalate Catalyst†. MEK peroxide is an extremely strong oxidizing agent and must be handled in strict accordance with the manufacturer's specifications. Precautions include, but are not limited to the following:

1. Store in a cool place below 70 °F and protect from direct sunlight at all times.
2. Keep away from heat, sparks, and open flames.
3. Do not add to hot materials. Explosive decomposition may occur.
4. Store in original container with special vented cap. Keep closed. Avoid shock and temperatures in excess of 70 °F. Keep containers closed.
5. Avoid contact. If skin contact occurs, flush with water at once. If eye contact occurs, immediately flush with water for 15 minutes then obtain immediate medical care.
6. Do not mix more than four hours' supply at one time. Clean catalyst pot with acetone before mixing new batch. Release pressure on pot when not using catalyst.

5.3 Acetone or MEK Solvents†. Both acetone and MEK solvents are volatile and explosive liquids with low flash points. Handle these materials in strict accordance with manufacturer's specifications.

Avoid spilling acetone or MEK solvents on absorptive materials such as wood floors, ground in work areas, and asphalt paving to prevent fire and explosive hazards.

Remove all acetone or MEK solvents from equipment after cleaning.

†WARNING: Do not confuse MEK Peroxide Catalyst with MEK Solvent!!

5.4 Vinyl Solvent Solution Coatings. These coatings contain highly flammable solvents that may be toxic, irritate the eyes, nose, and throat, dry or irritate the skin, and that are explosive in concentration. Safety precautions for handling these materials include:

1. Store materials in well ventilated areas, away from heating equipment, open flames, and away from direct sun- light.
2. Keep containers tightly closed at all times.
3. Avoid sparks or open flames near open containers.
4. Do not smoke while mixing or applying these materials.
5. Provide effective ventilation when handling or applying these coatings in closed or confined areas.
6. Use only vapor-proof and explosion-proof electrical equipment in confined areas.
7. Do not work in any area or closure when air is not clear and free of excessive solvent odor.
8. Use an approved type chemical respirator during spraying operations. (Use Binks No. 40–13, Mine Safety Appliance, or equal, organic type).
9. Exhaust from lowest level, where possible. Extinguish all pilot lights on water heaters, furnaces, or other equipment, on all levels.
10. Wear only rubber soled shoes and clothing free of ferrous metal parts when working in confined areas.
11. Always use drop cloths under materials supply cans, spray pumps and pots, and avoid dripping of cans or equipment in metallic or concrete closures.

5.5 Epoxy Coatings and Compounds. These materials contain flammable solvents that will dry or irritate the skin on contact. Solvent vapors may be toxic and may cause irritating agents may be irritating to the skin and mucous membranes.

Safety precautions for handling these materials include the following:

1. Store materials in well ventilated rooms away from heating equipment and other fire hazards, and away from direct sunlight.
2. Keep containers tightly closed at all times.
3. Avoid sparks or flames near open containers.
4. Do not smoke while mixing or applying these materials.
5. Provide effective ventilation when using materials in confined areas.
6. Use only vapor-proof and explosion-proof electrical equipment in confined areas.

7. Do not work in any closure when air is not clear and relatively free of solvent odor.
8. Use an approved type chemical respirator when applying coatings by brush or roller in confined areas. (Use Binks No. 40-13, Mine Safety Appliance, or equal, organic type.)
9. Use a fresh air hood (Binks No. 40-54 or equal) when applying these coatings by spray in confined areas.
10. Avoid contact of coatings or compounds with the skin for prolonged periods. Wash face, hands, arms, and other exposed areas of the body at least every two hours, using soap and water. Trust commercial protective creams for short periods of time only. Wash clothing regularly. Personal hygiene is highly important when working with epoxies.

5.6 Neoprene-Hypalon (Synthetic Rubber) Coatings. These materials contain solvents that are flammable and that may dry or irritate the skin. Concentrated solvent vapors are explosive.

Safety precautions for handling these materials include the following:

1. Keep container closed at all times.
2. Store materials in well ventilated rooms away from heating equipment and other fire hazards, and away from direct sunlight.
3. Avoid sparks or flame near open containers.
4. Do not smoke while mixing or applying these materials.
5. Avoid excessive contact of coatings with the skin.
6. If coatings are used in other than outside applications, follow the safety precautions given for vinyl coatings, above.

IV. Personnel Protective Equipment

1. Respiratory Protective Equipment

When industrial work methods or processes create hazards of exposure to harmful vapors, gases, dusts, mists, or fumes, the work areas should be enclosed or well ventilated to eliminate or minimize the hazards. If enclosure, ventilation, or other engineering methods of control are not possible, however, respiratory protective equipment should be provided for workmen exposed to possible danger. Even when the area is enclosed or well ventilated, a supply of appropriate protectors should be readily available for emergency work or repairs under unusual conditions.

The American Standard Safety Code for Head, Eye and Respiratory Protection, ASA Z2.1-1959, suggests in broad terms where protection is needed. The code does not spell out in detail the specific hazardous conditions requiring respiratory protection; instead it provides that respiratory protection "shall be provided where a process presents the hazard of exposure to harmful vapors, gases, dusts, mists, or fumes." A complete listing of all situations requiring respiratory protection would not be possible, but every process which generates air contaminants should be investigated to determine the degree of possible hazard.

1.1 Approved Devices. At the present time, the United States Bureau of Mines approves respiratory protective de- vices in the following categories:

1. Self-Contained Breathing Apparatus. These apparatus include the compressed oxygen cylinder and the com- pressed air cylinder, demand type.
2. Supplied Air Respirators. These apparatus include hose masks with blower, Type A; special hose mask without blower, Type B; air-line respirator, Type C; abrasive-blasting helmet, Type CE; dispersoid (dust, fume, and mist) respirators; and nonemergency gas respirators (chemical cartridge respirators).

1.2 Classification of Hazards. Because the selection of respiratory protective devices is based on the type of hazards encountered, the American Standard Safety Code for Head, Eye, and Respiratory Protection, ASA Z2.1-1959, classifies hazards as follows:

1. Oxygen deficiency
2. Gaseous contaminants:
   a. Immediately dangerous to life
   b. Not immediately dangerous to life.
3. Particulate contaminants (dusts, fumes, smoke, mists, fogs).
4. Combination of gaseous and particulate contaminants:
   a. Immediately dangerous to life.
   b. Not immediately dangerous to life.

It is suggested that self-contained breathing apparatus be used where oxygen deficiency and certain types of gaseous contaminant hazards exist and that supplied air respirators be used for the remaining types. It is always important to consult the plant or area safety engineer as to which type of protective device is best for a given condition, however.

1.3 Safety Rules for the Use of Respiratory Protective Equipment, General

1. If the wearer is to enter a confined space containing a hazardous atmosphere, first connect a strong lifeline to his body. The lifeline will serve as a means of guiding him to the exit, as a means of exchanging prearranged signals be- tween him and the man at the fresh-air base, and as a means of aiding in rescue operations in case of an emergency or accident. The lifeline should be held by two attendants, one of whom is wearing a similar apparatus.
2. Where a lifeline is used, a signal code to enable the wearer to communicate with the lifeline tender, and vice versa, is necessary. The following code is suggested:

Tender to Wearer	Wearer to Tender
1 pull—Are you okay?	1 pull—I am okay.
2 pulls—Advance.	2 pulls—I am going ahead.
3 pulls—Back out.	3 pulls—Keep slack out of line.
4 pulls—Come out immediately.	4 pulls—Send help.

3. If upon entering a contaminated area the wearer is able to detect the contaminant by odor or taste, or by eye, nose, or throat irritation, he should return to the fresh air immediately and ascertain what is wrong with the equipment or the manner in which it is being worn.
4. Bear in mind the time limitations of the apparatus and allow an adequate margin of time for return to fresh air.
5. The mouthpiece and nose clip, or the face piece, should not be removed until the wearer is certain that he is in respirable air.

1.4 Safety Rules for the Use of Hose Type Respirators

1.4.1 Hose Mask with Blower

1. Make certain that the hose mask is in good operating condition.
2. Set the blower in an assured source of respirable air.
3. Connect the proper length of hose (not over 150 ft) to the blower and to the face piece, making sure that all gaskets are in place and that the connections are tight. Where more than one hose line is to be used, each should originate at the blower.
4. Operate the blower for a minute or two at a rapid rate to blow any dust out of the hose and to make sure that air is being delivered to the face piece.
5. Adjust the body harness securely to the wearer. Connect a strong lifeline to the D-ring of the body harness.
6. Adjust the face piece to the wearer so that it makes a gastight fit with his face.
7. Operate the blower, and adjust the flow of air to the wearer's satisfaction. The blower must be operated continuously during the use of the mask.
8. Check on the prearranged signals between the wearer and the blower operator.
9. Enter the contaminated area cautiously.
10. Be careful that the hose and the lifeline are not endangered by sharp edges or falling objects, and remember that the wearer must retrace his steps and leave by the same route by which he entered.

1.4.2 Air-Line Respirators and Abrasive-Blasting Respirators

1. Make certain that the air supply is respirable. Pay close attention to the location of the intake to the air-supply device to make certain that the entering air is not contaminated from the exhaust of the compressor engine or from other sources. Provide a suitable filter to remove objection- able odors, oil, water mist, and rust particles from the air delivered to the air-supply line.
2. Make certain that the air-line respirator is in good operating condition.
3. Attach the proper length of air-supply hose to the source of compressed air and to the breathing tube.
4. Adjust the pressure of the air at the inlet to the air-supply hose so that it is within the proper pressure range.
5. Adjust the face piece, helmet, or hood to the wearer according to the manufacturer's instructions.
6. When the rate of flow of air into the face piece, helmet, or hood seems to be excessive, the wearer may decrease the flow of air by means of the air-regulating valve with which most air-line respirators are equipped. However, to prevent the contaminant in the surrounding air from reaching the wearer's breathing zone, the flow of air should not be decreased below 4 cubic feet per minute for face pieces, or below 6 cubic feet per minute for helmets or hoods.
7. Enter the contaminated area cautiously and leave by the same route.
8. In the case of abrasive-blasting respirators, make certain that the shatterproof eyepiece and the protective cover glass are in place. (Under no circumstances should regular window glass be used in place of the shatterproof eyepiece). Clean the inner and outer surfaces of the eye-piece. Make certain that the protective wire screen or perforated metal eyepiece is clean and in place.

1.5 Instruction in the Use of Respirators. For the safe use of any device, it is essential that the user be properly instructed in its selection, use, and maintenance. This is particularly important with respect to respirators. Competent personnel should give such instructions to the supervisors of all groups who may be required to wear respirators at their work. The supervisors, in turn, should instruct their men. No person should be allowed to wear a respirator of any type until he has received such instruction. Instruction should cover the following points:

1. An explanation of the need for using the respirator.
2. Its operating principle.
3. Steps to be taken to assure that it is in good operating condition.
4. Proper adjustment of the respirator to the wearer.
5. Proper use and maintenance of the respirator.

1.6 Care of Respirators. The life of the wearer may be dependent on the proper functioning and ready availability of respirators, so it is highly important that respirators be properly maintained and stored. Several rules can be fashioned for the adequate care and maintenance of this equipment:

1. All respirators shall be inspected at regular intervals to make sure that they are ready for use.
2. All rubber parts such as face pieces, mouthpieces, exhalation valves, breathing tubes, and headbands shall be inspected carefully for signs of deterioration such as hardening, checking, or tackiness. A check shall be made during this inspection to see that all gaskets are present and that they are held tightly in place. Metal parts shall be checked for signs of corrosion, and plastic and glass parts shall be checked for breakage.
3. When it is necessary to replace worn or deteriorated parts, only those made specifically for the device shall be used, and repair work shall be accomplished by experienced personnel only.
4. Respiratory protective equipment shall be cleaned and disinfected after each use. The manufacturer shall be consulted for the cleaning and disinfecting method best suited to his products.
5. All types of respirators shall be stored in clean and dry compartments under conditions of moderate temperature.

2. Goggles, Safety Eyeglasses

Safety goggles and safety eyeglasses are familiar protective devices to those who work in modern industrial plants. In most chemical plants and refineries, their use is mandatory.

There are many excellent devices on the market today. The American Standard Safety Code for Head, Eye, and Respiratory Protection, ASA Z2.1-1959, is the Code author- ity for devices of this type. The main requirements are that the goggles and eyeglasses fit well, are not cumbersome, provide for adequate straight-ahead as well as peripheral vision, and be manufactured of tempered, unbreakable glass, or unbreakable plastic.

Glass or plastic shields should be readily replaceable. Spare goggles, eyeglasses, and shields should be kept readily available. It is mandatory that these devices be kept clean.

3. Protective Clothing

3.1 Ordinary Work Clothing. Tears and rips in work clothing are potential causes of accidents. Torn clothing can get caught in moving machinery or on a ladder or scaffold, and may lead to a nasty fall. Mend tears and rips.

Cuffs on trousers are dangerous, since they might also catch on projections and cause crippling falls.

Floppy pockets, dangling ties, and other similar items of clothing can catch in moving machinery, or may catch on projections and cause a fall.

Oil or chemical-saturated clothing (or clothing saturated with paint or other flammable material) easily can lead to dangerous or fatal burns. Clothing saturated with these materials can also cause painful skin irritations and burns. Oil saturated clothing should be stored loose, exposed to air.

Defective, poorly designed, ill-fitting, or dirty clothing should not be worn to work. It is false economy to tolerate worn out or dirty clothing or to permit employees to wear to work old clothing not designed for safety under on-the-job conditions.

3.2 Protective Clothing for High Temperature and Highly Toxic Atmospheres.

Protective clothing capable of withstanding long operating temperatures of 500 °F, and capable of providing protection from many highly toxic atmospheres has been produced. This type of clothing is a complete suit constructed of woven Teflon laminated to a film of FEP fluorocarbon with a layer of reflective metal vacuum deposited onto the FEP. The suit is complete with gloves, steel-toed boots, and helmet-type headpiece, all locked to the suit by sealing ring arrangements.

Details of this suit construction and use can be obtained from the Snyder Manufacturing Company, New Philadelphia, Ohio, or the E. I. du Pont Chemical Company.

3.3 Hard Hats, Safety Shoes. Most industrial plants require that workmen wear rigid safety helmets and steel- toed safety shoes as a matter of basic safety protection. The files of industrial safety engineers and insurance companies contain a sufficient number of case histories to prove to the most intransigent workman that his safety depends on these devices of protection. Project superintendents and painter foremen should not permit a man to begin work on a job until he agrees to wear these items.

Steel toed safety shoes should have rubber soles, with no nails or brads exposed, when the painter is to work in enclosed spaces where flammable vapors may be present.

V. Training In Safety

1. Education Is the Key

When working equipment is in perfect condition, hazards of a given area are compensated for, and knowledge of safe applications of coatings is complete, then there is a sound foundation for painter safety. Patient and persistent education and training of the individual painter are the building blocks with which to construct an enviable safety record.

The individual painter must be educated by indoctrination. This can be handled only by constant discipline and the example of trained foremen, and by close control by the project superintendent. Trainees should be taught basic safety principles first, and then be placed with an experienced man for development.

Nothing can be taken for granted. Even experienced men need refresher courses in elementary safety practices, such as the proper placement of ladders, securing of all ladders, staging, and scaffolding, etc.; since it is a human tendency to become careless as familiarity with work progresses, even the best painters need to be reminded from time to time to avoid over-reaching, and to avoid pointing nozzles at other workmen. Constant vigilance must be exercised.

Monthly safety meetings, particularly for foremen and superintendents, are imperative. These meetings should include open discussion of all near-miss accidents, and recommendations for improvements in all phases of coatings application. Foreman and key painter personnel should be given the benefit of a formal safety course when one is avail- able.

1.1 Material for Periodic Safety Meetings. Much of the material and information in this manual is adaptable for presentation to a painter group during periodic safety meetings. Other information is available from NACE. Contact NACE Headquarters, P.O. Box 218340, Houston, TX, 492-0535, for further information.

It might be wise also, to invite safety engineers from industrial plants to meet with your men from time to time. These safety engineers can demonstrate safe and proper methods for lifting and handling materials and equipment, and can provide illustrations from their files of actual accidents and near-miss accidents that have been caused by carelessness, and by failure to wear hard hats, safety shoes, and safety goggles.

2. Responsibilities of Superintendents and Foremen

Painters in any crew depend upon superintendents and foremen to safeguard their lives. No other responsibility transcends this in importance!! With this responsibility in mind, it is suggested that superintendents and foremen be given the following instructions at the beginning of each project.

1. Maintain constant vigilance.
2. Be sure that each painter understands and accepts his personal responsibility for safety.

3. Be sure that you and your men are informed of all of the safety rules. Never let a man be injured because of failure to learn the necessary precautions!
4. Anticipate the risks that may arise from new equipment and materials. Secure expert advice in advance on such new hazards.
5. Encourage men to discuss the hazards of their work. No job should proceed if a question of safety remains unanswered. Be receptive to the ideas and suggestions of work- men; such suggestions may be the source of first-hand information and field knowledge that will prevent needless loss and suffering.
6. Insist with patience, persistence, and determination on men working safely. Enforce rules with disciplinary action if necessary.
7. Set a good example. Demonstrate safety in personal work and conduct.

VI. Appendix

1. Supplementary Data

1.1 Recommended Supplementary Reading. For those who are interested in pursuing the subject, the following treatise is recommended: "The Human Side of Safety," Louis H. Bornoff, Bright Publishing Company, Boston 16, Massachusetts.

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1. Use of safety manuals published by:
   a. E. I. du Pont de Nemours Chemical Company, Wilmington, Delaware.
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   c. Union Carbide Chemicals Company, New York, New York.
2. Review of preliminary material by the following:
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   b. The Safety Department of Monsanto Chemical Company, St. Louis, Missouri.
   c. The Medical Department of Continental Oil Company, Ponca City, Oklahoma.

17 Specifications

A coating specification is a formal, legally enforceable document that tells the contractor (applicator) what to do and where to do it, but generally doesn't tell him or her how to do it. It should be tailored to each specific job.

Irrespective of the type of coating job, a proper specification is the key to its success. A specification that describes the scope of the job, materials needed, the objective(s) of the coating, the key procedures required, the appearance of the finished coating, the standards by which the job will be judged, and the inspection requirements usually ensures a good coating job. A poor specification (i.e., one that is ambiguous, vague, lacks definition, or provides for a poor selection of materials) is an invitation to disagreements, possible lawsuits, and, above all, early coating failure. Even good specifications are sometimes disregarded, forgotten, unread, or made available only to the job estimator and not to the rest of the job crew. Such circumstances are also an invitation to early coating failure and costly, continual maintenance.

The task of writing any kind of specification is not easy. A coating specification is even more difficult because of the many variables involved. There are literally hundreds of materials to choose from, thousands of configurations of building materials, plus hundreds of specific types of exposures, unusual weather conditions, and interior and exterior surfaces. Added to these variables is a time frame within which the coating must be applied. Unfortunately, too many specifications are reduced to little more than the following. "Painting. After fabrication and dispatch to the jobsite, clean steel and paint with one coat of good quality primer and one coat of good quality enamel." A statement such as this is not a specification, but a meaningless document, which most likely will result in a protective system of the poorest quality, with a short life and continuing high maintenance costs for the life of the structure.

The procedure of writing an effective specification requires thorough planning for the structure, consideration of the needs and requirements of the coating, development of the specific procedures required for its application, consideration of environmental conditions during application, and development of a description of the finished product. A specification should be a practical document where the owner and designer effectively communicate to a coating contractor or coating superintendent what they want in a coating, when they want it, and what results they expect from the finished coating. The specification should not be unreasonable, but should take into consideration the problems that the contractor may encounter and must overcome in order to satisfy the specification.

A good specification should be written in such a manner as to provide a clear understanding for both the owner and the contractor regarding what is required of all parties. A good specification should and will invite cooperation between the owner and the contractor; thus, it is more likely to result in a satisfactory job. On the other hand, some specifications are written with an adversarial relationship in mind, which can lead to the dissatisfaction of both parties and a poorer than ordinary chance for a satisfactory job. Unfortunately, engineer/specifiers too often copy specifications from a previous job without regard to their accuracy, practicability, and adaptability to the current job, and without accountability for any advances in technology. Dissatisfaction, arguments, hard feelings, and ultimately legal actions arise from the use of poor specifications.

In order to aid corrosion engineers in writing good, sound specifications, *NACE A Guide to the Preparation of Contracts and Specifications for the Application of Protective Coatings*.[1] This is a detailed document and, as its title indicates, is a good guide to use in writing protective coating specifications. All parts of the document may not be applicable to any one specific job, and these parts may be eliminated or modified as desired. Even so, it should ensure that the content of the specification is as close to what is desired as possible. It should result in minimizing the opportunity for poor materials and work. Appendix 17A is an actual working specification that includes many of the requirements of a good specification.

A specification is, and should be considered, a legal document. It is a part of a contract between the owner and the contractor. While it is only a sheaf of paper, it can become extremely important in every detail if the job turns out to be a poor one and legal action results. Once legal action is taken, the specification, in all of its parts, often becomes the center around which the entire case revolves. A well-written specification is well worth the resulting effort and cost, primarily because it usually ensures a good job and good corrosion protection.

Even the best of specifications, however, are not infallible in ensuring the material, application, or protection intended. Any reliance on specifications must take into consideration their limitations and the dangers inherent in their use. The following statement, extracted from the *Steel Structures Painting Manual, Volume 22* discusses some of these problems.

> The use of specifications alone cannot guarantee performance; neither can strict compliance with the recommendations of the specifications prevent all future paint failures. For example, when hand cleaning is used as a method of surface preparation, it is impossible to guarantee

> that there will be no lifting of mill scale. Even when blast cleaning is used as a method of surface preparation, and the proper paint are used, paints may fail due to a great number of factors that cannot be controlled in every case. One can be safely assured, however, that if this good practice has been followed, the possibility of failure is reduced to the minimum consistent with the present state of the art.[2]

A specification is also a working document. It is important to understand this since, in many cases, specifications are more legalistic than practical. While the legal aspects of the specification are extremely important, the specification should be written in a way that the superintendent, the supervisor, and the workers can understand and use it to fulfill their part of the operation. The information contained should be straightforward, simple, and written in a way that is easily understood by all those who may be required to use it.

For example, the metric system of weights and measures is gradually being phased into the United States. However, personnel such as supervisors and applicators may not be sufficiently acquainted with such terms to interpret them properly from the standpoint of their particular part in the job. In Europe, figures for temperatures and coverage should be in metric terms since that is the system with which the people there are familiar. Where a specification is to be used in both areas, both terms should be included. A worker in the United States understands a mil of coating; however, 25 μ (microns) of thickness is generally used. One foot is easy for an American worker to relate to, while 300 mm usually means little or nothing to the worker. Thus, the wording of the specification should be geared to the area where it will be used, and the people located in that area should readily understand the terms and conditions.

There usually are three, and perhaps four, entities involved in a specification. These include the owner, possibly the engineering and design company, the manufacturer of the product to be applied, and the contractor who will apply it. All of these people or companies should have a part in creating the specification. It is obvious that the owner is vitally interested in and ultimately responsible for the specification. The owner should provide the technical expertise needed for creating an effective specification, either from within his or her own organization or from the outside, seeking the best possible advice from various sources (e.g., reliable engineering firms, coatings manufacturers, experienced consultants, and/or contractors).

An engineering firm usually is involved primarily in new construction; it is often given primary responsibility for developing the specification for the owner. Unfortunately engineers rarely receive formal training regarding coatings technology. As a result, their coating specifications are often selected from previous contracts held by the engineering firm and thus may not be applicable to the specific job involved. Since the specifications are the owner's ultimate responsibility, the owner should carefully review any engineering firm specifications being used to make sure that they provide the information needed for his or her particular purpose.

During the late 1990s engineering departments in both owner firms and engineering firms were often downsized to improve the firm's competitive capabilities. As a result, outsourcing of protective coatings specifications increased at a steady pace. This source of coatings expertise can be found in recently retired engineers operating their own small consultancies or in expanded coatings departments of large multinational corrosion engineering firms. The latter source is more likely to have the broad-based skills necessary for today's increasingly complex protective coating projects.

A reputable coating manufacturer should also have some involvement in specification development. It is the coating manufacturer's responsibility to provide the best information available on the use of their materials for the job that is contemplated. The manufacturer's technical department possesses the most current and knowledgeable source of material and application information for their materials. They should supply typical data about their coating (e.g., percent of solids, drying time, etc.) and practical information concerning the application of the specific material for a particular job. Some coating manufacturer's surface preparation and application instructions are separate from the technical data aheets (TDS). These are much more informative than the limited instructions that can be presented on a normal two-page TDS. If the use of the coating being considered is questionable, the manufacturer should step forward before the specification is written, and recommend a better material.

Ideally, a qualified coating contractor should also be involved in the development of a specification. However, except on maintenance projects, this is often impractical. Since the contractor is generally an authority on the application of coatings, his or her input can identify impractical or useless aspects of the specification. He or she should communicate this to the owner and help develop a more workable specification, which will provide the owner with the very best application possible.

The above entities should all be involved during the development of a specification so that both the best material and the best application procedures can result in the best possible job.

In many ways, there are two types of coating specifications. These are those involved with new work, and those involved with the maintenance of an existing coating. The specification for each may be quite different. In the case of a specification for new work, it may be drawn up by the overall architect or engineer for the job. In many cases, the specifications for new work may be much more detailed than those often used for maintenance work. Also, control of a specification for new construction is often with the engineering firm.

The specification for repair of an existing coating may be quite different, unless an addition to the structure is being made and repair of the existing coating is included in its specification. In this case, an engineering firm may also control and write the specifications. On the other hand, most specifications for maintenance coatings are developed in-house by the owner's engineering department or by the corrosion engineer involved in protecting the structure. This type of specification is often short and simple and thus more likely to result in trouble. The engineer drawing up the specification often has only a limited knowledge of coatings, and the corrosion engineer involved may be more familiar with cathodic protection than with the protection of the structure by coatings. This can lead to short, simple, and dangerous statements in the specifications such as "apply in accordance with the manufacturer's recommendation." On the other hand, proper maintenance specifications may be more critical than specifications for a new job, and thus may be more complicated. The reason for this, as brought out in Chapter 15 on the repair and maintenance of coatings, is that there are many more variables involved in coating repair than in a new application. In the case of a repair coating, failure has undoubtedly already occurred, so that the existing coating is damaged or contaminated enough to require remedial action. Cleaning of the coating, more difficult surface preparation, and the compatibility of the repair coating should be considered, as well as possible contamination from the atmosphere during the application process. Thus, the specifications for the repair of an existing coating on an existing structure should be much more detailed than is often necessary for the application of a new material. Even if the work is to be done by plant employees or a local contractor, a good specification for the guidance of these people and for proper inspection of the completed work is vitally important.

Parts of a Specification

In a specification for either new work or a repair coating, several different sections should be included. NACE Coating Inspector Training Program, Session 13 recommends the following sections.

- General
- Terms and Definitions
- Reference Standards and Codes
- Scope (includes the coating schedule)
- Safety
- Pre-Job Conference
- Surface Preparation
- Coating Materials
- Sampling Coatings
- Work Habits
- Application
- Work Schedule (sequence of work to be done)
- Repairs and Remedial Coating Work
- Inspection
- Documentation

These are covered in some detail as follows.

General

In the section providing general information, there should be a general description of the project. This should include the location of the work, the type of structure involved, the location of other structures in the area that may be affected by the application, and the degree of protection required for such structures.

General information should include a paragraph on the need for the coating. This is often left out of specifications. However, it is important in that it emphasizes to both the material supplier and the applicator the importance of the coating job. For example, if the coating is to protect against acid fumes, this should be stated so as to alert the coating manufacturer and the applicator that a superior coating is required, as well as a topnotch application.

The timing of the intended application is also important and should be outlined under general information. It may be even more important for a repair coating than it is for a new coating, since with a repair coating the application work must fit in with the operation of the structure during the repair period. This may mean that the application will have to be scheduled on weekends or on off-periods such as at night. This is important information, for both the manufacturer of the material and the applicator.

Terms and Definitions

A good specification defines specific words and terms in order to clarify their meaning for that particular job. Examples are:

"Shall " and "shall not " mean the provision is mandatory, and the contractor must comply with that part of the specification as written.

"Should " is not obligatory but it indicates a strong recommendation to the contractor to fulfill that part of the specification.

"May" means the contractor has options and should choose his or her preferred option.

"Specifying Engineer" means the person who can resolve nonconformance or make changes to the specification.

"Owner" means the registered person responsible for the overall operation of the facility or structure upon which this particular coating job is being done. "Owner's Representative " means the person to whom the responsibility for this particular coating job has been given.

Reference Standards

The specification should include a list of the published standards that are referenced by particular sections of the specification. These become, in part or in whole, the documents by which performance will be judged. It is particularly important for the inspector as it generally provides a pass or fail criteria for the inspector. The standard provides a method for a particular activity; it is the owner's responsibility to establish what the pass/fail criteria will be based upon the use of that method. The most common standards in use today are those developed in consensus committees by such worldwide organizations as NACE, SSPC, ASTM, ISO, AWWA, ANSI, ASTM, etc.

Scope

This section describes the work to be done, when and where it will be done, and what the contractor is to supply. There should be a listing here, or separately (such as in an appendix) of each item to be coated, as well as a list referring to all areas that are to be protected and are not to be coated. This section may also indicate the purpose of the coating project. An example is:

> The contractor shall furnish, at his or her cost, all labor, supervision, equipment, materials as are necessary to remove all existing paint, then cleaned and repaint the exterior surfaces of Tanks 1642, 1650, and 1626, adjacent to the new cooling tower, which is scheduled to commence operations within 270 days from the date of this bid proposal. All instruments, recorders, gauge glasses, and galvanized surfaces in the tank farm shall be covered and protected and shall not be coated.[3]

Safety

Many specifications begin and end this section with the generic phrase, "Work shall be done in a safe manner in accordance with all applicable federal, state, and local safety codes." This is hardly sufficient. The owner's safety manual normally has numerous provisions that apply specifically to this project. Unless these are delineated carefully in the specification, a serious accident can occur purely because the workers are unfamiliar with the plant and its particular hazards. If there are any special safety procedures required, they should be brought to the attention of all those involved through the specification.

Any requirement for special permits, such as confined spaces, tag-out and lock-out procedures, warning signals, safe havens, exit procedures, and so on, should be included in this section.

TABLE 17.1: Specifications for Surface Preparation (In Descending Order of Effectiveness)

NACE	SSPC	ISO/SWEDISH	BRITISH
No. 1 White Metal	SP 5 White Metal	Sa3 Visually Clean Metal	First Quality
No. 2 Near White Metal	SP 10 Near White Metal	Sa2½ Thoroughly Clean Metal	Second Quality
	SP 11 Power Tool to Bare Metal		
No. 3 Commercial	SP 6 Commercial	Sa2 Thorough Blast Cleaning	Third Quality
No. 8 Industrial	SP 14 Industrial		
No 4 Brush Blast	SP 7 Brush Blast	Sa1 Light Blast Cleaning	
	SP 3 Power Tool		St3 Very Thorough Hand/Power
	SP 2 Hand Tool		St2 Thorough Hand/Power
	SP 1 Solvent Wipe		
Note: See NACE No. 5/SSPC-SP 12 for Water Jetting Standard[5]			

The requirement for a contractor's safety manual should be included along with a provision that a copy is kept on the job site at all times. Posting of emergency phone numbers for fire, ambulance, medical aid, and other emergency numbers should be required in this section.

A more complete discussion of safety with specific recommendations is included in Chapter 16.

Pre-Job Conference

A good specification will provide for a pre-job conference well in advance of the job's start-up date so that all parties to the contract—the owner, contractor, coating supplier, inspector, specifying engineer, safety officer, and others—can convene to review standards, requirements, and work procedures for that specific project. It is not the first opportunity to clarify any misunderstandings but it sometimes is the last opportunity before substantial discrepancies can occur that lead to failure and legal consequences.

Discussions at the pre-job conference will often involve the scope, safety practices, cleaning operations, coating materials and their handling or storage practices, surface preparation equipment and procedures, application procedures, inspection (tools, methods, and sequence), submittals, and change orders (if any).

The pre-job conference is particularly important for the inspector, as this is where he or she can determine his or her authority and responsibilities in consensus with all the parties to the contract.

Surface Preparation

Various authors have attributed as high as 95% of all premature coating failures to inadequate surface preparation. While this is admittedly a very imprecise judgment, the fact remains that an inordinately large number of failures do occur because of some deficiency in this activity. The specifier must be as precise as possible to deal clearly with all parts of the cleaning and surface preparation process as he or she expects it to be done on this specific job. Pertinent paragraphs should deal with the following.

Pre-inspection

A procedure should be included for inspection, marking, and correction of all fabrication defects and/or process damages to the structure being prepared. The specifier may very well have prepared the specification from existing condition surveys, which are not inclusive of process changes or structural/coating deficiencies that have occurred since the condition survey was conducted. Pre-inspection provides a means to update the specification by written addendum to reflect the actual conditions on the job site.

Cleaning

Exactly which contaminants must be removed and the approved equipment, materials, and methods of removal should be included in this section along with standards by which the degree of cleaning will be judged. Too often, the cleaning statement is simply a reference to SSPC-SP1, "Solvent Cleaning,"4 without any thoughts to contaminants such as chlorides and sulfates. Both of these are water-soluble and the best method of removing them is with some type of pressure water washing, preferably following the application of a water-based biodegradable cleaner. These not only make the contaminants easier to remove, they also have both a temporary softening and a polarization effect on the previous coating system, both of which promote better adhesion of the new coating system.

Surface Preparation Materials, Methods, and Equipment

This section can be voluminous in its detail. It should include approved abrasives by type, size, cleanliness, and other factors; approved equipment by type, size, pressure, and so forth; as well as ambient conditions under which the surface preparation must be conducted, surface profiles to be achieved during abrasive blasting pass/fail criteria can be established. Should hand or visual or written standard for the quality of cleanliness must be specified.

The specification standards for proper surface preparation are relatively easy due to the work that has been done by several organizations, such as NACE and SSPC, to develop standards for such specifications. Thus, when specifying one of the accepted standards, one provides a means of obtaining the specified surface through the used of trained inspectors. NACE and SSPC surface preparation specifications have become recognized worldwide, and most applicators and contractors are prepared to prepare surfaces in accordance with them.

In general, there are two items that should be covered in a surface preparation specification. One is the type of cleanliness required for the coating to be applied. The specification for cleanliness is covered by the joint NACE/SSPC standards for blast preparation of steel and the SSPC specifications, which cover not only blast preparation, but also preparation by lesser means. These standards or specifications are covered in Table 17.1, appearing in descending order according to the degree of surface cleanliness of new steel. The development of the NACE No. 5/ SSPC-SP 12, "Surface Preparation and Cleaning of Steel and Other Hard Materials by High- and Ultrahigh-Pressure Water Jetting Prior to Recoating," is being used more often in maintenance repainting projects such as ship ballast tanks.

TABLE 17.2: Comparative Maximum Heights of Profile Obtained with Various Abrasives in Direct Pressure Blast Cleaning of Mild Steel Plates Using 80 psig Air and $^{5}/_{16}$ in Diameter Nozzle

		Maximum Height of Profile	
Abrasive	**Size[1]**	**In Mils**	**In Microns**
Large River Sand	Through U.S. 12, on U.S. 50	2.8	70
Medium Ottawa Silica Sand	Through U.S. 18, on U.S. 40	2.5	62
Fine Ottawa Silica Sand	Through U.S. 30, on U.S. 80	2.0	50
Very Fine Ottawa Silica Sand	Through U.S. 50, 80% through U.S. 100	1.5	37
Black Beauty (Crushed Slag)	Estimated at minus 80 mesh	1.3	32
Crushed Iron Grit	G-50	3.3	82
Crushed Iron Grit	G-40	3.6	90
Crushed Iron Grit	G-25	4.0	100
Crushed Iron Grit	G-16	8.0	200
Chilled Iron Shot	S-230	3.0	75
Chilled Iron Shot	S-330	3.3	82
Chilled Iron Shot	S-390	3.6	90

[1]Sizes listed are U.S. sieve Series Screen sizes or Society of Automotive Engineers grit or shot sizes.

Source: Steel Structures Painting Council, Mechanical Surface Preparation, Chapter 2, *Steel Structures Painting Manual,* Vol. 1.

As outlined in previous chapters on coating application and on surface preparation, most of the high-performance coatings should be applied over blast-cleaned surfaces. Where any corrosion is a factor, surface preparation specifications less than acid pickling (which is number 4 on the list) generally would not be satisfactory. As previously stated, the cleaner the surface, the better the performance of the coating applied over that surface. It should be noted, however, that dry abrasive blasting is not effective in removal of water-soluble contaminants such as chlorides and sulfates.

The second item that should be covered in a surface preparation specification is that of the surface profile. Much research has been done on this subject and it has been discussed throughout the industry and in technical literature on numerous occasions. Primarily, the surface profile must be practical and effective for the coating that will be applied over it. In writing the specification for surface profile, many specifiers select the blast media that normally gives the best surface preparation for the coating that is to be applied. However, this does not take into consideration the differences in field conditions. It also does not give the contractor the option to select the best combination of equipment and abrasive or water jetting that fits each particular situation. Therefore, it is recommended that a range of approved media options is given and the selection of which to use left up to the contractor as long as he or she achieves the specified degree of cleanliness and profile. Table 17.2 indicates the comparative typical heights of profile obtained by several abrasives. The development of impresser tapes such as Testex makes the recording of actual profile achieved easily measurable on the job site. Visual comparator discs are also used, but they are much more subjective and quite often cause controversy rather than solve differences in opinion.

Another item that is suggested for inclusion in a surface preparation specification is a requirement for the contractor to blast a section of the structure or work to be done and obtain approval for that surface before any coating is applied. This is an essential requirement since it allows all parties (i.e., the owner, general contractor, painting contractor, inspector, and actual workers) to visualize the type of cleanliness and profile that is required by the owner and by the coating that is to be applied over the surface. This can eliminate many arguments and difficulties after the job has been started. Where practical, this job standard should be sealed with a clear, non-yellowing, non-chalking coating until the end of the job, so that the understanding of the job standard does not drift with time.

Coating Materials

Selection of coating materials involves matching a coating with the environment and service conditions to which it will be exposed. The specifier must be able to assess each area to be coated, and rank each according to the anticipated operating conditions; then determine which coating to use in each environment. If he or she has good technical knowledge and a background in the industry involved in the project for which this specification is being written, he or she may be able to select the proper coating systems readily. If he or she does not (which is more often the case), he or she must rely on help from others. One such source is the coatings manufacturer's technical department rather than their sales department. Chemists and engineers serving in a technical capacity are better qualified to recommend the coating systems that have the best opportunity to work in a given environment. Sales personnel have as their primary obligation the achievement of sales goals set by their management. The pressure of achieving these goals can and have led to recommendations based upon economic factors rather than performance characteristics with predictably poor results.

Another source of information could be the table titled "Typical SSPC Painting Systems For Environmental Zones,"6 which lists various environmental zones of usage and recommends corresponding generic coatings. The selection may be based upon a generic formula such as SSPC Paint #20, AWWA C-204 Interior System #8, MIL Spec C15203, or others. If the structure that is to be coated is offshore, the NORSOK M5017 standard is a good reference to aid in the surface preparation, selection and application of coating systems. Another good reference is ISO 12944-5:2007.[8] The risk of using formula specifications alone without comparative tests lies in the fact that choosing by formula alone does not take into consideration the differences in job site conditions. What works in sunny California may be a disaster in wintry Minnesota. Another risk of using governmental formulae is the risk that they have not been updated and thus, do not have the benefit of the latest technology.

TABLE 17.3: Example of a Coating Manufacturer's Data Chart

Physical Data	Coating Data
Finish	Semi-gloss
Color	Aluminum
Applied over	Steel
Components	2
Volume solids (ASTM D2697)	90%
Dry Film Thickness per coat	5-8 mils, 125-300 µm
Coats	1
Calculated coverage at 1 mil (25 µm) 5 mils (125 µm)	1,444 ft^2/gal 35.4 m^2/ltr 288 ft^2/gal (7.1 m^2/ltr)
Allowance for Application Losses and Surface Irregularities	
Application	**Airless or conventional spray**
Pot life	8 h @ 70 °F (21 °C) 1.5 h @ 90 °F (32 °C)
Dry to touch	4 h @ 95 °F (35 °C) 12 h @ 70 °F (21 °C) 30 h @ 50 °F (10 °C)
Through dry	10 h @ 95 °F (35 °C) 24 h @ 70 °F (21 °C) 72 h @ 50 °F (10 °C)
Mixing Ratio	1 part resin to 1 part curing solution
Temperature resistance	200 °F (93 °C)
Flash point (Setaflash) Resin (Component A) Cure (Component B)	 112 °F (44 °C) 116 °F (46 °C)
Thinner	No. 65 < 70 °F (21 °C) No. 101 < 70 °F (21 °C)
Cleaner	Cleaner 12
Packaging 2 gal unit 10 gal unit	 1 gal resin/1 gal cure 5 gal resin/5 gal cure
Shipping weight (approximate) 2 gal unit 10 gal unit	 Resin: 12 lbs (5.5 kg) Cure: 8 lbs (3.6 kg) Resin: 60 lbs (27 kg) Cure 40 lbs (18 kg)
Shelf life	6 month from shipment date from each component stored indoors @ 40 to 100 °F (5 to 38 °C)

Source: Ameron Corp., Monterey Park, CA

The coating selection may be based on performance or physical criteria, such as percent solids by weight or volume, viscosity, weight per gallon, gloss, dielectric strength, permeability, abrasion resistance, pencil hardness, salt fog tests, etc., as determined according to the appropriate ASTM test methods. Unfortunately, many performance requirements prove to be less than satisfactory. There is no way to determine whether two materials will perform equally and satisfactorily without putting them through actual performance tests. Better choices may be made based upon side-by-side comparative tests of candidate coating systems. While this does not correlate directly to field history, it does indicate which of the candidate coating systems performs best in the tests chosen. The trick is to choose those tests that most closely represent the conditions that the coating systems are expected to resist at the job site.

Typically, a specification will list two or more approved coating systems by trade name for each specific environment on each job. This is a very acceptable procedure that has worked well in many instances. Unfortunately, too many specifiers, for one reason or another, add the statement "or approved equal" without ever stating a clear standard by which a proposed coating can be judged as "equal" or "not equal."

A statement regarding the storage of the material also should be included in the coating material section. Unfortunately, the material is often brought out on a job, left in the open, and, especially during a long job, subject to considerable weather changes during that period of time. This can lead to many material difficulties such as jelling of the coating or its transformation to a heavy, thixotropic consistency. Such exposure also may increase the settlement of pigments in the coating, which require substantial effort to bring them back into suspension.

Exposure conditions may even allow water to get into the coating. In one instance, 55-gallon drums of coating were left in the open during a period of considerable rain. The drums were left upright, and because of temperature changes, water was drawn through the bung in the top of the drum, resulting in coating contamination. The pigments in the coating were precipitated because of the water and could not be properly re-dispersed. The manufacturer was accused of supplying poor material. After the water was discovered, there was considerable rework of coated areas, which was quite costly. All of this could have been prevented by proper storage of the material in an area protected from the weather.

Sampling Coatings

The specifier may require the contractor or inspector to take retained samples of each batch of coatings delivered to a job site. The procedure, number of samples, labeling procedures, storage requirements, and so forth, should be clearly stipulated. Materials should be agitated or mixed prior to pouring off a sample. For multiple-component products such as epoxies and polyurethanes, obtain a separate sample of each component. Do not mix multiple-component product samples together. While not all coatings sampled are tested, the simple taking of samples does provide a measure of assurance that the proper coatings are being supplied. Should a problem develop, the retained sample becomes a valuable item for testing by an independent laboratory to determine the actual composition of the coating supplied to the job site.

Coating Schedule

The required coating schedule is often listed as an appendix. Where it appears is not mandatory as long as the areas to be coated, protected, not coated, etc., become an integral part of a good specification.

Work Methods

A good coating specification should not include a generic phrase such as, "All work shall be performed in strict accordance with these specifications and the coating manufacturer's current printed instructions for materials to be used on this project. Work shall be performed by skilled workers in a safe and professional manner." Such an open-ended phrase is subject to interpretation and misunderstanding.

The specification should define what is meant by "good work methods" by citing the requirements of such sources as SSPC-PA 1, or require painters to be qualified according to ASTM D4227[9] and D4228.[10] Another alternative is to require the contractor to qualify his or her operators according to the NACE International Guide to Qualification of Industrial Maintenance Painters.[11]

TABLE 17.4: Coating Application Requirements

Surface Preparation

Maintenance: Steel	Maintenance: Concrete	Immersion: Steel	Immersion: Concrete
1. Round off all rough welds and sharp edges. 2. Dry-abrasive blast according to Steel SSPC Specification SP-10-63 or SP-6-3. Use only steel grit (G-40 size), steel shot (S-230 size), graded flint, or silica sand (30-60 mesh). If reusing abrasives, clean them of contamination before reusing. Do not reuse sand or flint abrasives. Use air with minimum of 200 CFM (100 ltr/sec) per blast nozzle at minimum of 100 psi (7 kg/cm^2). 3. Apply coating as soon as possible to prevent blasted surfaces from rusting. Keep moisture, oil, grease, or other organic matter off surface before coating. Spot reblast to remove any contamination. Solvent wiping is not satisfactory.	Clean concrete surface, making them dry and free of previous coatings, disintegrated or chalky material, and surface glaze or laitance. Best cleaning is done by light sandblasting with 60–80 mesh sand and air at 50-60 psi (3.5–4.2 kg/cm^2). Note: Do not use form release agents, concrete curing compounds, or hardeners where a high-performance coating is to be applied.	Prepare surface in same manner as for maintenance except blasting should be according to SSPC Specification SP-5-63 to "white metal."	Prepare surface in same manner as described above for concrete in maintenance service.

Equipment Required

For Airless Spray	For Conventional Spray
· Standard airless spray equipment such as Grace Hydra-Spray or others using a 28:1 pump ratio · Fluid tip with 0.015 in. or 0.017 in. (0.38–0.43 mm) orifice. Air supply: 80-100 psi (5.6–7.0 kg/cm^2) in bound	· Pressure material pot with mechanical agitator · Separate atomizing air and fluid pressure regulators · Air supply: Compressor capable of supplying continuous volume of 20 CFM (10 ltr/sec) at minimum of 80 psi (5.6 kg/cm^2) to each nozzle · Air hose for gun 5/16 in. (7.9 mm) I.D. · Material hose, 1/2 in. (1.25 mm) I.D. · Industrial spray gun uch as DeVilbiss MBC 510 with a 24 D or 64D nozzle combination, 0.086 in. (2.1 mm) fluid tip, external atomization, 7-hole air cap.

Safety Equipment Required

1. Explosion-proof lights and electrical equipment
2. Fresh air mask, such as DeVilbiss P-MPH 527 and MPH 529, connected by 1/4 in (6.5 mm) hose connected directly to air source.
3. Exhaust fan capable of keeping solvernt vapors below 20% of the explosive limit or 1/4% by volume of solvent vapor in air.

English			Metric		
Tank Volume (Gallons)		Required Blower[1] (ft^3/min)	Tank Volume (kl)		Required Blower[1] (ltr/sec)
500–	5,000	1,000	4–	20	500
5,000–	20,000	2,000	20–	74	1,000
20,000–	100,000	5,000	75–	380	2,000
100,000–	250,000	10,000	380–	1,000	5,000
500,000	—–	15,000	2,000	—–	7,500
1,000,000–	2,000,000	20,000	4,000–	8,000	10,000

[1]All blowers to be suction type.

Application Procedure

1. Flush equipment clean with cleaner.
2. Thoroughly mix contents. Stir continuously throughout application.
3. Do not thin except for workability, and then with no more than 1 pint (0.5 ltr) of thinner per gallon of mixed coating.
4. Remove all dust from surfaces to be coated.
5. For conventional spray, regulate air pressure to 40 psi (2.8 kg/cm^2) to spray pot and 70 psi (4.9 kg/cm^2) to gun. NOTE Required pressures may vary with hose length and temperature.
6. Make even, parallel passes. Overlap each pass 50%, and apply a heavy, wet coat. Double-lap spray all welds, corners, etc. Immediately "cross-spray to achieve proper film thickness with no bare spots, pinholes, or holidays.
7. Allow first coat to dry at least 12 hours at 70 °F (21.1 °C) but not more than four days, before applying second coat. NOTE: Exposure to direct sunlight for more than 24 hours between coats will result in intercoat delamination.
8. Check for pinholes, bare areas, or holidays with nondestructive holiday detector. If coating is intended for use as a tank lining, check for pinholes, bare areas, or holidays with a nondestructive, field-calibrated sparking holiday detector, such as Tinker and Rasor high-voltage Model AP (approximately 2,500 volts). Also check film thickness with nondestructive dry film thickness gauge, such as Elcometer or Mikrotest. If film is not up to required thickness, add additional material.
9. To repair coating, or to add thickness, clean and remove all dust. Spray material on larger areas; brush may be used on smaller areas. NOTE: If coating has been applied for more than four days, a "tooth" must be provided on the surface before recoating—brush blast with 60–100 mesh sand or roughen with coarse sandpaper. See note under #7 above.
10. Before placing coating into service, allow film to dry one week at 70 °F (21.1 °C) if intended for immersion or tank lining service (provide normal ventilation). NOTE: if intended as a tank lining for potable water tank, coating should be flushed, rinsed, or filled and dumped with fresh water before service to avoid taste pickup
11. Clean all equipment with cleaner immediately after use.

Source: Ameron Corp., Monterey Park, CA.

Application

Application is the area of a coating specification that should be the most detailed and is therefore the most difficult to write. Often, however, this part of the specification simply states that the coating be applied in accordance with the manufacturer's recommendations. This is usually not sufficient since it only includes data put out in chart form by the manufacturer, an example of which is shown in Table 17.3. Such a chart provides a quantity of essential information; however, it cannot, because of its abbreviated form, cover many general conditions that are critical to the application of a coating. Manufacturers use this method of providing the essential information regarding a coating because of the many variables involved in application and the impossibility of covering all of these in any reasonably limited form.

In addition to this data chart, some manufacturers also supply more detailed application instructions. An example of this is shown in Table 17.4. In this case, detailed application instructions are provided, which give the essential information required for the proper application of the coating. However, even these specifications may not sufficiently cover all of the variables involved in a sizable or critical coating application. It must be remembered that every coating job is unique and therefore, such application instructions pertain only to a specific coating. If several materials are specified, as in a qualified products list, this information would not necessarily be applicable to all the coatings listed.

The applications section of a good specification should set forth the approved equipment and methods and criteria for acceptance of each coating system on this job. A good specification will state the minimum and maximum dry film thickness (DFT) of each coat in the system and the minimum and maximum allowable DFT of the total coating system. In addition, any special requirements such as stripe coating of welds, edges, nuts, bolts, and other parts, must be clearly stipulated.

Another important point for the general information section is the requirement that the superintendent or supervisor of the application crew keep a diary of job progress. This requirement also applies to inspectors, if they are involved. The diary should include (besides routine items such as weather) the areas coated, the coats applied during any period, and any exceptions to the specification. Such information might include potential problems such as moisture condensation on the coating shortly after application, welding in an area after the coating has been applied, or any unforeseen happening during the application. If there is a coating failure, such items can be extremely important in determining what may have caused the difficulty. If litigation results, such information can be extremely valuable to both the applicator and the owner.

The general information section of a specification may include any number of other specific items that are important to the owner or the design engineer. There are number of other specific items that are important to the owner or the design engineer. There are a number of application requirements that may be included, or at least considered, during the writing of a coating application specification

Weather

Weather is an extremely important condition that must be taken into consideration during any coating application. The specification should include maximum and minimum application temperatures above and below which the coating should not be applied. It also should include maximum and minimum humidity values above and below which the coating should not be applied. Wind is also a consideration since much of the coating may be lost due to the wind creating dry spray that is blown away, or it may create a serious overspray condition on the finished coating or on adjacent structures.

Dew Point

The dew point and condensation also should be taken into consideration in the specifications. It is generally recommended that coatings be applied when the surface temperature is within 3 °C (5 °F) of the dew point. Coatings should not be applied on wet or damp surfaces unless the coating is specifically recommended for that usage, and then only exactly as shown on the manufacturer's written application instructions, as adhesion will be affected. Surfaces subject to condensation or rain should not be coated until the surface has become thoroughly dry. If circumstances make it necessary to apply an epoxy over a wet or damp surface; brushing or rolling the first coat will increase the chances of success as the action of the brush or roller will force some of the moisture to be taken up into the interstices of the epoxy and expelled as part of the coating reaction.

Method of Application

The method of application may be outlined in a specification. Many coatings are preferably applied by conventional spray application; others may be preferably applied by airless spray; still others, as in the case of primers, may be better applied by brush in order to ensure a thorough wetting of the surface. The structure and the surface to be coated may require a specific application method. For example, a badly pitted tank may be better coated by airless spray rather than by conventional air spray since the material from an airless spray does not bounce or rebound out of small openings as it does from air spray. Also, a specific application of a coating may be such that only brushing or rolling can provide a satisfactory finished product. A specification for any coating job should include information on the method of application, even though the manufacturers of coatings supply considerable information in their application instructions.

Thickness

The number of coats to be applied is of vital importance since each specific coating may require more or fewer coats, depending on the severity of the exposure. The specification should not only cover the number of coats, but also should include the thickness of each coat to be applied and the total thickness of the completed coating. In this case, both maximum and minimum thicknesses should be specified, since it is almost physically impossible for an applicator to apply a specific number of mils of any coating.

Coverage

Specifying coverage rates in a coating specification has to be done with extreme care. The coverage of the coating will determine the thickness of each coat and the thickness of the finished product. Most coating suppliers provide the coverage of a coating on a theoretical basis. This is a necessity for them, again because of the variability of the applications for which the coatings are used.

Theoretical spreading rates are based on the volume solids of each coating and offer only a starting point from which to estimate practical coverage. It is always necessary to adjust the theoretical coverage rates because each job is characterized by conditions that will require more

or less coating. In the case of coatings over concrete, the coverage rates can vary widely and the manufacturer may very well recommend square footage per gallon rather than minimum and maximum DFTs. Specifications for application of coatings to ships' hulls are sometimes stated in square footage by frame numbers of the ship according to coverage recommended by the manufacturer.

Equipment Cleanliness

Cleanliness of equipment is well worth including in a specification. Hoses can pose a particular problem, since they usually are not cleaned as thoroughly as they should be. On any large job, it is preferable to specify that new hoses be used. In this way, contamination of the coating to be applied is kept to a minimum since only one coating would be used in those particular hoses on that job.

If new hoses are not practical, used hoses may be satisfactory if they are thoroughly cleaned with strong solvents prior to being used with the new coating. If this is not done, the solvents in the newer coating often swell and release the previous coating materials from the interior of the hose, seriously contaminating the coating to be applied, as well as providing for innumerable work stoppages during the application. Material pots, guns, brushes, and all other equipment should be specified as being clean and in proper working order.

Drying Time

The drying time between coats and the final drying time of the coating are extremely important, and while they are keyed to a specific coating at a specific DFT range and temperature, the minimum that should be included in the specification is a statement that the drying of the coating between coats and the final drying time should be in accordance with the manufacturer's recommendations. Otherwise, application may be undertaken during specific weather and temperature conditions that are outside of the parameters recommended by the manufacturer.

The specific conditions of the job determine the drying times for the coating. Where heating of the coating is required, as is necessary for some tank linings, the specification should be explicit in requiring that the minimum temperature be above the curing temperature of the coating at all points in the tank or container. Exterior supports, braces, manholes, valve flanges, and other similar places are heat sinks and therefore require more attention and heat than the plain areas. Many coating failures have occurred in such areas because of incomplete curing. Failures occur much more often because of incomplete drying or curing than because of over curing. An even, minimum overall temperature is essential for satisfactory solvent removal and resin reactions.

Pot Life

Pot life of the material also should be considered in the specification. Temperature and weather conditions affect the pot life of mixed coatings, and many of the two-part coatings will react over a period of time to the point where either the application is difficult, or the adhesion of the material applied will not be satisfactory.

The pot life naturally varies according to the specific coating, and the recommendation of the manufacturer must be considered as well as the practical temperature and weather conditions at the time of coating. Any coating that has a critical pot life should have a reference to the pot life in the specification with a definite limit set on the time period in which the material is useable. Such a reference acts as a "red flag" to the applicator, indicating those difficulties that can be encountered if the warning concerning the pot life is unheeded. A specific restriction against thinning or cooling as a means of extending pot life should be included.

Thinning

Thinning is a common point of contention since many applicators tend to over-thin materials in order to make them easier to apply. It must be remembered that when a coating is thinned, the total volume solids in the coating are reduced so that additional coats may be necessary in order to develop the proper coating thickness. Over-thinning can also cause resin or pigment precipitation, and use of the improper thinner may coagulate or gel the coating, making it impossible to apply. If it does not do this, the drying time of the thinner may be such that it will adversely affect the adhesion or the durability of the coating.

Many coatings are now produced ready for application so that thinning is not necessary when applied in accordance with the tip sizes and pressures recommended on the product data sheet (PDS). If thinning is allowed, the specification should include a specific type and amount of thinner in strict accordance with the manufacturer's recommendations, and the volatile organic compound (VOC) regulations.

Manufacturer's Instructions

The manufacturer's application instructions should always be made a part of the coating specification. With the advent of higher technology coating materials, many manufacturers are creating separate application instruction sheets from the PDS. These are as many as four pages in length and are very detailed. Any discrepancy between the requirements of the job, the job specifications, and the manufacturer's recommendations should be settled between the manufacturer and the owner prior to the time the specification is completed.

Coating Appearance

One item that is seldom included in a specification is a description of the final coating appearance. This can be done by specifying that the final appearance be in accordance with samples submitted by the coating manufacturer prior to the beginning of the job; by a written description of the coating detailing the color, texture, smoothness, and general appearance of the coating; or by specifying a sample application of the material by the contractor to be agreed upon by all parties prior to the beginning of the job. This last procedure is usually preferred since it provides a working sample that serves as a guide for both the applicator and his or her workers.

Color Between Coats

Another item that is also good to include in any specification is the change of color between each coat applied. Depending on the number of coats, these should be of a sufficient contrast in color with the previous coat. However, the next to the last coat should be reasonably close to the color of the final topcoat so that an even color for the entire coating is obtained.

Differentiating between the colors of various coats not only makes it easier for the painter to see where he or she has coated, but it also helps to eliminate holidays and other coating imperfections. It can also lead to better coverage per coat and a more even thickness than when coating with all the same color.

Specifications for Applicators

Another item that is seldom included in the specification, but which is well worth including, is the requirement that a copy of the specification and the manufacturer's instructions be given to each supervisor for reference. Too often, the only reference available to the applicator is the information on the label of the can, which may amount to little or nothing. A copy of the specification in the hands of the supervisor is also important from a legal standpoint, since this is evidence that those doing the work received a written description of the coating desired, the method of application, and the safety conditions required during the application. The fact that the coating applicator did or did not receive a copy of the coating specification has been the turning point in many legal proceedings where the coating application was in question.

Work Schedule

It is generally the responsibility of the contractor to establish his or her own work schedule and submit it to the engineer for approval prior to starting the job. However, the owner may have prerequisites for timing of certain work in certain areas. If so, these must be included in the specification. The schedule timetable normally includes such points as pre-inspection, pre-cleaning, repair of fabrication defects, surface preparation, application, inspection intervals, repair and remedial work, documentation, and reports.

This section should also clearly identify access points to the plant and job site and the allowable working hours for the contractor. Any other known restrictions and limitations should also be included.

Repair and Remedial Coating Work

This section should include a statement about the responsibility of the contractor to repair any damages or defects in his or her work. For example:

> Contractor shall identify damage to the coating and shall feather edge the coating around the damaged area a minimum of three (3) inches from the center of the damaged area in all directions. Contractor shall use 80 grit wet/dry abrasive coated paper to expose each coat of the coating system including the primer. The Contractor shall apply, by brush, the same number of coats as is found in the repair area. Total thickness of the repair shall be no less than 90% of the total thickness of the adjacent undamaged coating.[3]

Inspection

Generally, inspection should be required in the specifications. A clear, detailed specification and good inspection procedures are the best insurance for obtaining an effective coating application. Coating specifications vary; job conditions and circumstances vary from job site to job site. So do the duties of the person responsible for inspection of everything done in the course of a coatings job. Coatings inspectors on an offshore platform, for instance, are often given authority to do such non-inspection duties as ordering abrasives, coatings, thinners, etc., which rarely happens on an industrial site where the contractor has this responsibility. It is necessary, then, for this section of a good specification to spell out the responsibilities and authority of the inspector for this job and this job only. Besides the normal duties of inspecting pre-cleaning, mixing and application, documentation, and other steps, the specification may very well specify the extent of such duties as:

- When, where, and how many DFT measurements to take.
- Pass/fail criteria for all measurements such as using the SSPC-PA 2 guide.[12]
- Guidelines for completion and submission of reports.
- A comprehensive statement of the inspector's responsibilities and authority.
- An organizational chart showing the chain of command on that specific job site.

Inspection should be an in-process function that requires full-time observation of all cleaning, surface preparation, mixing, application, and curing of coating systems. All difficulties and improper work should be called to the attention of the applicators or contractor as quickly as possible so that they can be remedied prior to the application of the following coat. The inspector should be required to know the key application properties of the coating, and have the authority to make sure the work is performed in accordance with the specification.

A costly example of improper knowledge and/or insufficient attention to mixing requirements occurred during the hull coating and tank lining of a chemical carrier. The specified tank lining was a modified novolac epoxy and the hull primer was a surface-tolerant epoxy, both of which had product numbers very similar to each other. When the day shift inspector arrived on the ship one morning, he immediately checked the empty cans on the deck and found empty cans of the novolac epoxy base and empty cans of the surface-tolerant epoxy converter. Before he could stop the applicators, they had already coated a substantial portion of the tank. The only remedy was to allow it to cure sufficiently so it could be removed by abrasive blasting and re-coated. The cost of the re-blasting and re-coating was small in comparison to the extra costs of several days of extra drydocking charges for the ship.

There are many points to be considered during the application, ranging from inspection of the material as it arrives on the job, to inspection of the mixing of the material to make certain that it is fully dispersed, and that there is no settled material left in the bottoms of the containers. Each coat should be followed closely to make sure that the coating is applied according to the specifications. All pinholes, holidays, and missed areas should be eliminated from areas subject to immersion in liquids. Varying the color of each coat makes inspection of the application much easier and aids in eliminating many of the coating defects.

Finally, as part of the inspector's job, a diary should be kept of the work progress, including all of the pertinent activities and conditions found during each day. This is important since it provides a check for follow-up on rework items and a basis of fact for any problems that may arise at a later data. Such diaries are always invaluable during any legal proceeding. Inspection details should be included in the specifications.

Documentation

This section of the specification should list all the reports that are required, the frequency of reports and to whom they should be forwarded. This should include contractor's progress reports along with the inspector's reports of the work as it is accomplished. Blank copies of reports can be included.

Cost of Specifications

There is always some controversy over the additional cost of a job with a strong specification due to the fact that contractors may add to the contract price in order to cover possible additional work. Many contractors, particularly the poorer ones, prefer jobs that carry no specification whatsoever since this allows them freedom to do whatever they want or think is best. On the other hand, most good contractors welcome a strong specification because, in many ways, it reduces their cost by specifically and clearly outlining requirements. With a strong specification, there is usually much less rework, the cost of which is usually carried by the contractor.

While a strong specification may somewhat increase the bid price of a job over one which carries a more general specification, it will usually reduce the overall cost of the job due to the fewer requirements for rework and extra work and/or materials. Generally speaking, a strong specification is well worth any initial added expense as insurance that the job will be done properly and that many years of maintenance-free service can be expected from it.

References

1. "A Guide to the Preparation of Contracts and Specifications for the Application of Protective Coatings," NACE Publication 6J162 (Houston, TX: NACE).
2. Steel Structures Painting Manual, Discussion of Paint Specifications, Section 5, Vol. 2 (Pittsburgh, PA: SSPC).
3. NACE Coating Inspector Training Program, Session I.
4. SSPC-SP 1, "Solvent Cleaning" (Pittsburgh, PA: SSPC).
5. NACE No. 5/SSPC-SP 12, "Surface Preparation and Cleaning of Steel and Other Hard Materials by High- and Ultrahigh-Pressure Water Jetting Prior to Recoating" (Houston, TX: NACE).
6. "Typical SSPC Painting Systems for Environmental Zones: (Pittsburgh, PA: SSPC).
7. NORSOK M501, "Surface Preparation and Protective Coating" (Lysaker, Norway: Standards Norway).
8. ISO 12944-5, "Paints and varnishes –Corrosion protection of steel structures by protective paint systems-Part 5: Protective paint systems" (Geneva, Switzerland: ISO).
9. ASTM D4227, "Standard Practice for Qualification of Coating Applicators for Application of Coatings to Concrete Surfaces" (West Conshohocken, PA: ASTM).
10. ASTM D4228, "Standard Practice for Qualification of Coating Applicators for Application of Coatings to Steel Surfaces" (West Conshohocken, PA: ASTM).
11. International Guide to Qualification of Industrial Maintenance Paints (Houston, TX: NACE).
12. SSPC-PA 2, "Procedure for Determining Conformance to Dry Coating Thickness Requirements" (Pittsburgh, PA: SSPC).

APPENDIX 17A

Typical Offshore Work Specification

1.1.1 Scope

1.1.2 The specification covers the basic requirements for cleaning, surface preparation, material selection, application, and inspection of external coatings to the metal surfaces of piping, structures, vessels, buildings, and packaged equipment located on ABCD offshore platforms.

1.1.3 This specification does not apply to internal coatings, pipeline coatings for submerged service, cathodic protection, or fabrication requirements, unless specifically listed in the specification and contract documents for each specific platform.

1.1.4 Definitions

1.1.5 The term "structure" is used in this specification in a general sense to mean any item including the list of items given above owned and operated by ABCD. It shall not include subcontractor structures or equipment operated on ABCD platforms.

1.1.6 "ABCD" as used in this specification means ABCD and its affiliates. "CONTRACTOR" means a company or individual under contract to perform specific work or services for ABCD.

1.1.7 OWNER shall mean ABCD and its authorized representatives with responsibilities for the work being performed under each specific contract.

1.1.8 COATING SUPPLIER shall mean the coatings manufacturer or an authorized technical representative of the coatings manufacturer whose material has been chosen for each specific platform.

1.1.9 INSPECTOR shall mean a NACE-Certified Coating Inspector retained or employed by ABCD.

1.2 Conflicting Requirements

1.2.1 In case there is any conflict between the specification, the inquiry, or purchase order, the accompanying data sheets and drawings, and any other supplemental specifications, the CONTRACTOR shall notify ABCD in writing of the basis of the conflict and justification for any deviations from this specification. Until such time as resolution is received by the CONTRACTOR, the more stringent requirements of the conflict shall apply.

1.3 Contractor requirements

1.3.1 The CONTRACTOR shall furnish all labor, materials, and equipment necessary for the cleaning, blasting, ventilating, coating, curing, and inspection of surfaces to be coated. It is the responsibility of the CONTRACTOR to perform all work in a manner meeting the requirements of all health and safety regulations applicable to the specific work site.

1.3.2 The CONTRACTOR shall provide a Competent Person, Lead as a member of his or her crew on jobs involving removal of lead-based paint. Such persons shall have a training certificate from SSPC or equally qualified source meeting the requirements of EPA.

1.3.3 It is the responsibility of the CONTRACTOR to meet the requirements of this specification, to use equipment capable of meeting these requirements, and to perform all inspections necessary to insure compliance prior to inspection by the OWNER's representative.

1.3.4 In addition to the CONTRACTOR's inspections, ABCD or its designated representative(s) may perform any inspection necessary to verify compliance with this specification. Inspection may include any and all work, equipment, inspection equipment, materials, or procedures and may be conducted at any time ABCD chooses. CONTRACTOR shall provide accessibility to all the coatings work for inspection purposes.

1.3.5 The CONTRACTOR shall correct any work which ABCD or its designated representative(s) have determined to not be in compliance with the requirements of this specification. Corrections shall be made without additional cost to ABCD.

1.3.6 It is the responsibility of the CONTRACTOR to perform all work in a manner meeting the requirements of all health and safety regulations applicable to each specific work platform.

1.3.7 The CONTRACTOR must have a proven procedure to document and maintain accurate records. Records must be kept on all aspects of the coating job including the results of all quality control testing. These records shall be made available for audit at ABCD's request. Contractor must submit copies of inspection forms to ABCD for approval prior to beginning each job.

1.3.8 The failure of ABCD or ABCD's inspector to discover or reject defective work or materials does not constitute acceptance of such work or materials by ABCD.

1.3.9 The provision of this specification shall also apply to any work performed by subcontractors to the CONTRACTOR on each specific platform.

1.4 Pre-Job Conference

1.4.1 A Pre-Job Conference must be held at least one week prior to the beginning of any work on each specific platform. Mandatory attendance is required of the CONTRACTOR, the INSPECTOR, the COATING SUPPLIER, and the OWNER's representatives (including the Safety Officer) for each specific platform.

1.4.2 The CONTRACTOR shall review his or her safety practices, cleaning and surface preparation operations, coating material and solvent storage and handling practices, application procedures, inspection tools, methods and sequence, and any proposed change orders. He or she shall obtain concurrence in writing from all parties prior to starting the work on each platform.

1.5 Coating Supplier Technical Service Requirements

1.5.1 The COATING SUPPLIER is required to provide on-site evaluation of the work being done, at the OWNER's request. The SUPPLIER is required to attend all project meetings with the CONTRACTOR, including the Pre-Job Conference. The COATING SUPPLIER may be required to provide the following technical assistance:

- Be on site when the coating application begins.
- Be on site when there is a major coating system change.
- Respond to any material or application problems.
- Visit the site periodically during material application.
- Provide a written report to the OWNER's representative after each on-side visit.

2.0 Codes and Standards

Except as amended in this specification, the latest approved editions of the following codes and standards shall form an integral part of this specification.

- SSPC-SP 1, "Solvent Cleaning"
- SSPC-SP 2, "Hand Tool Cleaning"
- SSPC-SP 3, "Power Tool Cleaning"
- SSPC-SP 11, "Power Tool Cleaning to Bare Metal"
- SSPC-VIS 1-89, "Visual Standard for Abrasive Blast Cleaned Steel"
- SSPC-VIS 3-93, "Visual Standard for Power and Hand Tool Cleaned Steel"
- NACE No. 2/SSPC-SP 10, "Near White Blast Cleaning"
- NACE No. 3/SSPC-SP 6, "Commercial Blast Cleaning"
- NACE No. 4/SSPC-SP 7, "Brush-Off Blast Cleaning"
- NACE WJ-1/SSPC-SP WJ-1, "Waterjet Cleaning of Metals—Clean to Bare Substrate"
- NACE WJ-2/SSPC-SP WJ-2, "Waterjet Cleaning of Metals—Very Thorough Cleaning"
- NACE WJ-3/SSPC-SP WJ-3, "Waterjet Cleaning of Metals—Thorough Cleaning"
- NACE WJ-4/SSPC-SP WJ-4, "Waterjet Cleaning of Metals—Light Cleaning"
- RCRA, "Resource Conservation and Recovery Act"

3.0 Materials

3.1 Coating Materials

3.1.1 Appendix B provides a list of approved coating systems by coating supplier or manufacturer. The CONTRACTOR may indicate a supplier preference; however, ABCD reserves the right to make the final selection. Once a supplier has been chosen for a specific project, that supplier shall remain the supplier throughout the project. Paint systems of one supplier shall not be mixed with systems or products of another unless approved in writing by ABCD.

3.1.2 Coating systems in Appendix B are listed according to specific service or use as outlined in Appendix A. Substitution of materials by the CONTRACTOR is not permitted. All thinners, catalyzing/curing agents, and other additives shall be as specified by the coating manufacturer for use with the specified coating system. Use of special curing accelerators is not allowed.

3.1.3 Colors are indicated where appropriate. In all cases, each coat must be contrasting to preceding and succeeding coats. The color of the finish coat is project-specific and will be provided by ABCD. All coatings must be free of lead and chromates or other toxic contaminants listed in RCRA 40 CFR 61.

3.1.4 The CONTRACTOR shall supply all coating materials, catalysts, and thinners unless other arrangements have been made and approved by ABCD.

3.1.5 Store coating materials in their original containers with their original labels visible and readable. Storage conditions shall be as specified by the manufacturer's data sheet. Use each material within its shelf life as defined by the manufacturer.

3.1.6 Do not use coatings which have exceeded their shelf life or which have deteriorated in storage. Deterioration is indicated by formulation of a surface skin, by gelling, color change, or by settling of solids which cannot be mixed into a smooth consistency.

3.1.7 CONTRACTOR shall obtain copies of the manufacturer's product data sheet and MSDS for each product. This information must be available at the job site.

3.2 Abrasive Materials

3.2.1 Abrasives shall be either sharp steel grit, a mixture of steel grit and steel shot, coal slag, garnet, or aluminum oxide and meet the following requirements:

- Contain less than 1% free silica.
- Be free of harmful quantities of toxic metals.
- Contain less than 50 ppm water soluble chlorides.
- Contain less than 200 ppm water soluble sulfates.
- Be free of clay, limestone, shells, undersize and oversize particles, organic material, and other detrimental foreign material.

CONTRACTOR must obtain certification from the abrasive supplier that the abrasive meets these requirements. A copy must be submitted to ABCD prior to abrasive blasting.

3.2.2 No substitution of blasting media shall be made without written approval of ABCD.

3.2.3 The abrasive must be of proper size to achieve the cleanliness and anchor profile requirements of the coating manufacturer for each coating being applied.

3.2.4 Reclamation and reuse of blast media shall not compromise surface cleanliness or surface profile as required in this specification.

3.2.5 Surfaces which are abrasive blasted using a nonapproved abrasive shall be reblasted with the proper abrasive at no additional cost to ABCD.

3.2.6 "Wet or Dry" type abrasive paper must be used where hand sanding (abrading) is required. Abrasive paper residue must be removed with tack rags, air blow down, or vacuuming immediately prior to painting. Sanding residue must be removed by use of tack rags, air blow down, or vacuuming, as appropriate, prior to applying coating.

3.2.7 Industrial Grade Baking Soda or impregnated polyurethane foam pellets may be used for cleaning certain substrates, provided specific written approval has been given by ABCD prior to using either cleaning materials.

4.0 Extent of Surface Preparation and Coating

4.1 All carbon or low alloy steel exposed to the atmosphere shall be coated unless specifically exempted in the specification for each platform.

4.2 Unless otherwise specified by ABCD, do not coat nonmetallic surfaces, plastic, or plastic coated items (unless required to prevent UV degradation), metal jacketing or weatherproofing on insulation, stainless steel instrument tubing, galvanized surfaces, transite, nickel alloys, aluminum alloys, copper alloys, duplex stainless steel, austenitic stainless steel, and grease fittings.

4.3 Do not abrasive blast or coat items such as internal surfaces of piping and equipment, rubber hoses, belts, flexible braided connectors, nameplates, gauges, valve stems, motor shafts, pneumatic controllers, glass, sight glasses, level gauges, and regulators. Remove, mask, or otherwise protect such items from all effects of abrasive blasting and coating application.

4.4 Do not abrasive blast or coat items which require further cutting, welding, assembly, drilling of bolt holes, or similar work unless specifically directed to do so by ABCD.

4.5 Do not coat galvanized surfaces except to repair defects in the galvanized finish or to provide a desired protection or color finish coat as directed by ABCD for each specific platform.

4.6 Flange protectors and nut protectors shall be removed for surface preparation and coating. They shall be reinstalled after completion of the coating application. The areas marked as "No Blast—No Coat" shall be masked off to prevent damage. The CONTRACTOR shall not break open any flanges for surface preparation or coating unless specifically directed to do so in writing by ABCD.

4.7 Bolt holes in flanges require no special attention. They do not require surface preparation and coating application, nor do they require masking to prevent blasting and coating application.

4.8 Any surface that cannot be accessed for coating after assembly shall be prepared and primed before final assembly. Landing surfaces for grating are to be fully coated before grating is installed. Landing surfaces for equipment, pipe spools, support brackets, and areas under U-bolts are to be coated with at least the primer and intermediate coat before placement of the equipment.

4.9 Rotating equipment such as compressors, electric motors, blowers, and electric generators shall be protected from all effects or damage from abrasive blasting or coating application. If such equipment is in operation, it shall be protected by use of filter media, protective housings, or other methods as directed by ABCD. Equipment which is in operation shall be protected in a manner that does not cause it to overheat.

5.0 Surface Preparation

5.1 Pre-Cleaning of Surfaces

5.1.1 Prior to any other surface preparation, all oil, grease, drilling fluids, salt, and/or other contaminants should be removed by solvent cleaning in accordance with SSPC-SP 1 or by application of an ABCD approved water-based biodegradable cleaner followed by pressure washing at a minimum of 1,000 psi. Scrubbing with stiff bristle brushes may be done, provided the final low pressure rinse with fresh water is employed to remove all cleaning residues.

5.2 Compressed Air

5.2.1 Air used for abrasive blasting and spray painting shall be free of oil and water. CONTRACTOR shall perform a blotter test at the nozzle or conventional air spray paint gun at least daily to verify the purity of the air according to Section 7.7.3. Air pressure for abrasive blasting to remove coatings or corrosion shall be 85-100 psi (6-7 bar) at each nozzle. Air pressure for brush or sweep blasting may be reduced as necessary to achieve removal of loose coatings and contaminants without causing excessive damage to sound coatings.

5.2.2 The CONTRACTOR shall provide adequate traps, separators, and other equipment to assure the specific quantity and cleanliness of air at no extra cost to ABCD.

5.3 General Requirements of Surface Preparation

5.3.1 The degree of surface preparation required for each coating system shall be as specified in Appendix B with reference to the specific platform areas shown in Appendix A.

5.3.2 The blast profile (surface roughness) shall be as specified in Appendix B for each coating system being applied.

5.3.3 Blast nozzles for total or spot removal of coatings or corrosion shall be 7/16 in diameter venturi carbide, boron nitride, or other size and type approved by ABCD. Nozzles must be replaced whenever the venture wears out in excess of 1/16 in. Blast nozzles for sweep or brush blasting may be of any type or size that can be used at an oblique angle from a distance of 2-3 ft from the surface without creating excessive damage to sound coatings.

5.3.4 Dry abrasive blasting shall be used unless approved otherwise in writing by ABCD. Rust inhibitors or other surface treatments shall not be applied to any surface. Abrasive material must conform to Section 3.2.

5.3.5 Do not perform abrasive blasting when the steel is less than 5 °F (3 °C) warmer than the dew point of the air. Do not blast surfaces that will become wet before coatings can be applied and achieve initial cure.

5.3.6 Blast cleaning shall be performed with sufficient lighting (minimum 20 candlepower) to permit the operators to see their work and to permit thorough and accurate inspection of blasted surfaces.

5.3.7 Blast cleaned surfaces shall meet the cleanliness and surface profile requirements listed in Appendix B for the coating system specified. Verify cleanliness, anchor profile depth, and anchor profile density as described in Paragraphs 7.7.4 and 7.7.5. Record measured profiles for each item blasted.

5.3.8 Remove ALL blasting residues from all surfaces to be coated immediately before painting using, as appropriate, shovels, brooms, compressed air, and vacuum cleaners. Compressed air used for cleaning shall be free of oil and water as specified in Section 5.2.1.

5.3.9 Blasted surfaces shall be primed the same day that they are blasted unless the blasted area's humidity is controlled to 50% or lower relative humidity. Surfaces that show flash or pinpoint rusting shall be brush blasted to achieve original specified cleanliness prior to painting.

5.3.10 When working large areas that cannot be completed in one day, CONTRACTOR shall leave 6 in of blasted steel free of all coatings around the edge of the blasted area. When blasting adjacent to a previously coated or primed area, feather a minimum of 1 in into the adjacent coating and overlap the primer to cover the entire feathered area.

5.3.11 Abrasives used in removal of lead-based paints must contain additives (such as Blastox) to lower the amount of leachable lead to 5 ppm or less during the removal process.

5.4 Alternate Surface Preparation Methods and Equipment

5.4.1 Equipment that cannot be abrasive blasted because of the danger of damage to the equipment shall be solvent cleaned and prepared for coating application by power tool cleaning. Polyurethane foam pellets or industrial grade baking soda may be used with prior written approval of ABCD. Surface cleanliness must meet the requirements listed in Appendix B. Use devices that roughen the surface such as 3M Clean 'N Strip or RotoPeen. Avoid devices that polish the surface.

5.4.2 If previously painted, the equipment may be prepared for coating application by hand and power tool cleaning in accordance with SSPC-SP 2 or SP 3 followed by application of appropriate system in Appendix B for the area delineated in Appendix A. This applies to items such as electric motors, winches, gear housings, etc.

5.4.3 Wet abrasive blasting or water jetting may be used for limited areas provided these are approved in writing by ABCD prior to start of the job on each platform. Fresh water must be used with an inhibitor approved by the manufacturer of the coating system being applied and by ABCD. Any inhibitor used must be metered accurately into the make-up water at the minimum levels recommended by the coating manufacturer. Injection of inhibitor at the blast nozzle is expressly prohibited.

5.4.4 Areas cleaned by water jetting shall be inspected for acceptance in accordance with either visual surface preparation standards WJ-1 thorough WJ-3 or Nonvisual standards SC-1 through SC-3 contained in NACE No. 5/SSPC-SP 12 as specified by ABCD for each specific platform.

5.4.5 Sound coatings that are cleaned by use of water-based biodegradable cleaners followed by pressure washing shall utilize power washing equipment capable of operating at a minimum of 3,000 psi with abrasive injection controlled at the nozzle so as to clean spot rust down to NACE No. 3/SSPC-SP 6 Commercial Blast followed by continued cleaning with fresh water only.

5.5 Defects in Steel Surfaces

5.5.1 Steel defects revealed during abrasive blasting (slivers, laminations, cracks, pitting, etc.) shall be reported to ABCD for evaluation. If structurally unacceptable, appropriate repair will be required. If harmful to the performance of protective coatings, the CONTRACTOR shall grind smooth or otherwise repair as directed by ABCD. The repair area shall be reblasted and coated after repair. Crevices that cannot be seal welded or caulked with ABCD approved caulking compound must be protected by an application of 100% solids epoxy penetrating sealer according to manufacturer's directions prior to application of the coating system specified for that area of the platform.

5.6 Prevention of Damage to Abrasive Blasting

5.6.1 Peripheral Equipment

The CONTRACTOR shall assure that all gauges, sight classes, instruments, instrument tubing, instrument tags, vessel ID plates, navigation aids, and other items of equipment designed by ABCD are protected from damage during abrasive blasting. Appropriate masking and/or protective shielding shall be employed.

5.6.2 Rotating Equipment

Rotating equipment shall be protected from damage by selection of surface preparation procedures in consultation with the OWNER'S representative on each platform. Appropriate shielding, masking, use of filter media, choice of alternate soft abrasives, and other protective measures shall be employed by CONTRACTOR to protect such equipment. Section 5.7 includes further requirements for equipment protection.

5.6.3 Overblast and Overspray

Organize and plan work to prevent overblast or overspray damage to surrounding coated items. Protect surroundings as needed using barriers, tarps, etc. Level and type of protection required is site specific. CONTRACTOR must have a plan approved by ABCD prior to beginning the job. CONTRACTOR shall repair all overblast and overspray damage at no additional cost to ABCD.

5.7 Protection of Sensitive Equipment

5.7.1 This section defines procedures to be employed to protect the OWNER'S sensitive equipment during coating maintenance operations. The OWNER reserves the right to inspect and approve protection measures employed by the CONTRACTOR at any time.

5.7.2 Class I: Standard Procedures

Engine air intakes, crank case breathers, electric motor cooling air intakes, air conditioners, etc. are to be covered with a double layer of 1-in R-85-T sticky filter media. Install with the sticky side in. Change the outer layer as often as required to keep inner layer clan. Change inner layer when soiled. Do not cause overheating by excessive restriction of air flow. Use chicken wire, hardware cloth, etc. if necessary to provide support for filter and to provide larger area for air flow. Protect sight glasses, gauges, windows, chart boxes, etc., with replaceable semi-rigid clear plastic sheet (to allow visibility), plus tape, polyethylene sheet, etc.

5.7.3 Class II: Dust Restriction

Follow all requirements of Equipment Protection Class I. In addition, construct a rigid framework completely enclosing the designated area and cover the framework with a durable mesh material to control abrasive particles and dust. All gaps in the enclosure must be closed. Use a mesh with 16-20 threads per inch or 250-300 openings per in^2.

The structure must provide acceptable access to OWNER's personnel for routine work functions. The structure must be able to withstand normal weather conditions without damage.

Class II protection must be installed as specified before any abrasive blasting begins on the platform. It shall be maintained in good condition for the duration of the job and removed after completion of the job without damage to the structure or the coating system.

5.7.4 Class III: Dust Exclusion

Follow all requirements of Equipment Protection Class I. In addition construct a framework completely enclosing the designated area and cover the framework with a heavy, fiber-reinforced polyethylene or similar impervious sheet material to prevent the passage of dust or abrasive particles. All gaps must be closed to provide complete isolation of the interior.

The enclosed work area must be equipped with exhaust fans with ducts to discharge dusty air and particulate matter to a point designated by the OWNER.

If the work involves removal of lead-based paint, the residue of removal operations must be collected and stored for disposal in accordance with EPA 30 CFR regulations.

If sensitive production equipment is enclosed, it must be pressurized with clean, filtered air. The air volume must be sufficient to meet air flow requirements (combustion air, cooling air, etc.) of the equipment enclosed.

The structure must provide acceptable access to OWNER'S personnel for routine work functions whenever surface preparation or painting work is not underway. The structure must be able to withstand normal weather conditions without damage.

Class III protection must be installed as specified before any abrasive blasting begins on the platform. It shall be maintained in good condition for the duration of the job and removed after completion of the job without damage to the structure or the coating system.

6.0 Coating Application

6.1 Coating materials shall be as specified in Section 3.1.

6.2 Mixing

6.2.1 Do not split kits or use partial kits. Only mix full kit components as supplied by the coating manufacturer.

6.2.2 Mix each component of a coating to break up all solids and to produce a smooth uniform liquid. After each component is fully mixed, combine components as specified on the manufacturer's data sheet and blend thoroughly. Use only air driven or explosion-proof electric power mixers.

6.2.3 Thin coatings only as necessary and only to the extent recommended by the manufacturer using only the manufacturer's recommended thinner. Measure the amount of thinner carefully and record. Mix thoroughly at low speed until a uniform, creamy consistency without streaks of color is achieved.

6.2.4 Mixing shall comply with the manufacturer's data sheet unless specific alternative written instructions have been provided by ABCD. Induction times, if any, shall comply with the manufacturer's printed recommendations.

6.3 Temperature, Humidity, and Moisture Limitations

6.3.1 Do not apply coatings when the air temperature, steel temperature, or relative humidity is outside the range permitted on the manufacturer's data sheet or when the steel is less than 5 °F (3 °C) warmer than the dew point of the air.

6.3.2 Do not apply coatings if the surface will be rained on or will collect condensation before the coatings reach their minimum recoat time as recommended by the manufacturer.

6.4 Surface Condition

6.4.1 Apply coatings only to clean, dry surfaces that are in their specified state of surface preparation (according to the requirements of Appendix B) at the time of coating application. Surfaces that show signs of oxidation, rust bloom, or other deterioration shall be reblasted to the original specified cleanliness before application of coating.

6.4.2 Coated surfaces held for more than 36 h before recoating shall be washed with fresh water and allowed to dry thoroughly before recoating.

6.4.3 Coated surfaces below +25 ft of the mean water line shall be washed with fresh water prior to application of each coat after the primer until such time as a chloride level of less than 50μm/cm2 is achieved. Primer and intermediate coat shall not be coated over until approved by the INSPECTOR.

6.4.4 All coatings shall be applied in a uniform and continuous film free of holidays, skips, runs, sags, and other defects (as determined by visual inspection).

6.5 Application Equipment and Conditions

6.5.1 Apply coatings by conventional, air-assisted airless or airless spray. Use spray guns, fluid tips, fluid needles, air caps, atomizing tips, hoses, packing, and other equipment that are specified on the coating manufacturer's data sheet. Brush application of a spot primer is acceptable provided the specified thickness is achieved. Roller application of a non-skid

deck coating is permissible if specified coverage rates are followed and the manufacturer's data sheet allows roller application. Non-skid deck coatings containing holidays (as determined by a close visual inspection) shall be removed and reapplied.

6.5.2 When using conventional spray, use pressure pots with two independent regulators, one for the pot pressurization air, the other for the atomization air. All air must meet requirements of Section 5.2. Do not use a fluid hose longer than 50 ft. Keep the pot and the painter at the same elevation.

6.5.3 Use an air-driven agitator on the pressure pot operating at low speed when applying coatings containing zinc powder, glass flake fillers, or non-skid fillers. See the manufacturer's data sheet for specific information.

6.5.4 Spray equipment including guns, hoses, pots, etc. shall be thoroughly cleaned after each use, or between shifts, as required to prevent contamination of coating materials by residues in the spray equipment.

6.5.5 Prior to spray application of primer and intermediate coat to pitted steel that has been abrasive blasted, use a mitt, roller, or brush to force the primer and intermediate coat into the pits. (NOTE: Omit this procedure with inorganic zinc [IOZ] primer only.)

6.5.6 Stripe coating: Brush apply a thin coat of primer to all edges, welds, threads, bolts, threaded surfaces, and other rough or irregular surfaces before spray application of the full coat of primer. When IOZ is the primer, strip coat using the intermediate coating after the IOZ has been applied and cured.

6.5.7 Do not use any coating material that has reached its pot life as defined in the manufacturer's data sheet.

6.5.8 Apply all coatings without runs, sags, blisters, dry spray, over-spray, entrained trash, and entrained blast abrasive.

6.5.9 Apply each coat at the thickness specified in Appendix B. Verify by measuring dry film thickness (DFT) according to Section 7.7.6. Use National Institute of Standards and Technology Certified Calibration Standards for Non-Magnetic Coatings on Steel for calibration of Type I pull-off gauges. Use plastic shims provided by the manufacturer of Type II Constant Pressure Probe Gauges. Calibrate in the specified thickness range of the coating being measured. Record coating thickness measurements in the inspection records for each item coated.

6.5.10 Applied coatings must meet the DFT requirements of Appendix B as measured in accordance with Section 7.7.6. If coatings are applied too thick, the surface must be reblasted to bare steel and recoated in full. If epoxy coatings are found to be too thin, the surface must be reblasted and recoated. If an IOZ is applied too thick, only those areas that are mudcracked must be reblasted and recoated.

6.6 Cure of Coatings

6.6.1 Allow each coat to cure as specified on the manufacturer's data sheet before application of successive coats.

6.6.2 Solvent-based IOZ primers require moisture for proper cure. If the relative humidity is below 50%, allow the IOXZ to air dry for 1 h, then mist the surface with potable water. Do not keep the IOZ wet constantly, rather constantly mist and dry the surface for a minimum of 12 h. Allow the surface to dry for 3 h minimum prior to the application of additional coating materials.

6.6.3 Do not apply additional coats of polyurethane over finish coats that have either dulled or wrinkled from early exposure to moisture. Affected areas must be removed with power tools, scraping, solvent cleaning, or other appropriate means to expose clean, noncontaminated intermediate coat followed by reapplication of polyurethane finish coat. Repairs must be done within the manufacturer's recommended recoat interval of the intermediate coat.

6.7 Repair of Damage

6.7.1 Repair damage to any coat before application of additional coats.

6.7.2 Where damaged area exposes the substrate larger than 8 in (200 mm) in each direction, repair by abrasive blasting to SSPC-SP 6 or SSPC-SP 10 (as required in Appendix B). Feather a minimum of 1 in into sound coatings surrounding the repair area. Do not damage surrounding coatings or equipment during repairs. Take special precautions to prevent damage to over-blast. Apply appropriate coating system from Appendix B.

6.7.3 Damage to coatings that do not expose bare metal or exposure of metal is less than 8 in in each direction may be repaired by abrading the coating and metal with power tools suing 3M Clean N Strip, 3M RotoPeen, or equivalent followed by application of the appropriate intermediate or finish coats in accordance with Appendix B. The original anchor profile must be maintained or replaced.

6.7.4 Power and tool cleaning may be used at ABCD's discretion for repairs larger than 8 in if ABCD determines that such repair is more practical than abrasive blasting.

7.0 Quality Control and Inspection

7.1 The CONTRACTOR is responsible for the quality of all work performed and for assuring compliance with these specifications. CONTRACTOR is responsible to stop operations and promptly notify ABCD when conditions develop that could adversely affect the quality of the completed work.

7.2 ABCD may inspect any work, equipment, material storage, or any other aspect of the project. ABCD's inspectors shall have safe access to all work and storage areas, but will not interfere with CONTRACTOR's normal operations.

7.3 The CONTRACTOR is to provide all inspection and calibration equipment needed to perform the quality control and testing functions outlined in this specification. The equipment needed shall include, but not be limited to the following:

- Surface sensing thermometer
- Sling psychrometer with psychrometric tables
- Materials to perform blotter test per paragraph 7.7.3
- Hypodermic needle pressure gauge for measurement of blast nozzle pressure
- A blast nozzle orifice gauge
- Telescoping inspection mirrors for inspection of areas that are difficult to see
- Surface Cleanliness Comparators, SSPC-VOS 1-89
- Testex Press-O-Film Replica Tape and Spring Micrometer

- Surface profile comparator
- Wet film thickness (WFT) gauge
- DFT gauge
- National Institute of Standards and Technology (NIST) Certified Coating Thickness Calibration Standards for Nonmagnetic Coating on Steel
- Titration papers that measure pH in the range of 2-13
- Titration papers that measure chlorides down to 30 ppm and sulfates down to 200 ppm
- Battery operated light meter capable of measuring available light at the working surface

Specific information on the above items and their use is given in Section 7.7. In all cases, equipment shall be as specified or approved equivalent.

7.4 The CONTRACTOR must record the results of all quality control checks and testing, including but not limited to those listed in Section 7.7. CONTRACTOR must submit sample copies of inspection forms to ABCD for approval prior to beginning job. Records shall include the identification of the structure, equipment, building, etc., and any physical inspection results, such as Testex tape, etc. An example set of acceptable inspection forms are attached as Appendix E.

7.5 The quality control inspections and tests specified in this Section 7.0 are considered to be a minimum. Further testing may be required to follow up when inspection results are not acceptable or when other problems arise.

7.6 Work not meeting the material or quality requirements of this specification, as determined by ABCD, must be repaired or redone at CONTRACTOR'S expense.

7.7 Required Inspections

CONTRACTOR shall perform the inspections listed below and record the results on the inspection forms. ABCD representative will confirm results.

7.7.1 Coatability

All surfaces to be coated shall be inspected for coatability prior to blasting and coating. All surfaces to be coated that have chloride contamination in excess of 50 µg/cm2 or sulfate contamination in excess of 200 µg/cm2 must be power washed until they meet these minimum levels of contaminants and allowed to dry prior to coating. All defects shall be corrected before proceeding with the coating application.

7.7.2 Ambient Conditions

The steel surface temperature, ambient air temperature, humidity, and dew point shall be checked and recorded at least every 3 h (but always immediately before painting) during all blasting, coating, drying, and curing procedures. Steel temperature must be monitored continuously and recorded during forced curing. Readings must comply with this specification at all times.

Measure air temperature, relative humidity, and dew point with any suitable sling psychrometer and corresponding psychrometric tables, or approved meter. Measure steel temperature with any suitable surface-sensing thermometer such as Pacific Tranducer Corp. (PTC) Model 312F or other approved meter and recording device as required.

7.7.3 Compressed Air Supply

Perform a blotter test by directing a strong stream of compressed air at a clean white absorbent material or at a smooth plastic or metal surface. No oil, water, or discoloration is to be visible in either case. Test the air at the farthest point downstream of oil traps and dryers. This test must be performed at least daily and more often if deemed necessary. In all cases, this test must be performed immediately before application of any coating.

7.7.4 Surface Cleanliness

Inspect the surface cleanliness after blasting and prior to coating application using visual comparators according to SSPC-VIS 1-89 or VIS 3, as appropriate. The surface must meet the cleanliness requirements of Appendix B.

7.7.5 Surface Profile

The surface profile of blasted surfaces shall be inspected prior to the application of the coating using Textex Press-O-Film replica tape. Use according to the manufacturer's instructions. The profile depth must be as specified in Appendix B. The density of the blast peaks and valleys and the appearance of the blasted surface must be comparable to that of the Clemtex, Elcometer, or KTA Surface Profile Comparator. Report results and attach replica tape to inspection report.

7.7.6 Dry Film Thickness

Determination of dry film thickness (DFT) shall be based on a sufficient number of spot measurements needed to verify compliance with the requirements listed in Appendix B. ABCVD reserves the right to make as many measurements as needed to determine compliance. As a minimum, one spot measurement per 50 ft2 (3.6 m2) is required to assure compliance.

A spot measurement is defined as the average of three gauge readings taken in close proximity to each other. The gauge readings must be no closer than 0.5 in (12 mm) and no further apart than 3 in (75 mm). Each gauge reading shall be at least 80% of the specified minimum thickness and less than 120% of the specified maximum. The average of the three gauge readings constitutes a spot measurement. The spot measurement must fall within the specified DFT range given in Appendix B.

Thickness measurements must be made with a magnetic type DFT gauge for ferrous substrates such as Mikrotest III or IV, Quantix 1500, Positector 6000, Elcometer 335, or other as approved by ABCD. The gauge must be calibrated according to the gauge manufacturer's instructions using the National Institute of Standards and Technology (NIST) Certified Coating Thickness Calibration Standards for Nonmagnetic Coating on Steel or the calibrated plastic shims provided by the manufacturer of the instrument being used. Calibrate gauge before and after each use as a minimum. If calibration has drifted, CONTRACTOR must repeat measurements until data agree with previous measurements.

7.7.7 Coating Integrity

The coating shall be examined for blisters, runs, sags, dry spray, and foreign material after the last coat has dried and before it has cured. No coating containing blisters, runs, sags, dry spray, or foreign material shall be accepted.

7.7.8 General Cleanliness Inspections

A cleanliness inspection shall be performed prior to each application of coating and prior to final cure to ensure that the applied coating is free of all visible foreign materials. All tape, polyethylene floor covering, padding, masking material, etc. must be removed prior to beginning the final cure.

7.8 The following is a list of inspection hold points. CONTRACTOR must cease operations on a particulate structure at these hold points and obtain the approval of the on-site ABCDS representative before proceeding. The inspection points are:

- Verification of surface cleaning before abrasive blasting
- Verification of cleanliness after abrasive blasting and prior to any coating application
- Verification of coating quality and thickness after each coat of material prior to application of additional coats

At the hold points listed above, the ABCD representative will confirm that the CONTRACTOR has made the proper inspection and that the results of that inspection conform with this specification. The existence of these hold points do not release the CONTRECTOR from conducting the necessary inspections. Other required hold points may be determined later at ABCD's discretion, provided the CONTACTOR receives prior notice.

CONTRACTOR shall blast and coat only properly sectioned off areas of the platform at any one time and shall not proceed to work on other sections until prior section is completely coated by the CONTRACTOR, and accepted by ABCD unless specifically approved in writing by ABCD.

8.0 Safety and Environmental

8.1 It is the responsibility of the CONTRACTOR and any subcontractors to perform all work in a manner consistent with all applicable health and safety regulations applicable to the specified site. The omission of any applicable safety regulation in this specification does not relieve the CONTRACTOR or any subcontractors of the responsibility of compliance. The CONTRACTOR must have copies of all applicable regulations governing the work procedures available to all workers and subcontractors at the work site.

8.2 The CONTRACTOR must provide safe access to the surfaces to be cleaned, blasted, coated, or inspected. All scaffolding, rigging, ladders, etc., must comply with all applicable regulations. Scaffolding and rigging shall provide easy and safe access to all surfaces for surface preparation, coating application, and inspection.

8.3 The CONTRACTOR shall assure that every worker under his or her supervision and every worker employed by his or her subcontractors possesses and uses the following minimum safety equipment, plus any additional requirements set forth by the OWNER or the specific platform Safety Officer at the Pre-Job Conference.

- A NIOSH approved hard hat.
- Safety glasses with side shields
- Steel toe leather shoes or work boots
- Leather gloves during all abrasive blasting operations
- Washable cotton or replaceable Tyvek coveralls during all lead-based paint removal work
- A safety harness for elevated work with a maximum lanyard length of 8 ft (2.4 m)
- A life vest for over0wter work or for use on areas of each platform as designated by the OWNER
- NIOSH approved respirators and breathing devices commensurate with the level of solvent vapors and particulate matter in the work area occupied by the workers

8.4 The CONTRACTOR shall take all necessary precautions for the safety of all persons and employees on the platform or accompanying work boats, jack-ups, etc., utilized by the CONTRACTOR for each specific platform. Such precautions shall comply with all safety rules and regulations of the OWNER and applicable federal, state, and/or local codes, laws, and regulations necessary to prevent damage or injury to persons or property.

8.5 The CONTRACTOR shall submit a written drug and alcohol control policy along with an accident, injury, and loss prevention program during the Pre-Job Conference. Such program, once approved by the OWNER, shall be maintained and enforced by the CONTRACTOR at all times.

8.6 The CONTRACTOR shall enforce a schedule of safety meetings at the beginning of each work day, which will inform all employees and the specific platform's person in charge of daily operations exactly what work will be done during the day, what areas he or she will occupy, and the tagout, lockout procedures necessary for the platform equipment in that area of work.

8.7 The CONTRACTOR shall post all necessary emergency medical treatment facility phone numbers in a conspicuous location readily accessible by all members of the work crew.

8.8 Abrasive Blasting

8.8.1 All blasting equipment must comply with all applicable safety regulations. All blast nozzles must be equipped with a "deadman" automatic shutoff device. Blasting hoses, air movers, and other equipment must be grounded to dissipate static charges.

8.8.2 Lighting shall meet all applicable codes and requirements for the area where it is in use and shall provide adequate visibility (minimum 20 foot candles) for the blasting process and for safe movement of workers and inspectors.

8.8.3 All personal protective clothing and equipment must comply with all applicable safety regulations and must function properly during use.

8.8.4 All pressurized equipment (compressors, air accumulators, blast pots, etc.) must be equipped with automatic pressure relief devices to prevent over-pressurizing.

8.8.5 All pressurized connections must be secured with devices to prevent accidental disconnection (i.e., quick connect blast hoses must have the safety wire installed).

8.8.6 Dispose of all spent abrasive, empty abrasive bags, etc. in a manner consistent with all applicable safety and environmental regulations. Keep the work area free of debris to permit safe access.

8.9 Coating Application

8.9.1 The CONTRACTOR shall assure that all coating materials are handled in a safe manner that meets the requirements of the coating manufacturer's product data sheet and Material Safety Data Sheet, along with all applicable federal, state, and/or local codes, laws, and regulations. The CONTRACTOR shall supply all equipment necessary to meet these requirements and assure that they are properly used, cleaned, and maintained by his or her employees and the employees of his or her subcontractors.

8.9.2 Lighting and wiring in coating work areas shall meet all applicable codes and requirements for the area where it is in use and shall provide adequate visibility (minimum 20 foot candles) for the coating processes and for safe movement of workers and inspectors.

8.9.3 Store all flammable materials in a manner conforming to all laws and regulations. Store away from electrical equipment, motors, generators, compressors, or other possible sources of ignition. Post warning signs for flammable materials. Prohibit smoking near the storage areas. Ground all containers containing flammable materials.

8.9.4 Electrically ground all spray equipment to prevent accumulation of static charges.

8.9.5 Hand tools used in the vicinity of flammable materials must be non-sparking.

8.9.6 Keep all sources of ignition such as fire, internal combustion engines, welding, and persons smoking at a safe distance from the work area during all coating mixing, application, and drying. CONTRACTOR'S electrical equipment is to be kept at a safe distance from coating work areas. It shall be placed in a well-ventilated, nonhazardous area.

8.9.7 Ventilation

Maintain continuous air movement through enclosed areas during all coating application and drying. The ventilation system shall be explosion proof and shall provide sufficient air movement to keep the atmosphere below 20% of the lower explosive limit (LEL) at all times. The air shall be vented in compliance with all safety regulations. Use air-driven fans or venture type eductors to pull vapors and overspray out of the paint area when force ventilation is necessary. Solvent vapors collect in low areas; design ventilation to move air through such spaces. Position fans to draw contaminated air out of the work area and allow fresh air to flow in to replace it.

8.9.8 All personal protective clothing and equipment must comply with all applicable safety regulations and must function properly during use. Painters and helpers working in the coating application area shall were proper breathing protection for the coating being applied and for the work space where it is being applied.

8.10 Water Disposal

8.10.1 All unused mixed materials and all waste materials and spillage shall be immediately disposed of in a manner consistent with all applicable safety and waste disposal regulations. Debris from removal of lead-based paint shall be treated as hazardous waste whenever it contains more than 5 ppm of lead or chromate.

8.10.2 All cans that contained coating materials or thinners, or that were used for mixing materials, must be disposed of properly in accordance with all applicable safety and environmental regulations. In addition, all rags and other items contaminated with coating materials or thinners must be stored in such a manner as to prevent self-combustion and disposal of in a similar manner.

8.10.3 Dispose of all residue from removal of lead-based paints in accordance with applicable federal,, state, and local regulations including EPA 30 CFR.

9.0 Documentation of Work Performed

9.1 The CONTRACTOR shall prepare a detailed work schedule prior to mobilization. This schedule shall be kept on each platform and available for review at any time by the OWNER'S representative. This schedule shall indicate the total work hours estimated to be required for completion of all contract items.

9.2 The CONTRACTOR shall maintain a daily record of work performed. These records shall be available for the OWNER'S review on each platform. The following data shall be recorded daily.

- Area treated (ft2) and work performed on this area (e.g., degrease, abrasive blast, paint, etc.)
- Work hours used per task (rig, wash, blast, coat, etc.)
- Quantity of each material consumed
- Total platform area treated to date, its percentage of total contract job area, and percentage of total work hours expended to date.

  Forms supplied by the OWNER shall be filled out to record this information and turned over to the OWNER'S representative weekly.

9.3 Monthly job status summaries shall be provided to the OWNER. These shall list the following items:

- Percentage of total contract scope of work completed to date
- Incremental percentage of total contact scope of work completed since previous report
- Percentage of total estimated man hours for contact scope of work items performed to date
- Incremental percentage of total estimated man hours for contract scope of work items performed since previous report
- Total man hours since the last report spend on contract work, extra work, standby due to weather, and standby due to OWNER'S operations
- Total man hours lost due to reportable injuries to date
- Total man hours lost due to reportable injuries since previous report

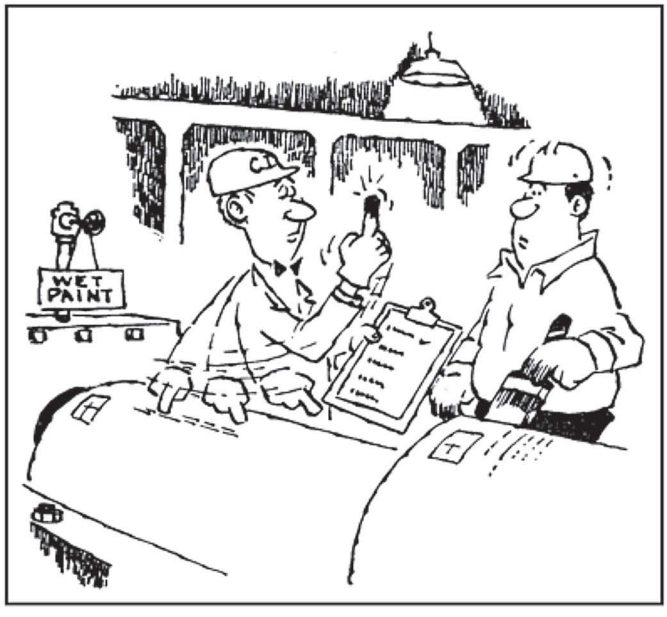
9.4 CONTRACTOR shall prepare hazardous waste manifest and chain of custody form for all hazardous waste disposed from the platform. One copy must be given to the ABCD representative on the platform whenever a shipment of hazardous waste is removed from the platform. A copy of the manifest and chain of custody must be returned to the ABCD representative after the hazardous waste has been properly treated and disposed of with signatures of each party handling, treating, or disposing of the hazardous waste.

18 Inspection and Training

The best coating available is of little value if it is not carefully and properly applied. Thus, coating inspections are specified to ensure proper application. It has been stated, "A specification must be complied with if it is to serve a useful purpose…a good specification which is adhered to will produce optimum coating life and is economically advantageous."[1] This is because a good specification includes an inspection requirement to ensure a high-quality coating application that will result in long coating life under even severely corrosive conditions.

Proper inspection is a primary key to effective coating performance and therefore should be a requirement of every good specification, as well as a periodic requirement over the lifetime of the coating. Effective inspection during the life of a coating can extend its useful life several times over by initiating coating maintenance and repair before major coating failure results.

Comparison of the results obtained when proper inspection has been carried out during coating application has shown that the life expectancy of the finished coating can be increased by a factor of two or three by the introduction of proper inspection procedures. It is shortsighted to develop detailed specifications and requirements for a coating application, yet fail to properly inspect the work to be sure that the specifications have been met. The primary purpose of inspection is to ensure compliance with the specifications that were established for the job.



Coating quality depends on the level of inspection.

Unfortunately, inspection of the coating application is frequently overlooked by the owner of a structure, in spite of the fact that inspection is the area of the job where he or she is most likely to receive less than he or she specified. In fact, the application of protective coatings is often considered an indefinite and rather haphazard operation where quality control is more the exception than the rule.

Most other engineering operations, such as the installation of equipment, routinely require a thorough inspection of the installation process and end results. However, installation of the material that will protect the equipment against the atmosphere, chemicals, and other destructive elements is often carelessly left to the discretion of the subcontractor who does the work. Instead, both owner and contractor should consider coating application as a manufacturing operation that creates a new product and therefore, naturally requires thorough inspection.

Failure to provide inspection is also common in contracts for maintenance coating work, although it is no more excusable in this case than it is with new work. As stated by S.T. Thompson:

> The implementation of a good maintenance painting program depends upon four cornerstones: Good specifications, quality materials, qualified contractors, and effective inspection. Failure in any of these areas, like the proverbial weak link in the chain, will result in decreased performance and increased costs— often substantial.[2]

Actually, inspection of maintenance coatings may be even more important than for new work because of the increased number of variables. In fact, it is these variables, all of which have a substantial effect on the quality of the protective coating, that dictate the need for competent inspection throughout the application process. The coating material, mixing of the coating (particularly where there are two or more parts included in the finished material), thinning, surface preparation, coating application, weather conditions during application, individual coat and total coating thicknesses, and surface treatment after coating application are all variables that must be carefully controlled if a high-performance coating is to perform properly. Without in-process inspection, conformance with application specifications is difficult to determine. The final coating appearance can be quite deceptive, giving no indication as to the probable effectiveness of the finished product.

In this age of critical labor-intensive operations, quality assurance is extremely important. The assurance of quality usually is dependent on in-process quality control, involving inspection of the basic material and its use or application to ensure the long life and effectiveness of the product. There is no installation operation where this is more critical than in the application of high-performance coatings. It is a well-known adage in the coating industry that even an improperly selected coating or poor-quality paint can provide good service if it is applied carefully and properly, while a high-performance coating can be completely ineffective due to a poor and careless application. This is the reason that inspection plays such an important role in a coating program.

As discussed in the previous chapter on specifications, the quality of a coating applied to an industrial plant, chemical plant, refinery, food plant, paper mill, offshore marine structure, or nuclear energy installation is dependent on two important items. The first of these is the coating specification, which dictates the product to be used as well as its installation. The specification must be strong, stating the need and requirements for the final coating as well as providing a measure for the evaluation of the completed coating to ensure that the desired results are obtained. A strong specification is indispensable and should include the requirements for in-process inspection.

The second important item (and the key step in ensuring a successful coating job) is proper inspection. Inspection is necessary to ensure that the intent of the specification, as well as its details, are carried out. The coating operation is usually the last phase in any construction or maintenance job. Thus, the pressure to complete the coating, either during operation or prior to the start-up of a new operation, is the cause of many coating failures. Without good specifications and thorough inspection, and under the above conditions where pressures to complete a job are extremely strong, serious errors and costly mistakes can be made during a coating installation.

Variables Involved in Quality Control

As previously discussed, there are so many variables involved in coating applications that it may seem surprising that any good applications are ever obtained. First of all, environmental conditions vary from hot, dry weather to cold, humid weather. Coupled with these outside variables are the variables inherent in the material itself, which can range from a fast-drying vinyl to a slow-curing polyamide epoxy. There are also variables associated with those doing the application work. For instance, one person may be proficient at applying one type of coating, while another may be much better at applying a second type of material. Inspection to provide in-process quality control is the only way in which variables such as these can be properly controlled.

Another possible variable is the degree of understanding regarding the specifications or the design engineer's coating requirements. In many cases, the general character and physical properties of a coating are not fully recognized by engineers, architects, contractors, and, more often than not, the actual owners. Many of these people regard a high-performance coating as no more than an average type of paint. While it is true that there may be no difference in the application equipment used, there is quite a difference in the handling and processing of the various coating materials.

A coating is a highly complex material. It is formulated from as many as 20 different materials mixed (or in some cases reacted) together, yet the end product is a very thin film of only a few microns or thousandths of an inch thickness. As such, it must adhere to the surface; protect the surface from penetration or corrosion; and resist abrasion, high humidity, weather, water, chemicals, precipitated salts, or actual immersion in corrosive or aggressive solutions. In all cases, the coating is a thin film separating two reactive materials. Understanding the complex nature of coatings emphasizes the need for good specifications and inspection procedures.

Inadequate specifications also represent a variable, as discussed in the previous chapter on specifications. Many specifications are so inadequate as to be nearly useless in obtaining the desired coating. This is often caused by a lack of communication. However, poor specifications are often caused by engineers using antiquated specifications that are completely improper for the job at hand.

Selection of the lowest bid, irrespective of the quality of the bid, also presents a difficulty as far as quality control is concerned. Even though the bid may be a legitimate one, once problems begin to occur, there is the inevitable trend toward a reduction in quality to make up for the losses caused by various problems. Even small variations in the application process can make substantial differences in the end product. Efforts to reduce labor costs through quick applications inevitably lead to a lack of proper care during the application, which further deteriorates the quality that is necessary for the use of high-performance coatings.

Another difficulty from a quality standpoint is that too often the superintendents, managers, and even owners fail to understand the importance of corrosion control and the role that coatings play in preventing corrosion. Because painting is such a commonplace activity, supervisors and managers often do not realize that it is the greatest single factor in the cost of maintaining corrosion-free industrial structures. Thus, little attention may be paid to proper inspection of the final job. While this situation is not true in every case, it is common enough to be considered a serious difficulty with regard to coating quality.

The lack of proper inspection is another variable that can also cause serious problems. Even when a good specification calling for thorough inspection has been written, the personnel selected to provide the inspection often are not knowledgeable enough to interpret the specifications in either a practical or satisfactory manner. In addition to the fallacy that almost anyone can follow and inspect a coating job, another reason that paint inspectors are so often poorly qualified is that relatively few qualified guidelines applicable to the coating of industrial structures are available. This has been changing in recent years due to the extensive work on surface preparation and coating application by such organizations as NACE International and SSPC.

Types of Coating Inspectors

There are many types of coating inspectors. One is an inspector supplied by the coating manufacturer. This type can be very effective and helpful, particularly if they have had extensive field experience, are allowed to be on the job full-time, and are knowledgeable about the application of the supplier's products. Such a combination of knowledge, experience, and full-time availability is rarely available from a coatings manufacturer for the entire duration of a coatings project.

Another type is an inspector obtained from an independent consulting firm. They are usually trained as inspectors and thus have had extensive experience on numerous coating application jobs. While they can be very effective inspectors, those obtained from general contract inspecting companies may be more experienced in setting up equipment than in actual coating inspection. Such individuals may be more interested in the details of the specifications than in their overall intent. In fact, some adhere to specification details so narrowly that a serious friction develops between the inspector and the contractor, while others are so lax, mainly due to little or no coating knowledge that little benefit is obtained from their services.

A corrosion engineer assigned to a coating application may serve as a good inspector. This is because these engineers are familiar with the company, the reason for the coating, the corrosion problems involved, and may even have taken part in writing the specifications. Rarely, however, has that engineer received in-depth training in all the aspects of proper coatings inspection.

A retired painter or coating supervisor also can serve as a good inspector since he or she is familiar with application procedures and common applicator problems. However, they can sometimes be less than objective in their observations, depending on the attitudes and work habits developed over many years of field work.

Unfortunately prior to 1983, there were few inspectors who were thoroughly trained for the job. The good ones were self-made, as a result of an interest in coatings and long application experience. This situation has changed dramatically since the establishment of the NACE Coating Inspector Program (CIP), begun in 1983. This intensive series of week-long training sessions plus a peer review focuses on both the technical knowledge needed by a qualified inspector and the practical hands-on experience with surface preparation, application, and inspection equipment. As of early 2013, there had been over 30,000 persons from many parts of the world trained in one or more of these sessions. Approximately 20,000 had completed all the sessions and passed the peer review, thus becoming a NACE CIP-certified Level 3 Coating Inspector.

Another problem in obtaining a high-quality coating application lies with the applicators themselves. This is explained further in a chapter in an SSPC publication on inspection.[3]

> The painting inspectors' problems will often be magnified by incompetence and lack of knowledge on the part of the painters themselves. Very rarely do painters have much detailed knowledge concerning the materials they use. This is particularly true in the case of the newer paint products. It cannot be assumed even that the painter will know what thinner is to be used in the particular type of paint he is applying. Not infrequently the man applying paint will be found to be not an experienced painter at all but a handyman who knows only a little about the many different jobs he does. The inspection difficulties inherent under such conditions need not be detailed. Personal prejudices of the painters must be overcome, since, if they feel their "long experience" is being ignored, the quality of the painting is apt to suffer.
>
> Despite the rather dark picture just presented, improvements in the quality of painting through the sensible employment of competent inspection procedures is distinctly attainable and should benefit all concerned except those few contractors who construe laxity in inspection as an opportunity to reduce cost.[3]

It should be noted that SSPC has pioneered several training courses aimed directly at the contractors and their field personnel, including two weekly courses in protective coatings and lining technology, as well as courses in project estimating and managing. NACE has also had a protective coatings and lining course for a number of years, which has been expanded into three week-long courses leading to a certification as a Protection Coatings Specialist. While these courses include sessions on inspection instruments, the focus is more on coatings technology and project management training.

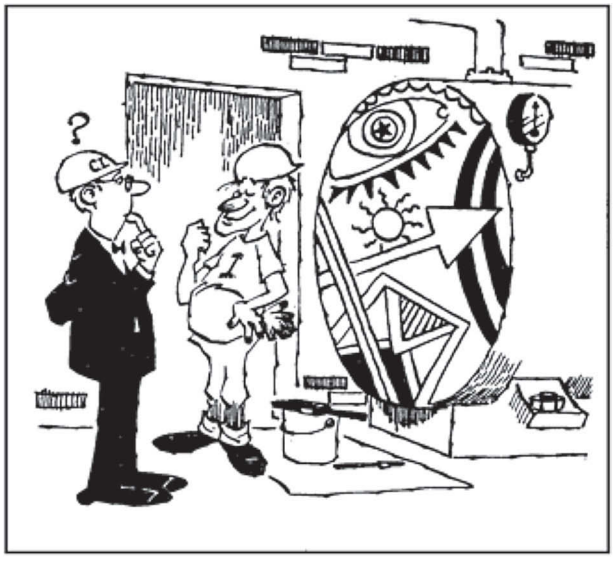
Good coating inspection is based on the concept of in-process quality control. This means that every step in the application of a coating, from surface preparation to final drying or curing, is monitored to ensure its conformity with specifications. This in-process concept is important since coating inspection is too often done on a spot-check basis where the inspector may appear at the job site periodically to make a cursory examination of the situation. This type of inspection is not in-process quality control and does not lead to the type of application that is required for high-performance coatings. While it is better than no inspection, continuous inspection of all steps involved in the application process is important for the best quality work. When each step is properly monitored, the quality of the end product is nearly always assured.

What Should a Qualified Inspector Know?

With this in mind, what should a qualified inspector know to provide the proper level of inspection for high-performance coatings?

Intent of the Specification

It is assumed in this case that the specification has been written. However, for an inspector to properly interpret the specification, it is necessary that he or she have a thorough understanding of the intent of the specification. As previously discussed; the specification should be a compilation of information provided by architects and engineers, company personnel (preferably a corrosion engineer), the applicator, and a top executive of the company. Each of these groups has a somewhat different perspective on what constitutes a proper coating job. It is the inspector's responsibility to enforce the specifications in such a way that will satisfy all of the parties concerned with the application.



It depends on whose standards are followed as to whether a coating job is satisfactory.

The architects and engineers generally are interested in the protection of the structure and its appearance. Company personnel tend to be interested primarily in the operation of the structure and the costs involved in its maintenance. The corrosion engineer's interest lies in the resistance of the coating to the atmosphere. Company executives may be interested in the general appearance of the structure and how it affects the overall company image.

If the inspector understands the intent of the specification and then makes sure that each step is accomplished in accordance with that intent, the requirements of the specification are more easily met. In so doing, the requirements of each individual involved also should be satisfied.

If dealing with an industrial structure in an acid atmosphere, the inspector should understand that the corrosion of any steel or concrete structure in such an atmosphere can be quite rapid and possibly catastrophic. The inspector should then interpret the speci-

fication in light of that knowledge. If the coating is for appearances only (which is unlikely where a high-performance coating is used), the principle of sidewalk inspection might be applied, which means that overall appearance must be good, irrespective of hidden areas. For instance, the appearance of the underside of an automobile generally does not matter. However, this certainly is not true where a corrosion problem exists, since any area left uncoated in that case could cause serious problems.

Substrate

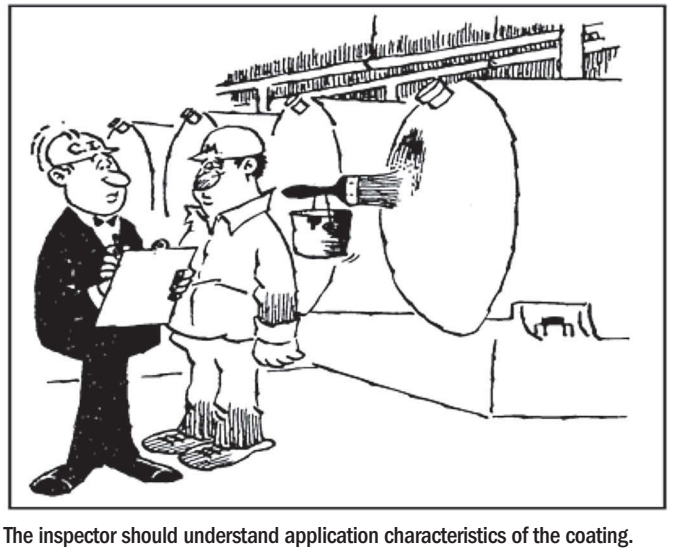
The inspector should have a good knowledge of the substrate over which the coating is to be applied. The underlying surface (whether it is wood, aluminum, concrete, steel, galvanizing, or a specialty steel) is extremely important from the standpoint of coating durability. For instance, there are potential adhesion problems wherever a coating is applied over stainless steel (SS). On the other hand, if there were an imperfection in a coating applied over SS, the reaction at the imperfection would be considerably less and therefore, less important than if the substrate were hot-rolled steel. Concrete surfaces, because of both their reactivity and their variable surface, present different problems than when coating a dense, smooth, clean steel surface. The coating that might easily be continuous over a steel substrate might not provide a continuous surface over a concrete substrate. The substrate can easily make the difference between a satisfactory coating application and a poor one, so that the inspector should be knowledgeable in this regard.

Surface Preparation

A good inspector should have a sound knowledge of surface preparation; not only for steel, but also for other surfaces such as galvanizing, concrete, and aluminum. The inspector should know the application characteristics of coatings over each type of surface, as well as the type of surface preparation that will provide the best base for a coating over the various substrates. While this subject of surface preparation has been thoroughly covered by NACE, ISO, and SSPC, the standards and information presented by these groups usually is not sufficient unless augmented by some practical experience in the field with various types of surface preparation on various substrates. For example, the field inspector may be required to rule on the difference between a white metal and a commercial blast according to the appearance of the surface. He or she must also know how the coating involved will react over such surfaces in order to provide practical evaluation of the surface preparation. The inspector should be thoroughly familiar with the equipment used to obtain the various grades of surface preparation. This not only includes blasting equipment, but should include the equipment for water jetting hand preparation of surfaces as well. There is nothing quite so impressive as an inspector who is able to pick up the equipment and perform the proper type of surface preparation as a demonstration of how the work should be done. The inspector should also know the results of the surface preparation (i.e., knowing the coating that is to be applied and the type of surface preparation available). He or she should be able to evaluate the effectiveness of the coating over such a surface and provide advice as to how to obtain the best possible coating application under given circumstances.

The Effect of Design

The coating inspector should be completely familiar with the design of the structure and with the effect that the design is going to have on the application and effectiveness of the coating, and on the degree of abrasive blasting or surface preparation possible. Unfortunately, structures are often designed without any consideration of coating application. They are designed with bolts and rivets, sharp corners, edges, hidden areas, crevices, and similar problems, which are all areas that can cause serious problems from a coating standpoint. The inspector should have a full knowledge of the application procedures that are required to obtain a full, thorough coverage of such problem areas. He or she should understand that coatings will tend to pull away from corners and edges, as well as from surface protrusions such as weld spatter. He or she should also realize that a coating must be applied from several different directions wherever bolts, rivets, or similar protrusions are encountered. This type of information will aid the inspector in properly evaluating the coating application and in obtaining the best possible job.



The inspector should understand application characteristics of the coating.

Coating Characteristics

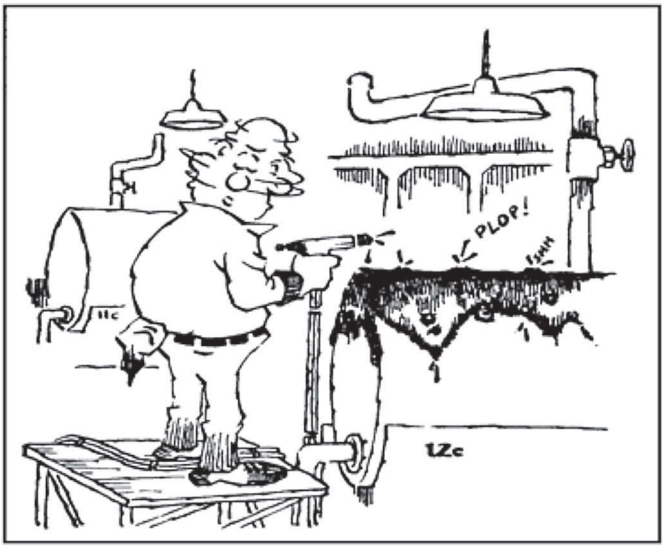
The inspector should have a good knowledge of various coating characteristics that can affect the application as well as the finished product. He or she should know, for instance, that vinyl coatings are generally relatively thin films and that additional care is required on rough areas or edges and corners in order to obtain full thickness. He or she should realize that epoxy coatings generally require a catalyst or an additive in order to cure properly; that such coatings have a limited pot life; and that, if that pot life is exceeded, adhesion characteristics are often insufficient. The inspector should know the different application characteristics of each different coating specified for the job he or she is inspecting. He or she also should know the general wetting characteristics of these coatings in order to evaluate their effectiveness over various types of surface preparation.

Even though the coating inspector may not be involved with the coating selection or specification, his or her knowledge of coating characteristics and basic properties influence the success or failure of the coating application. His or her knowledge usually comes from actual field experience with coatings. In fact, the coating inspector should have practical experience with high-performance coatings so as to provide the best evaluation of any given job.

Application

The coating inspector should have an excellent knowledge of the application procedures generally used for high-performance coatings. He or she should know the characteristics of air and airless spray, and should be familiar with the procedures used to properly apply coatings with such equipment. Such knowledge can help the inspector in the evaluation of the job and in making timely suggestions to the contractor if application problems occur.

Application procedures frequently need to be changed during a job in order to obtain a proper coating. For example, if there is excessive overspray, a knowledgeable inspector should be able to suggest methods to correct the situation. If application is by air spray, perhaps the use of airless spray would overcome the situation without reducing the effectiveness of the coating or the labor involved from the contractor's standpoint. The inspector should also know that the mishandling of either air or airless spray may cause pin-holing in various coatings. Thus, he or she also should know what to do about pinholes if they develop. The inspector should realize that if pinholes are in the coating, spraying an additional coat over the surface does little to overcome the situation. He or she should realize that working a coating into the pinholes by brushing is the only method that will obtain a satisfactory application. Otherwise, removal and reapplication of the entire coating system may be necessary.



Application procedures may have to changed during the job to obtain proper coating.

Another thing the inspector should be aware of is that, if there is high humidity, some coatings will tend to blush or absorb water into the coating surface. This can result in a less than effective coating, and in many cases, can change the coating adhesion characteristics of a following coat. This type of application expertise can best be gained through practical experience.

As part of his or her application knowledge, the inspector should thoroughly understand the application equipment, how it works, and its effect on various types of coatings. He or she should recognize the difficulties inherent with various types of application equipment. This is particularly important from a safety standpoint. For example, airless spray is under very high pressure and applicators must keep their hands away from the spray area of airless equipment. A number of accidents have occurred where the jet from an airless spray impacted a finger, hand, or arm with the jet, driving the coating into and through the skin, causing serious injury. A whipping air hose or an abrasive blast nozzle can cause serious injury to both the surface to be coated and the personnel in the area. Inspectors should understand this and be able to react quickly should a blast hose be dropped accidentally.

Cleanliness

Another item that the inspector should be aware of is the cleanliness of the equipment. Lack of cleanliness has been the cause of more poor applications than almost any other problem. Equipment that has been used for oil paint, alkyds, or similar materials, and is then switched over to high-performance coatings, almost inevitably causes contamination of the coating and work stoppages. The same is true where organic coatings have been used, followed by inorganics. The inspector can easily save the contractor time and effort by making sure that the equipment is in proper order.

The Contractor

The coating inspector should also be able to recognize the contractor's problems, such as contending with poor structural design or learning how to apply a new type of coating. The experienced coating inspector may be able to help the contractor salvage a job that has gone sour and save money for both the contractor and the owner. In many ways, a good coating inspector can be the contractor's best friend. He or she can act as a consultant, teacher, helper, and, above all, an intermediary who promotes understanding between the contractor and the owner.[4]

The inspector, in all cases, should avoid developing an adversary relationship with the contractor. This happens all too often, with the contractor feeling that the inspector is interfering with the work, and the inspector feeling that the contractor is trying to speed the job up, use less material than is required, and generally exercise less than the required amount of care during application. This kind of a situation can best be avoided if the inspector makes a determined effort at the beginning of the job to develop the proper relationship with the contractor, making sure that his or her own activities on the job are helpful and practical. This does not mean that the inspector should allow the contractor to do things that are not proper. If the contractor feels that the inspector is being fair and that his or her objections or suggestions are sound, a good relationship can develop.

The Representative of the Owner

The inspector is often the only representative of the owner with whom the contractor will have any major contact. The inspector must have sufficient knowledge of the job, the specification, and the coating materials to act as the interpreter of the specification and as an intermediary between the contractor and the owner in order to ensure that the owner receives the kind of job for which he or she contracted. The inspector must be sufficiently political to give in on items that are of little consequence and yet hold firm on those which are going to make a substantial difference in the effectiveness of the job. Communication is often a problem between the owner, the material supplier, and the contractor. The inspector can be the intermediary between all parties, providing the communication that is necessary to obtain the proper job. In this case, a pre-job conference can be the beginning of this type of open communication. As stated by Bayliss in Quality Control of Protective Coatings:[5]

It is easy to draw up a list of the qualities required of the ideal painting inspector but again one must take a practical attitude. The job is not the most congenial, for instance including long hours and long periods away from home. The work like painting itself can be unpleasant and even with an element of danger. In practice the difference between a good and troublesome job is often a measure of the inspector's personality. A bad inspector is like a bad policeman and is either too petty and rigid or the reverse. Good quality control should result in the satisfaction of all parties that everybody has done the best they can, to the best of their abilities.[5]

One item that must be mentioned at this point is that during an application, particularly where the inspector is new to the contractor and to the personnel, the inspector will, as a rule, be constantly tested during the first part of the job by both the workers and the contractor to see whether or not he or she is knowledgeable and whether or not his or her suggestions are practical. If the inspector makes a favorable first impression, the job usually proceeds well, producing good results. If, on the other hand, he or she is not able to make a proper first impression, it is more likely that he or she will be baited and deprecated, and that almost anything he or she does will be sidetracked, overlooked, or carried out in a poor fashion. This situation can only result in a poor application and therefore, poor overall results.

Areas of Coating Inspection

Material Inspection

The inspection of materials purchased for a coating application depends, to a great degree, on the method of purchasing. Several methods were outlined in the previous chapter on specifications. If a material is purchased according to the formula specification (which is usually the case where government purchasers are involved), considerable laboratory material testing is necessary to determine conformance with specifications. This kind of testing requires considerable laboratory equipment, personnel, and detailed procedures, which cannot be carried out by the inspector in the field.

Trade name, or equal specifications, also require laboratory testing to determine whether or not the materials are equal. Since the field inspector cannot do this type of testing, it must be handled by the company, an independent testing laboratory, or by a governmental agency.

Materials purchased on a qualified products list are usually pretested. This involves a long laboratory procedure to determine if the materials on the qualified products list meet a series of performance requirements for the purpose involved. Once the materials are on the qualified products list, no additional laboratory testing is necessary, unless it is desired by the agency purchasing the material. Again, these would be laboratory tests so that the field inspector would not be able to contribute in this area.

Materials purchased by trade name usually require no laboratory testing. Some purchasers may require infrared scans on different batches of materials to determine their equality. However, because these materials are backed by the manufacturer's name and reputation, there usually is little call for testing. A good discussion of materials inspection appears on Chapter 5 of the *Steel Structures Painting Manual*[3] as follows.

This section presumes that the paints are purchased on a specification basis, generally through competitive bidding. If paint has been purchased outright as the trade name or proprietary products of a single manufacturer, there is usually no point in testing it, since there is no agreement between paint supplier and buyer as to what the detailed characteristics of the paint must be. Similarly, there is little reason to test paint purchased on a 'similar or equal' basis because the determination of similarity and equality is for all practical purposes impossible within the time usually allotted for such testing work. The following discussion presumes also that certificates of compliance with the specifications and certified test reports, originating from the paint manufacturer, are of limited value to the purchaser. When the buyer does not necessarily accept the lowest bid from any source but instead purchases the specification paint from a reputable concern in whom he has developed confidence, then such certifications may be acceptable.

The scope of testing and/or plant inspection of paint purchased on a specification basis must be determined by the buyer. His judgment in this matter will be influenced by: the volume of paint involved, the bid price per unit of supplied paint, whether competitive bidding was employed, whether there has been past experience with the particular supplier, the manufacturing facilities and reputation of the supplying organization, and lastly, the type of paint being furnished. The first of these considerations needs little explanation—the economic feasibility of testing several hundred gallons of paint is apparent when compared with the cost of testing forty or fifty gallons. When several thousand gallons of a paint item are involved, still more expense can be justifiably incurred in determining whether the material complies with the specifications. The need for considering the second point—unit bid price—in determining the scope of testing will be apparent to those who have received competitive bids on paint items. It is not unusual to receive quotations on a large quantity paint item ranging from the bare cost of materials to several times that figure. If the supply contract is awarded at a bid price which appears so low as to preclude reasonable profit, the buyer should take great precautions to insure that the material complies with the specifications. Although the private organizations can reject those bids which appear abnormally low, this highly desirable course of action is often nearly closed to municipal, state and federal government agencies. The effect of the buyer's past experience with a particular supplier on the scope of the test work to be performed requires no explanation.

Similarly, the supplier's manufacturing facilities and reputation may be important factors in determining whether or not the furnished materials should be tested thoroughly. The last consideration, i.e., the type of paint being furnished, has a bearing on the thoroughness of the test work, as will be seen from the following examples. A relatively simple oil type paint such as that conforming to Federal Specification TT-P86c, Type I (red lead-linseed oil paint), may be adequately tested merely by examination of the finished product. However, the buyer of a phenolic type red lead paint conforming to Type IV of the same specification could hardly be assured of full compliance with the specification without testing a separate sample of the phenolic varnish and the resin and oil used in making up the varnish, in addition to the paint. Indeed, some formulations for certain paints are so drawn up as to require inspection in the plant if the buyer is to be assured of obtaining the desired material.

In deciding how thorough the testing work to determine compliance with a paint specification should be, one additional group of factors should be given careful consideration: the contemplated exposure condition, the cost of making the surfaces to be painted accessible for repainting, the cost of surface preparation, and the cost of paint application. For example, a partially submerged miter gate in a navigation lock can be made accessible and the surfaces prepared for painting only at great expense. Clearly, the coating of such surfaces should make use only of those materials whose compliance with the specifications is beyond question. Conversely, the need for absolute assurance of paint quality is not so urgent for easily accessible steelwork subject to a rural atmospheric exposure.

As a general statement, it can perhaps be said that buyers who do not contemplate thorough testing of their specification paints should deal only with paint manufacturers with whom they have had satisfactory experience in the past and/or those who have an excellent reputation for

integrity and ability. If he does not resort to comprehensive testing of specification paints, the purchaser should probably disregard the lower prices associated with competitive bidding and buy from a technically competent manufacturer who believes a satisfied customer to be the most profitable one in the long run.

It is only fair to point out in closing this general discussion that not all of the trouble experienced in obtaining satisfactory specification paints is the fault of the paint manufacturer. Some of the specifications are so poorly written and so clouded with contradictions as to defy the interpretive ability of anyone except, and often including, the writer.[3]

Field Inspection of Materials

The inspection of materials on the job is only cursory at best. There are, however, a number of worthwhile steps that can be taken. The inspector should check the labels on the container to determine whether or not the material bears the designation and number that are detailed in the specification. It is important to check all containers, particularly on a large application job. This is because errors can be made in the shipping of materials, and the applicators could easily use these wrong materials, particularly if the material and the label on the container are the same color.

It is also worthwhile to check the date on the container, which indicates the shelf life of the coating and the date beyond which the coating should not be used without further testing to see that its consistency and other properties are satisfactory. It is also important to read the label of the container or the material safety data sheet to determine the level of safety hazard that may be involved in the use of the material.

Once the containers are open, the inspector should check for material problems, such as viscosity, livering, gelling, pigment separation, and very hard pigment settling, as well as for the solvent to be used if thinning is required. Most of these items can be checked purely by observation. If any abnormalities are found, these should be checked out with both the owner and the paint manufacturer to determine if the material is satisfactory. It is far better to run a check on the material before it is applied than to run one afterward.

A material that is gelled, even though mechanically mixed, will probably have gel particles distributed through the coating, which can create a weak point for failure. For example, solvent vinyl coatings that have been packed in an unlined steel container will often gel around the edges of the container. This is an irreversible gel, and if it is mixed into the coating and applied, it not only makes for a poor appearance, but it also creates an unsatisfactory coating from a resistance standpoint.

Some materials also settle very badly in the container, making it difficult to properly mix them back into proper suspension. Unfortunately, applicators often leave the badly settled materials in the bottom of the container and use only the liquid above. Of course, when this is done, the coating lacks solid content and the material applied is not in accordance with the formulation. The resulting application is a poor one from a resistance standpoint. Coating buckets have been found on the job with 1 to 3 in (25 to 76 mm) of pigment settling, which was never applied on the structure. Unless such settled materials are gelled or livered, they usually require some additional work to re-disperse the pigments and therefore, bring the coating back to a proper consistency.

Inspection of Surface Preparation

All of the information presented in Chapters 9 and 10 on surface preparation and coating application are applicable to the inspector at this point. As previously discussed, the performance of the best coating is usually no better than the surface preparation. If a high-performance coating is applied over a pitted surface with rust in the pits, little satisfaction is going to be obtained from the material. It is also true that once the coating has been applied to a surface, it is very difficult to determine the quality of the surface preparation. Coatings easily cover mistakes and improper surface conditions. It is only after the coating is in service that these imperfections become significant.

Unfortunately, in the case of surface preparation, the inspector is saddled with a considerable responsibility in determining whether or not the surface was properly prepared for coating. One of the best ways to deal with this situation is for the inspector, the owner, and the applicator to clean a section of the surface to the satisfaction of all parties. The inspector can then use this degree of surface preparation in determining whether the surface conforms to the specification. A viable alternative is to use the SSPC visual, photographic standards for abrasive blasted steel (VIS-1) or power tool cleaned steel and coatings (VIS-3).

In surveying surface preparation work, the inspector should check for a number of different items. One, he or she should check to see that the surface preparation conforms to the specifications. In the case of NACE No. 1/SSPC-SP 5[6] for white metal blasting, the inspection is relatively easy, since the surface must be of one color. On the other hand, near-white blasting or commercial blasting is much more difficult since closer evaluation is needed before a decision as to whether or not the blasting conforms to the specification can be made. Again, this is an area where a pre-application conference and demonstration help to ensure a proper evaluation. Even so, inspection of old, heavily pitted surfaces, or those covered with old coating residues, involve many decisions that are difficult to make.

Pitted surfaces are particularly difficult because the surface is uneven and rust and contamination can remain in the pits, especially after the first blasting. This is more noticeable in areas where there are chlorides, because the chloride residue often is not readily visible until sufficient humidity is absorbed from the air and the pit begins to darken in color. If this is the case, the surface will have to be cleaned by water jetting to obtain the desired cleanliness,[7-10] as dry abrasive blasting does not do an adequate job of removing chlorides. It will be up to the inspector to advise the owner that this is the case. Contractors and blasters are often reluctant to go over the surface a second time because of the time and effort required. Some blasters complain that the surface is difficult to clean, that pitted steel cannot be cleaned properly, and that heavy scale is almost impossible to remove. Complaints such as these usually are not valid. If the blaster worked methodically across the surface, taking a ft^2 area at a time and cleaning it thoroughly, these problems should not exist. Again, the inspector is the one responsible for advising the owner, and possibly the contractor, that the surface is either satisfactory or unsatisfactory.

In one case during the coating of a tanker, the blasting contractor claimed that oil and contamination were bleeding out of the surface because he would no sooner leave the surface than black areas would appear, particularly in the pits. There was no dehumidification on the job and condensation and absorption of moisture was very rapid. The problem was actually that the contractor was not thoroughly cleaning the surface, and the chlorides or chloride salts embedded in the surface were absorbing moisture and changing color very rapidly. This can be a difficult situation for an inspector to handle, and he or she must have the courage of his or her convictions and the backing of the owner in order to obtain proper results.

The inspector should check for surface impurities, both before and after blasting, since they are the cause of a considerable number of coating difficulties. It is often necessary to wash the surface with water or dilute phosphoric acid and to re-blast in order to obtain the desired surface. The inspector must also be aware of the problem of humidity and condensation. The changes in temperature as the day passes can rapidly make a change in the possibility of moisture condensation on the surface. The surface temperature generally does not change as rapidly as the air temperature, and once the air temperature begins to drop, the humidity increases and the possibility of condensation becomes greater. Situations have been encountered where the surface has changed from dry to covered with condensation in a matter of 15 minutes.

The temperature of the surface is also important to note. Hot surfaces are often difficult to coat under such conditions because the solvents in the coating boil off rapidly, creating pinholes or poor adhesion. A warm surface is often advantageous during coating application. Cold temperatures cause the coating to dry and cure slowly. Temperatures that are too cold may inhibit the coating from curing, causing it to remain soft and sticky for considerable periods of time. On the other hand, water-based materials on cold surfaces may slide or refuse to evaporate properly, with the ingredients in the coating separating, leaving the coating open to early failure. This is true with water-based organic as well as inorganic coatings.

The inspector should also watch for damage to adjacent coatings during the surface preparation process. If a surface is being blasted, the adjacent coated surface can be badly damaged by the blaster waving a blast nozzle over into the coated area. While it may not be immediately obvious, these areas corrode rapidly as soon as the coating is put into service. Thus, ongoing inspection during the actual blasting process is needed to protect against such damage.

Inspection of other types of surface preparation may be even more difficult. For instance, if the process of acid pickling is thoroughly monitored and clean solutions are used, there is usually little difficulty. However, mill marks may have been painted on the steel, there may be pitting of the steel surface, or the surface may be spotted with oil and grease. Since all of these conditions create difficulties in the actual coating process, inspectors should be on the watch for them. Surfaces should be inspected and such items as mill marks, oil, paint, and similar impurities should be removed prior to the pickling process.

Pickling smut also poses a problem during the pickling process. The smut is a black deposit on the surface of the steel usually caused by poor pickling practice. It must be thoroughly washed off from the surface during the rinsing process and usually requires scrubbing with brushes for proper removal. Application of a coating over a smutty surface only leads to poor adhesion and coating difficulties. Under usual pickling conditions, the solutions are hot and the steel comes from the pickling process through a hot rinse bath. In this case, the steel is hot or warm as it comes out, the surface dries quickly, and it is an ideal time to apply the primer or first coat.

Surfaces prepared by power sanding and other power tools are also difficult to interpret. The inspector should realize that more contamination of the surface remains when using these types of preparation, and that a completely clean surface is impossible to attain by such means. Such surfaces usually are found during maintenance coating operations and cover only limited areas. Nevertheless, they should be as clean as possible, with all possible rust and contamination removed. The lower the level of contamination, the greater the chance for the coating in the repaired area to perform properly.

In any evaluation of surface preparation by blast methods, the inspector should pay particular attention to the type and size of the abrading media. As stated previously, surface preparation is most affected by the blast media, since this is the way in which the surface is cleaned and the surface profile obtained. The size and type of the blast media, therefore, primarily determines the conditions of the blasted surface. Surface cleanliness and profile can be affected by the pressure of the blast nozzle. The force that drives the blasting media against the surface determines the profile. A low blast pressure should provide for less profile than a higher blast pressure.

Most blasting operators operate their equipment with a nozzle pressure of between 90 and 100 psi. However, the length of the blast hose and size of the compressor also can make a difference in the actual nozzle pressure. The inspector should realize this and make sure that the blasting air pressure at the nozzle is sufficient to properly clean the surface and obtain the necessary profile. The blasting air pressure should be determined at the nozzle and not at the gauge on the compressor, due to the variables in the length of the line and restrictions such as moisture traps, and so on. Air pressure at the blast nozzle can be determined using a hypodermic needle air pressure gauge. The needle of the gauge is inserted through the blast hose as close to the nozzle as possible, and the pressure reading should be taken with the nozzle in operation and the abrasive passing through the nozzle.

The inspector should also be aware of the cleanliness of the abrasive. Tator and Trimber describe a valuable method of evaluating the cleanliness of the abrasive in their paper entitled "Coating (Paint) Inspection Instrument Types, Uses and Calibrations."[11] The method is useful with not only metal abrasives, but synthetic and siliceous abrasives as well.

> Although there is no inspection apparatus for determining the cleanliness of the abrasive used, a visual inspection must be made to assure that it is not damp or contaminated. When abrasive recycling systems are used, a simple test for the presence of oil or grease contamination should be made. Drop some of the abrasive (e.g., teaspoonful) into a small vial of water (pill bottle size) and shake vigorously. Inspect the top of the water for a film of grease or oil which will be present if the abrasive is contaminated. Dirt and dust in the abrasive can be assessed in the same manner. Small abrasive "fines" will be held by surface tension at the meniscus and a dirty abrasive will color the water or cause turbidity. However, water-soluble contaminants such as salt will not be detected using this test. If water-soluble contaminants are present, a litmus paper test of the water in the vial will tell if they are acid or alkaline. If neutral, the only field method to detect their presence is to evaporate the water and look for salt crystals.[6]

The inspector should also understand that the air used for either blast cleaning, blow-down, or for the application of coatings should be free of contamination. There should be adequate moisture and oil traps in the lines to make certain that the air is both oil- and water-free. Even a small amount of oil and water is unsatisfactory. There have been incidences where there was so much water in the lines that once the air was turned on, water flowed from the air line for several minutes before any air was available. Even after the water was blown out, the air was not entirely satisfactory. There also have been instances where an oil-water emulsion was sprayed out of the air line, indicating a poorly operating compressor and creating a situation that was entirely unsatisfactory for either the surface preparation or the application of the coating.

It is relatively easy to determine the cleanliness of the air by simply blowing the air from the air line into a clean rag. If there is contamination in the line, it will easily show on the rag as either moisture or oil. If the air is clean, there should be little or no contamina-

tion on the rag surface. Should contamination be visible, the in-line moisture and oil traps should be investigated to make sure that they are operating properly.

There is a relatively easy test to determine whether or not a blast-cleaned surface is oil-free. This is described as follows.

> An oil-free steel surface blasted with clean abrasive can be easily wetted with water. A representative area of surface thus cleaned when wiped with a clean, water-saturated cloth, should support a continuous film of water and there should be little or no tendency for the water film to draw up into globules or otherwise demonstrate the usual surface tension phenomena associated with water on oil metal surfaces. Such a surface is said to be free of "water break" if a continuous film of water is maintained. The water may also be applied by spraying or dipping. The ability, then, of a steel surface to support a break-free film of water is a positive indication of the absence of oil contaminants. It should be noted that the water-break test is quite sensitive and is suggested only for the specific case in which one wishes to determine if a freshly blasted surface (without further treatment) is free of oil contamination. Even a steel surface that has been thoroughly cleaned with solvents by the usual specified shop or field methods will generally not support a continuous film of water. In fact, the solvents themselves may leave sufficient hydrophobic residue to prevent the formation on the steel surface of a break-free water film.[3]

Such a test necessarily requires a re-blast or re-preparation in the area where water is applied.

Application Inspection

Unfortunately, the nature of the materials and operations involved in coating do not permit the owner who has contracted a coating job to make a few observations of the finished work and then determine whether or not he or she has received the full measure of coating performance. Once finished, an intrinsically poor coating job may appear, upon superficial examination, to be equal to a job of the highest quality. Moreover, the deficiencies of the former may not be apparent for an extended period of time, too late for the owner to negotiate for corrective action, beyond a guaranteed period. Observation of coating operations as they proceed is the only practical way in which the owner can be assured that he or she is obtaining the coating job that was specified.3

Observation is the inspector's primary tool, and one of the inspector's primary points of observation is the coating applicator. The inspector should realize that the average applicator knows very little about the makeup of coatings, particularly the high-performance type of coatings that are used under highly corrosive conditions. Thus, he or she is much more likely to make mistakes in thinning and in the application of such coatings than in the past when paints were much more simple in character. The inspector should also realize that the personnel actually performing the work will probably never read the provisions of the specifications, so that the only information they have concerning the coating is what is printed on the can. Many applicators believe that they know all about coatings application, even though their information has been derived from the actual use of only one or two types. In many cases, even the contractor's supervisory personnel have not had access to the actual specifications. Thus, the inspector may have the delicate job of educating both the supervisors and the applicators with regard to the specific coating that is being applied.

One of the most obvious duties involved in inspecting a coating application is to check both the job specifications and the manufacturer's specifications, not only to make sure that he or she is fully aware of all details, but also that the two specifications agree. If there is a major discrepancy between the two, these should be reconciled at the pre-application conference between the owners, manufacturer, contractor, and inspector.

One of the first steps in the inspection of an application is the inspection of the surface over which the coating is to be applied. While surface preparation has previously been covered, the inspection of the surface should include assurances that the prepared surfaces are free of any dust, dirt, or abrasive residue from blast cleaning and that the surface is ready for application of the coating. If the coating work is to be done on an exterior surface, the prepared surfaces should be coated with the first coat prior to nightfall in order to prevent turning of the surface or moisture condensation. Blast-cleaned surfaces should not be allowed to stand overnight without first being coated. If the surfaces to be coated are on the interior, there may be times when they can be allowed to stand overnight prior to coating. Even in this case, however, it is not a good practice, and the inspector should thoroughly re-inspect the surface the following morning prior to the application of any coating.

Inspection of the surface prior to application applies not only to bare steel, but also to previously primed or coated surfaces. It is important that each coat in the system be applied over a perfectly clean, dry surface, and that the previous coats be touched up for any damage prior to the application of the following coat. Care should be taken to make certain that the surface is free from precipitated salts or other impurities between coats.

Before the application of any coating, the inspector should assure the proper mixing and thinning of the coating prior to its use. Inspectors should make sure that the material in the containers is the proper one for the job, and that the solids in the bottom of the container are thoroughly mixed into a uniform, lump-free condition. If two-component materials are being used, each of the components may require proper mixing in order to thoroughly incorporate all of the materials into a uniform liquid. Following the mixing of each component, the mixing of the two components in the proper quantities should be observed. The mixture of the two materials should, when completed, be uniform in color, texture, and so forth. If thinning is called for in the specifications, the inspector should check to be sure that the proper thinner and the proper quantity of thinner are being used.

Applicators invariably tend to over-thin paint, since this makes it easier to apply by either brush or spray. The inspector must realize that over-thinning tends to produce thin films, thus requiring additional coats to make up for the difference in solid content. The average specification will call for no more than a pint of thinner per gallon of the original coating. This usually will adjust the viscosity to the needs of varied weather conditions or use of specific application equipment.

Once the coating is ready to be applied, the inspector should know the coverage that is expected from the coating, and in this case he or she should know the practical as well as theoretical coverage. From this, the inspector should be able to determine the wet film thickness (WFT) to be applied and the dry film thickness (DFT) of the final coating. With this information, the inspector can then check during the application for the thickness of the material as it goes onto the surface. With some experience, an inspector can actually determine quite accurately whether or not the material is being properly applied, even when standing some distance away from the surface. If he or she stands in such a position to see the gloss of the coating as it is being applied, the inspector can determine if it is being applied evenly, if the passes are being overlapped properly, if there are thin spots or holidays being left, or if the material is

being applied as dry spray. All of this is part of the observation process during actual application. Inspectors should also make periodic checks of the total coating thickness with a WFT gauge. This is an easy instrument to use, and it should be used directly in the area where the coating is being applied.

The actions of the applicator (i.e., how he or she handles the gun or the brush, the amount of coating being applied, whether or not he or she is flicking the gun at the end of a pass, and the gun distance from surface) are all important observations. The inspector can probably do more to ensure a proper application at this point than at any other point in the operation. It is at this time that the inspector should observe all application conditions very closely.

The inspector should include checking each coat for imperfections such as holidays, pinholes, runs, blistering, and overspray. If at all possible, such imperfections should be taken care of immediately prior to the movement of the applicator away from a particular area. Before the coating is dry, runs can be easily brushed out, holidays can be recoated, pinholes can be brushed, and the gun can be adjusted for overspray conditions. If the imperfections are taken care of at this point, prior to the coating being dry, a solid, uniform coating is assured. If the coating has been allowed to dry and then inspected, it is necessary to repair each of the above types of imperfections at that time, prior to the application of an additional coat. The coating should be repaired for damage as well as for imperfections, prior to the following coat. Each coat should be checked for curing and drying conditions and the inspector should determine that the drying time is proper both between coats and for the final coat. He or she should make certain that there has been no condensation on the surface or fallout of contamination between coats. If such conditions have occurred, each coat should be cleaned prior to additional coats. Finished surfaces should be inspected. This inspection should cover overspray, pinholes, runs, holidays, and any area that appears to be rough or improperly applied. All such imperfections should be marked and repaired prior to acceptance of the coating.

During the application, the inspector should be aware of temperatures; not only the ambient temperature of the atmosphere, but also the temperature of the metal. The relative humidity should be checked to assure that condensation and moisture is not possible on the surface during the application. When the temperature is close to the dew point, even the evaporation of the solvent in the coating can reduce the surface temperature condition to the point where moisture can condense on the surface. When this happens, the coating may blush (which is the absorption of the condensed moisture into the coating), causing a poor film. The minimum air temperature usually permitted for the application of coatings is 40 °F (5 °C), and the temperature of the steel should never be much lower than that. Under certain conditions, and with certain coatings, the temperature limits can be lowered, but it is generally not good coating practice to coat when the metal temperature is below 35 °F (1 to 2 °C).

Coating during below-freezing temperatures, although possible with some coatings, is always dangerous since any moisture that may have been on the surface turns to either frost or ice and will cause immediate delamination of the coating. High temperatures are also a problem. Generally, coatings should not be applied when metal temperatures are greater than 125 °F (50 °C). Some special coatings may be applied at higher temperatures, although these are usually the exception. The temperature at which it is uncomfortable to place a hand on the surface, and usually not possible to hold it for any period of time, is 125 °F.

The temperature of the surface and the air is always a concern during an application. The contractor may want to continue coating even though the minimum or maximum temperature has been exceeded. At this point, the inspector must determine whether it is possible to exceed the limits or whether, because of conditions, the quality of the coating will suffer. Generally, it is best not to permit any broadening of the temperature range since coating problems only multiply at each end of the range.

If coating is done on the exterior surfaces, weather changes are always a problem, and may be harmful to the freshly applied coating. Rain, sharp decreases in temperature, increases in wind conditions, and increases in humidity should be carefully watched. If possible, the application should be halted prior to any damage to the coating or, at least, time should be provided for the applied coating to dry before damage can occur due to such changes.

As previously discussed, condensation is a particularly difficult factor to not only observe, but also control. A surface can change within a matter of minutes from being dry to being so wet that you could write your name in the condensation. This is the reason that humidity should be checked periodically, making certain that the dew point is sufficiently removed from the ambient temperature that condensation cannot take place. Anytime that the steel temperature is lower than the ambient outside temperature, condensation problems are possible. This is particularly true where there are heavy steel masses, such as heavy plate or heavy cross sections of steel. The temperature of the steel, after being exposed overnight, takes a considerable period of time to increase to the ambient exterior temperature. In fact, in many cases it does not rise to the air temperature even over an entire day's period. This makes the surface thermometer an extremely handy tool for the inspector. Each day's work should be finished in considerable advance of the time when it is possible for condensation to occur on the surface in order to allow a reasonable drying period.

The inspector should have information concerning the drying time of the various coats being applied. Chlorinated rubber or vinyl coatings, which dry by evaporation, often can be recoated within a matter of minutes. This is sometimes necessary because of contamination fallout. Since they dry primarily by the evaporation of solvents alone, this rapid recoating is not a major problem. However, coatings (such as epoxies) that are internally cured usually require some additional time for curing prior to a following coat. The inspector should know this time so that he or she can judge whether or not the application is being conducted properly.

Also, with coatings such as epoxies, too long of a drying time between coats can also be a detriment and may cause intercoat delamination. This is especially true with coal tar epoxy coatings. Overnight cure is usually satisfactory for most coatings prior to a second coat. However, in the case of coal tar epoxies, if there is moisture condensation on the surface during the night, intercoat delamination may easily occur when the following coat is applied. Under these conditions, the surface must be protected from moisture if the coating is to be allowed an overnight cure before application of a following coat.

In inspecting the coverage of the coating, the inspector should be guided more by the DFT than the coverage per gallon, since it is the DFT that is important from the standpoint of resistance. The coverage does not indicate whether or not the coating has been applied smoothly and evenly, and it cannot account for losses due to application conditions such as wind. The DFT of the coating should be measured in numerous spots over the surface in order to determine the average thickness of the coating. Particular care should be taken in areas of possible thin application, as well as areas that may be overly thick since a thick film (particularly in the curing-type coatings) may become brittle and lose adhesion because of its thickness alone. Measuring the film thickness for each coat provides time prior to the second coat for any film thickness deficiency to be corrected.



FIGURE 18.1: A knife or sharp putty knife is an essential inspection tool.



FIGURE 18.2: A geologist's 10X magnifying glass, which is an essential inspection tool.

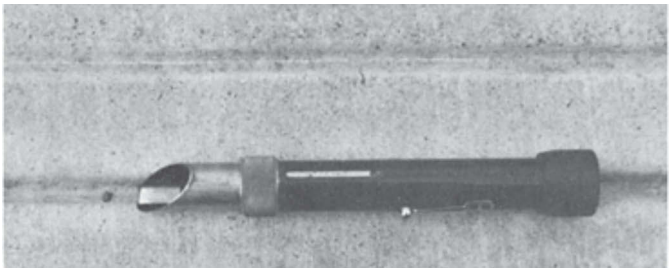


FIGURE 18.3: A 30 to 60X field microscope.

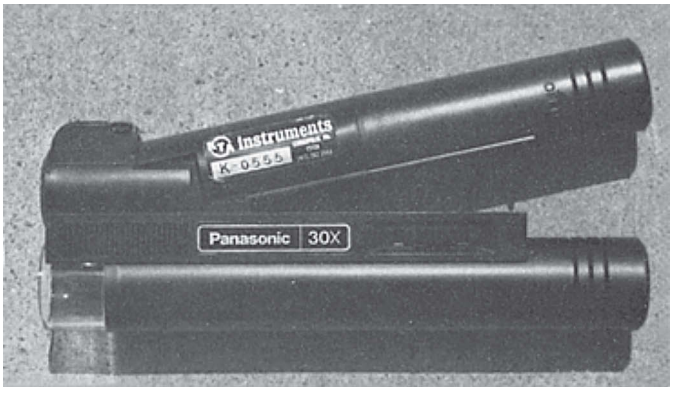


FIGURE 18.4: A 30X magnification Panasonic light scope.

Inspection Equipment Knife

There are several items of inspection equipment that should be available to the coating inspector. A knife or a very sharp putty knife is essential in determining the adhesion of a coating (Figure 18.1). If there are any questions with regard to the adhesion, a knife cut should be made through the coating to the steel to determine the degree of adhesion. The knife should be held at an angle to the coated surface and a cut made that tapers down through the coating to the substrate. If the coating is satisfactory from an adhesion standpoint, the cut should come off as a ribbon and the edges of the cut should be smooth, with no evidence of interface between the coatings and substrate. If the coating shatters from the surface, the adhesion is poor.

The putty knife can be used in the same manner by taking a corner of the knife and making a linear gouge in the coating down to the substrate. With some practice, the inspector can become very adept in determining the adhesion and flexibility characteristics of the coating with a knife. Of course, in all cases where such a cut is made in the coating, it should be repaired immediately.

The knife can also be used in the crosshatch or cross-cut tape adhesion test described in ASTM D3359.[12] This test consists of a series of crosscuts made in the coating. A 1-in square is made on a side, with cuts approximately either 1 mm or 2 mm apart made at right angles across the square depending on the thickness of the coating film. Masking tape is then rubbed onto the area and removed. The adhesion is judged by the number of squares that are delaminating from the surface.[13] This test is not effective on thicknesses in excess of 5 mils (125 μm). In such a case the X cut version of ASTM D3359 should be used.

Magnifiers

Another item that is extremely valuable for inspection of both prepared surfaces and the coating is a 10-power magnifying glass. This is a small glass that can be conveniently kept in a pocket for use at any time. An amazing amount of information can be gathered from the use of this small tool. Thus, it is recommended for use by every inspector to make the evaluation of contamination in pits, corroded areas, pinholes, or other coating imperfections much easier (Figure 18.2).

There are also some small, hand-held microscopes that are valuable inspection tools. In fact, some will change magnification from 30 to 60X (Figure 18.3). One of the most practical scopes is the Panasonic Light Scopet, which has a light source and 30X magnification (Figure 18.4). Thirty-X is as high as is practical for hand-held field inspection instruments. Such microscopes are very effective for the fine study of surfaces, both before and after preparation, and for imperfections in finished coatings. A great deal of information on coating failures can also be obtained with this instrument.

Other Equipment

There is also an illuminated magnifying glass, which is much larger and requires flashlight batteries. They are usually five-power in magnification and cover a much larger area than the smaller glass. They are valuable in evaluating surfaces, and since they are self-illuminating, it is easier to inspect surfaces that may be in dark or dimly lit areas.

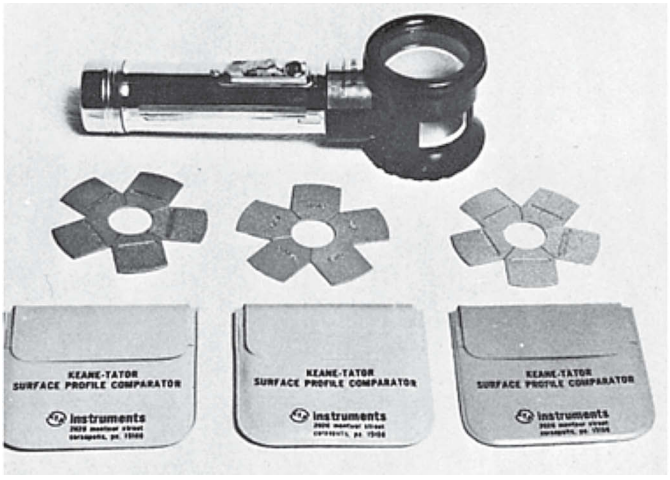


FIGURE 18.5: The Keane-Tator surface comparator. Source: KTA-Tator, Inc., Pittsburgh, PA.



FIGURE 18.6: Elcometer 125 Surface Profile Comparators. Source: Elcometer, Inc., Rochester Hills, MI.



FIGURE 18.7: Elcometer 224 surface profile micrometer or depth gauge. Source: Elcometer, Inc., Rochester Hills, MI.

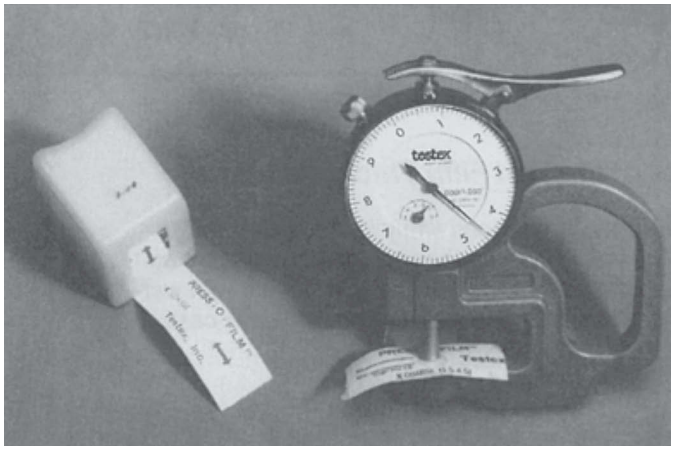


FIGURE 18.8: Presto-O-Film replica tape and spring loaded micrometer. Source: S.G. Pinney & Associates, Inc., Port St. Lucie, FL.

This equipment is also part of the Keane Tator Profile Comparator[†] This consists of a reference disc with five segments, each of which has a representative blast profile on the surface. The disc is laid on the prepared surface, and the profile of the blasted surface is compared with the reference disc profile. Using the illuminated magnifier, a good comparison of the two surfaces can be obtained, making it possible to determine by comparison the profile of the blasted surface (Figure 18.5).

There are actually three surface profile discs available, depending on the type of abrasive that is used on the job (i.e., sand, shot, or steel grit). Since the surface character and profile are quite different with each of these blasting media, the correct disc must be used in order to properly determine the profile. Each disc is designated by letter and number. The number indicates the depth of the profile in mils, and the letter indicates the type of blasting media (e.g., "S" for sand, "GS" for steel or metallic grit, and "SH" for steel shot). A second number is also present, indicating the year that the master disc was formed, which generally is not that significant. For example, 1S70 indicates that the leaf of the disc was prepared using sand that created a one mil profile and that the master disc was made in 1970.

For those involved in the use of international standards emanating from Europe or the United Kingdom, there is a similar set of comparative discs for grit and shot prepared by Elcometer that conforms to the requirements of ISO 8503.[14] These discs are square in shape with four different ranges of profile from fine to coarse (Figure 18.6).

Another field instrument that is useful in determining the average profile depth is a depth micrometer. This consists of a needle or a pin that projects out from the flat base of the micrometer, and the distance that the needle or pin extends from the flat micrometer base is read on a dial in mils or microns. Practically, the flat base is supposed to rest on the profile peaks and the pin extends into the valleys, giving the profile depth reading. It is necessary to take a number of readings with this instrument in order to obtain an average profile. This kind of an instrument is also useful in determining the depth of pits and other depressions in a metallic surface (Figure 18.7). However, great care must be taken not to drag the pin across the surface as it either dulls or bends the needle, which makes readings inaccurate.

[†]Trade name.

Another method of determining the surface profile is through the use of a replica tape, which consists of resinous film on a mylar tape (e.g., Presto-O-Film Replica Tapet). The tape is pressed firmly onto the blast-cleaned surface, and the resins on the surface of the tape deform under the pressure used to apply it to the surface. The resinous layer is penetrated by the profile peaks to the tough mylar backing so that when removed, it is an exact replica of the profile of the blasted surface, and it can then be measured with a light spring-loaded micrometer. The thickness of the mylar tape is subtracted from the micrometer reading, thus providing the average profile on the blasted surface (Figure 18.8). The backs of the tape are self-adhesive, making them very appropriate for posting into the daily reports of the inspector as a permanent record of the profile.

It is important for the inspector to realize that there is no direct correlation between any of the above methods.

A particularly effective piece of inspection equipment is the telescoping mirror. With its adjustable head and telescoping handle, it is particularly effective at checking behind nuts, bolts, and angles, where the human head cannot reach.

A viscosity cup is worthwhile in working with the liquid coating if it is necessary to determine the viscosity or consistency. There are two types: the Zahn Viscosity Cup and the Ford Cup. These are small cups with a known volume and with a sized orifice in the center. Each measures the time it takes the measured amount of coating to pass through the orifice. The faster the flow, the less the viscosity.

The viscosity cup is a good laboratory instrument and can be used to determine the viscosity of a coating fairly accurately. For a coating inspector on the job, it is also practical to check the coating viscosity between batches or where there may be a question of over thinning. It is strictly a comparison instrument when used outside the laboratory, and its use is only necessary where the consistency of the coating is questionable. The coating manufacturer should be consulted concerning the orifice size and the time involve for the coating to pass through the orifice, both un-thinned and thinned.

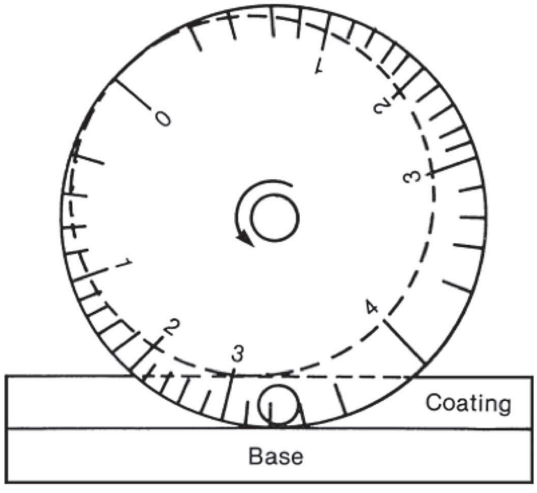


FIGURE 18.9: An inter-chemical wet film thickness gauge.

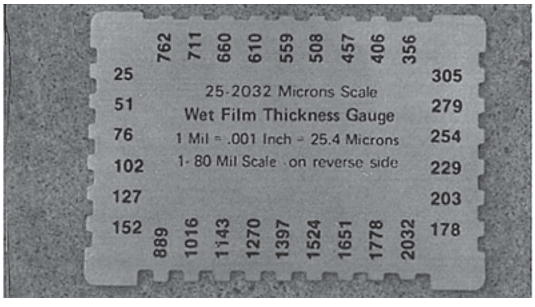


FIGURE 18.10: A notch type wet film thickness gauge.

Wet Film Thickness Gauge

There are two types of WFT gauges. The first is the inter-chemical direct reading wet film gauge. This is a circular gauge that is rolled across the surface on the two outer rings. The center is an offset ring, calibrated in thousandths of an inch or mils so that when the gauge is rolled on the surface, the point at which no liquid coating appears on the inner ring shows the WFT of the coating. This is read on the exterior of the gauge. This is a simple instrument that is very effective in determining the wet film thickness (Figure 18.9).

The second type of WFT gauge is an even simpler one. It is the notch-type gauge that is made with two end points with progressively deeper notches or steps in between. Each step is a difference of 1 mil (25 µm), so that when this is pressed into the coating, the WFT is determined by the last step that is wet by the coating (Figure 18.10).

With either of these instruments, surface irregularities can distort the reading so that care should be taken during their use. Also, since they are an in-process check on the amount of coating being applied, they will not always yield an exact measurement. For example, if the coating has been allowed to dry for several minutes prior to the use of the gauge, the wet thickness will measure less than when the coating was just applied. Neither can the wet film be exactly that calculated from the solid content of the coating due to evaporation and overspray between the spray gun and the surface. It is, however, a reasonable measure of the film thickness of the coating and provides a good evaluation of the uniformity of the material being applied to the surface. It is not effective on highly pigmented coatings such as inorganic zinc and non-skid epoxies.

Dry Film Thickness = Wet Film Thickness x $\frac{\text{vol\% non volatile}}{100}$

Correct for Losses by Multiplying Wet or Dry Film Thickness by $\frac{\text{100-\% loss}}{100}$

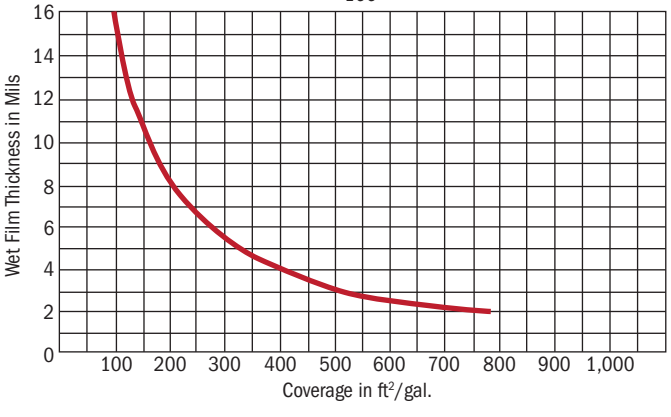


FIGURE 18.11: Wet film thickness obtained at various coverage or spreading rates. Source: "Good Painting Practice," Chapter 4, vol. 1, *Steel Structures Painting Manual* (Pittsburgh, PA: SSPC, 1982), p. 98.

The WFT can be converted to the coverage of the coating in square feet per gallon by use of the chart in Figure 18.11. The WFT, it must be remembered, is the actual amount of material being applied to the surface. Therefore, the spreading rate for coverage shown in the chart would be the practical and not the theoretical coverage of the coating. A WFT gauge has the advantage of determining a thin film application or an overly thick film application at the time it is being applied rather than after it is dry. Thus, the coating coverage can be corrected at the time of application and a much more even, uniform coating obtained.

Using the chart in Figure 18.11, it is possible to determine the coverage of the coating being applied, and from that, the approximate DFT that will be obtained. For example, if the WFT reads 8 mils, the coverage from the chart is 200 ft²/gal. As was previously determined, the coverage of a 100% solids coating is 1,600 mil ft²/gal. If the coating in the example is 50% solids by volume, it would contain 800 mil ft²/gal. The coating is being applied at 200 ft²/gal, so that the DFT should then be 4 mils. The formula is a simple one.

$$\text{Dry Film Thickness} = \frac{\dfrac{1600 \text{ mil ft}^2/\text{gal}}{\text{\% solids by volume}}}{\text{actual coverage in ft}^2/\text{gal}} \tag{18.1}$$

$$\text{DFT} = \frac{\dfrac{1600}{50\%}}{200} = \frac{1600}{200} = 4 \text{ mils} \tag{18.2}$$

This provides the approximate DFT that is actually being applied.
Tator and Trimber, however, have a different perspective.

> Wet film thickness gauges are only of value if one knows how heavy a wet film to apply. The wet film thickness/dry film thickness ratio is based on knowing the solids by volume of the specific material being measured. The old theory of doubling the desired dry film thickness to establish the wet film to be applied is only correct if the solids by volume of the coating material is 50%.
>
> The solids by volume of the coating material is information that is readily available from the manufacturer and is commonly included in their product data sheets. The basic formula is DRY FILM THICKNESS = WET FILM THICKNESS × % SOLIDS BY VOLUME. A more workable variation of the formula showing the required wet film thickness for the desired dry film thickness is as follows:

$$\text{Wet Film Thickness} = \frac{\text{Desired Dry Film Thickness}^{6}}{\text{\% Solids by Volume}} \tag{18.3}$$

As an example, if the desired dry film thickness is four mils (0.004 in) and the % solids by volume is 65% (0.65 in), the WFT would be: WFT 0.006 (6 mils) = 0.004 (4 mils)/0.65 (65%).

The above formulas are accurate providing the solids-by-volume of the material is not changed. The percentage will change, however, if any thinner is added to the coating. When thinner is added, the total volume of the material is increased without any corresponding increase in the amount of solids. Therefore, the thinned material will result in a lower percentage of solids by volume. Thus, when comparing thinned vs. un-thinned material in order to achieve a comparable dry film DFT, a heavier wet film application of the thinned material will be required. In order to evaluate what the new WFT should be, the new percent solids by volume of the coating material after thinning must be determined. The following formula should be used to determine the required WFT when the material is thinned.

$$\frac{\text{Desired Dry Film Thickness Wet Film Thickness} = (\text{\% Solids by Volume})}{(100\% + \text{\% Thinner Added})} \tag{18.4}$$

Again using the above example the desired dry film thickness is 4 mils (0.004 in.). The coating is thinned to one qt. per gal; the wet film thickness then becomes:

$$\text{Wet Film Thickness} = \frac{\dfrac{0.004 \text{ (4 mils) } 0.004}{\text{0.65 (65\%) or 0.52}}}{100\% + 25\%}$$

$$\text{Wet Film Thickness} = 0.0077 \text{ mils or, from a practical standpoint, between 7.5 and 8 mil}^{11} \tag{18.5}$$

Dry Film Thickness Gauge

The measurement of the DFT of a coating is probably one of the most important measurements that can be made. This measures the total dry thickness of the film as applied to the surface, and is therefore the working thickness of the coating. There are a number of methods of measuring DFT. The most valuable are the nondestructive test instruments, which are based on a magnetic principle. There are a number of quite accurate electrically operated thickness gauges that are primarily for use in areas where power sources are available and where the instrument can be reasonably close to the coating being tested, such as on product finishes like washing machines, refrigerators, and other appliances. However, this type of gauge is not practical for a field inspector working with steel tanks or similar structures.

For the field inspector, there are four principle types of magnetic or electronic instruments. While they are somewhat less accurate than the electric gauges, they have the distinct advantage of portability and can be used on almost any steel structure with accuracy sufficient enough to indicate whether or not the coating is applied within the limits of the specification. The magnetic ones are effective at measuring nonconductive coatings over ferrous steel substrates, the electronic eddy current ones are effective at measuring nonconductive coatings over nonferrous metals such as SS and aluminum. Newer electronic gauges are effective at measuring nonconductive coatings over such nonferrous substrates as concrete, fiberglass, wood, ceramics, and other such materials. Nondestructive DFT gauges come in several types.

Lift-off Magnetic Gauges (Type I)

Elcometer 211™, Mikrotest III™ or IV™, and Positest™ are common examples of these instruments. All are single-point instru-

ments using the magnetic pull-off principle (Figure 18.12). They nondestructive and the thickness is read on a movable dial. They are lightweight, easily carried, and are some of the most popular thickness gauges in use.

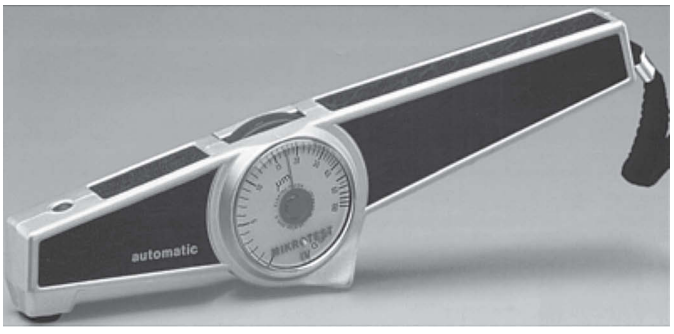


FIGURE 18.12: A Mikrotest III™ magnetic pull-off thickness gauge. Source: Corrpro Companies, Inc., Houston, TX.

Positive Pressure Single Point Gauges (Type II)

The Elcometer 456™ (Figure 18.13), PosiTector 6000™ (Figure 18.14), and Quanix 1500™ are examples of three nondestructive, magnetic, or eddy current thickness gauges. They are a more advanced type of instruments for measuring coatings on either ferrous or nonferrous substrates (the ferrous models use the magnetic principle, the nonferrous models use the eddy-current principle). They are small, easily hand- held with a single-point contact, and read the thickness in mils or microns on digital scales. They are accurate instruments and will give quick readouts while being moved over a coated surface—something that other easily portable gauges do not do. Where many thickness readings are necessary, these instruments are undoubtedly the quickest and easiest to use. The more advanced versions can store up to 10,000 readings and print out lowest, highest, average, and mean readings in mils or microns.



FIGURE 18.13: Elcometer 456 Positive Pressure (Type II) Dry Film Thickness Gauge. Source: Elcometer, Inc. Rochester Hills, MI.

Pencil Gauges

Pencil gauges are also magnetic pull-off gauges operated by a permanent magnet in a spring. They are about the size of a small pen or pencil and are handy gauge because of their size. However, they do not provide as accurate a reading as other types of gauges described earlier.

These instruments generally should be calibrated for use with the thickness of coating that is to be measured. Calibration merely consists of placing a standard with approximately the same thickness as the coating to be tested on the bare metal surface to be coated and adjusting the instrument until it reads the correct thickness. The instrument should be checked at least to determine its variance from the standard.

It also should be considered that the magnetic gauges will not read as accurately over a blasted surface as they will over a perfectly smooth steel surface. This is because the thickness of the coating varies between the peaks and valleys, and with the magnetic principle, the variation in the reading could be the depth of the profile. If the instrument is calibrated on a blast-cleaned surface, the test measurements will be more accurate and will generally read the thickness of the coating somewhere between the low and high points in the blast pattern. This, of course, is quite different from readings obtained on a perfectly smooth surface.

Steel surfaces that are badly pitted are also difficult to read with any of the magnetic equipment due to the extent of variation in the steel surface. It should also be considered that red rust is nonmagnetic, so that if a coating is applied over a rusty surface, the thickness of the rust will increase the thickness of the reading. Care is necessary, then, in using these instruments to make sure that the coating being checked was applied over a clean, smooth surface. Edges, weld areas, and rough conditions interfere with an accurate reading with these instruments.

All gauges based on permanent magnets will accumulate steel or other magnetic particles at the magnetic contact, causing inaccurate readings unless they are removed. These magnetic thickness gauges are capable of fairly fast readings, so that any number of readings can be taken over a relatively short period of time. This is an advantage since it allows the inspector to check many spots and thus obtain a good measure of the average coating thickness that is being applied. The general accuracy of the magnetic thickness gauges when they are properly adjusted, and in good working order, is between plus or minus 10% of the actual coating thickness. While there can be much larger variations due to external sources, the accuracy is much greater than the judgment of an applicator. A 10-mil film would have an accuracy of plus or minus 1 mil, which is entirely practical from an overall inspection standpoint.

There also are a number of destructive methods by which to determine the coating thickness. One of these, the depth gauge micrometer, was discussed previously. In this case, the coating can be scraped from the surface and the micrometer used to determine the thickness of the coating at that point. If it is possible to obtain chips or to peel the coating from the surface, a standard micrometer or a spring-loaded micrometer can be used. Both of these provide an accurate measure of coating thickness.

The P.I.G. (Paint Inspection Gauge, formerly Tooke Gauge) is a hand-held unit that uses a precision cutting tip to cut a groove in the coating (Figure 18.15). The groove is



FIGURE 18.14: A PosiTector 6000 nondestructive thickness gauge. Source: Corrpro Companies, Inc., Houston, TX.



FIGURE 18.15: A Tooke coating thickness gauge, which is a destructive gauge that requires coating repair after use. Source: Corrpro Companies, Inc., Houston, TX.

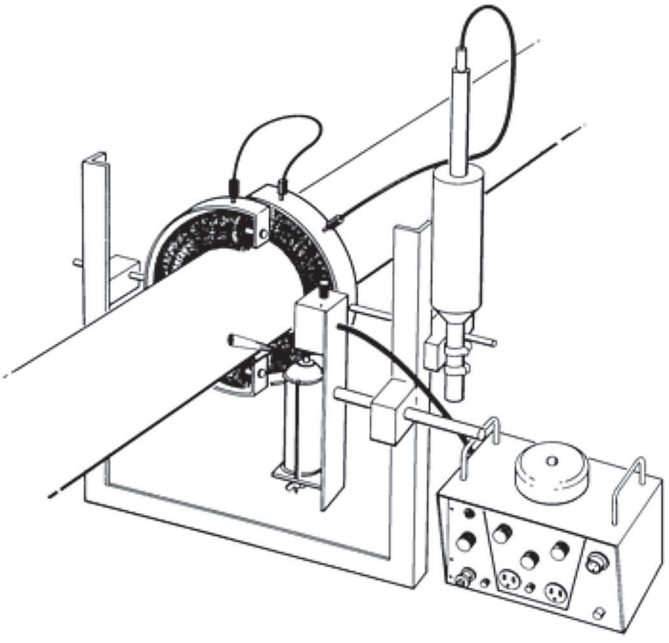


FIGURE 18.17: Automatic holiday detector for pipe coatings using a circular high voltage probe. Source: Tinker and Rasor, San Bernardino, CA.



FIGURE 18.16: A low voltage wet sponge holiday detector. Source: Tinker and Rasor, San Bernardino, CA.

made with a known angle

and is then viewed perpendicularly with a microscope. The microscope is calibrated, and the actual coating thickness can be determined from the scale in the eye-piece. The advantages of this instrument are that it can be used for determining the thickness of multi-coat systems, it can determine the thickness of the individual coats, and it can be used to read coating thickness on nonmagnetic surfaces. This allows the thickness of coatings on aluminum, copper, or concrete surfaces to be determined. The disadvantage of all destructive thickness testers is that the damaged area must be properly repaired after use.

Holiday Detectors

Where coatings are to be used in critical corrosion service, or as linings where sensitive or corrosive solutions will be in direct contact of the coating, inspection with a holiday detector is usually required. There are two principle types of holiday detectors: the low-voltage, wet sponge type and the high-voltage units. For relatively thin films, the low-voltage holiday detector is most useful. In this case, relatively low voltage direct current is passed into a wet sponge, which is passed over the coating surface. As the sponge contacts a pinhole or other coating imperfection, contact is made with the steel substrate and an audible alarm rings so that it is possible to locate the imperfection in the coating.

These are simple, nondestructive, easy-to-use testers that do not damage the coating even at the point of electrical contact. These units are designed for thin films (up to 20 mils [500 μm]) (e.g., a normal thickness of vinyl, epoxy, etc.) where the wet sponge can supply enough water in the pinhole to make electrical contact. These are used wherever an imperfection-free lining or coating is required. They are self-contained, battery operated, and only require a ground contact with the base metal for them to operate. Figure 18.16 shows such a unit in operation with the wet sponge on the coating surface and the ground lead attached to the flange of the tank.

The second type of holiday detector, the high-voltage unit, is available in a number of different forms, depending on the area of surface to be covered. One is a hand-held unit approximately the size of a flashlight, with a pointed probe that is passed over the coating surface. When the probe approaches a holiday or pinhole in the coating, the spark jumps from the point of the probe to the coating imperfection. This makes for a very accurate determination of the pinpoint imperfection. Some units require a 110-V alternating current power source; others are self-contained, battery operated, and are effectively operated in remote areas. Such units can operate with voltages from 500 to 200,000 V. Both the thickness and the dielectric strength of the coating impose limitations on the voltage used.

There are also larger units, using the same principle, with a wide rake-type probe that can cover several feet of surface at a time. In this case, the probe is made up of a section of conductive plastic or many fine wires and when an imperfection is found, a spark jumps at that point. These units may operate at somewhat higher voltages than the hand-held units (up to 35,000 V) and are primarily used on thicker films such as vinyl sheet linings, tape wrapping, high film thickness epoxies, or coal tar (hot-applied) coatings. Where heavy coatings are applied to pipe, circular brushes that cover the entire circumference of the pipe can be used. The unit is rolled over the

pipe exterior to pick up any possible coating defects. Many types of such units are available, and are extremely useful in the inspection of coatings, particularly those that have pore-free requirements. Figure 18.17 shows a circular unit for the automatic inspection of pipe coatings.

Some difficulties may be involved in the use of the high-voltage equipment. For example, when a coating contains conductive pigments, for example, graphite, aluminum, or copper, the high-voltage spark will pick out the conductive particles in the film and indicate an imperfection. If the high-voltage spark is left on the particle long enough, it will burn a hole in the coating at that point. Also, because of the high voltage used, thin continuous areas of coating can be penetrated, causing a hole where none existed before. However, this also can be an advantage since such thin areas are potential failure areas.

Thermometers

A piece of inspection equipment that is useful under many circumstances is the surface thermometer. This thermometer is a dial-type unit that can be placed on the surface and that will directly read the surface temperature. This can be important in determining substrate or coating temperatures, particularly when the weather is unusually hot or cold and the temperature of the substrate is unknown. It can be very important to know when the substrate is approaching the temperature of condensation.

The thermometer is also a useful instrument in determining the high temperature of steel. This is particularly true where it is in the sun, such as on a roof deck or a similar area subject to direct rays of the sun. This is important because excessive temperatures can cause blistering of many coatings during the application process. Figure 18.18 shows one type of surface thermometer that is easily portable for field work and can be placed on almost any surface for a quick reading.

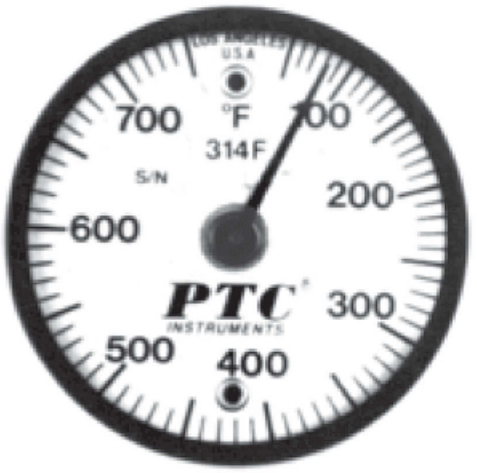


FIGURE 18.18: A surface temperature thermometer. Source: Corrpro Companies, Inc., Houston, TX.

Hygrometer

The combination of a thermometer and a hygrometer is a valuable inspection tool, particularly where there may be problems of dew or condensation. With the combined use of both instruments, it is possible to determine the probability of condensation on steel surfaces. This is done through use of a chart such as the one shown in Table 18.1. (While the same chart was also shown in Chapter 10, it is duplicated in this chapter as a reference for the inspector.) In this case, it is only necessary to know the metal surface temperature, the temperature of the surrounding air, and the relative humidity. If the relative humidity, as indicated by the hygrometer is above a certain point, condensation is likely. For example, as indicated by the chart, if the air temperature is 70 °F (21 °C), the metal surface temperature 60 °F (16 °C), and the relative humidity above 56%, the probability of moisture condensation on the steel is high.



FIGURE 18.19: A hygrometer and temperature indicator.

Another useful piece of inspection equipment is called a sling psychrometer (Figure 18.19), or a wet and dry bulb thermometer. These are essentially two thermometers; one is covered with a wick or a sock that is saturated with water, the second is the dry bulb that gives the ambient air temperature. The most common type of psychrometer is referred to as the sling psychrometer or whirling hygrometer. In this case, the operating principle is to wet the wick on the wet bulb thermometer and then sling or revolve the thermometers through the air for a sufficient time to determine the cooling effect caused by the evaporation of the moisture on the wet bulb thermometer. After the two temperatures are determined, a psychrometric chart or table is used to determine the relative humidity and dew point temperatures of the air. This instrument is commonly used in the field to determine relative humidity. The combination of surface hygrometer and thermometer is more likely to be used on fixed fabrication site.

Adhesion Tester

The inspector is sometimes called upon to determine the adhesion of a coating on a numerical basis. The Elcometer Model 106t adhesion tester (Figure 18.20) can be used in the field and will provide a measure of the adhesion in lb per in^2. It consists of a pulling unit with aluminum test dollies that are attached to the coating surface with a contact adhesive. After the adhesive has cured, the coating may or may not be cut down through to the substrate (depending on the type and thickness of coating being tested) around the periphery of the dolly. The tensile unit is then put into place and attached to the dolly and the unit is tightened by hand. The test unit applies a direct tensile to the dolly, breaking it from the surface when the adhesion of the coating is broken. The point of the break is read on the scale of the instrument in lb per in^2.



FIGURE 18.20: An Elcometer adhesion tester, which provides numerical readings in pounds per square inch. Source: Corrpro Companies, Inc., Houston, TX.

TABLE 18.1: Percent Relative Humidity Above Which Moisture Will Condense on Metal Surfaces Not Insulated

Metal Surface Temp.	4 °C 40 °F	7 °C 45 °F	10 °C 50 °F	13 °C 55 °F	15 °C 60 °F	18 °C 65 °F	21 °C 70 °F	24 °C 75 °F	27 °C 80 °F	30 °C 85 °F	32 °C 90 °F	35 °C 95 °F	38 °C 100 °F	40 °C 105 °F	43 °C 110 °F	46 °C 115 °F	49 °C 120 °F
1 °C 35 °F	60	33	11														
4 °C 40 °F		69	39	20	8												
7 °C 45 °F			69	45	27	14											
10 °C 50 °FF				71	49	32	20	11									
13 °C 55 °F					73	53	38	26									
15 °C 60 °F						75	56	41	17	9							
18 °C 65 °F							78	59	30	21	14	9					
21 °C 70 °F								79	45	34	25	18	13				
24 °C 75 °F									61	48	37	29	22	16	13		
27 °C 80 °F									80	64	50	40	32	25	20	15	
30 °C 85 °F										81	66	53	43	35	29	22	16
32 °C 90 °F											81	68	55	46	37	30	25
35 °C 95F												82	69	58	49	40	32
38 °C 100 °F										83	70	58	50	40			
40 °C 105 °F											84	70	61	50			
43 °C 110 °F												85	71	61			
46 °C 115 °F													85	72			
49 °C 120 °F														86			

Source: *Corrosion Control Principles and Methods*, Section 7 (Pasadena, CA: Ameron Co.).

When this instrument is used, not only is the tensile adhesion value of importance, but the actual break from the surface is also important. If the break from the surface is clean, this indicates a possible adhesion problem. If the coating itself is broken, it means that the cohesive strength of the coating is less than the adhesion strength to the substrate. The break may also be in the adhesive itself. If this is the case, it indicates that the adhesive strength of the coating is greater than the strength of the adhesive.

Since this type of test is time consuming, a number of tests over a broad area are usually not practical. It is also a destructive test, so, as with all destructive tests, the area tested must be patched with the original coating in order to ensure that full corrosion resistance is obtained. Figure 18.20 shows the pulling or tension unit by which the dollies are pulled from the surface by direct tension. Other field units made by Hate, Dyna, and others are practical for on-the-job measurements where numerical adhesion ratings are desired or required. The applicable standard for this test is ASTM D4541.[15]

Inspector's Diary

The diary of an inspector is an important document. Not only is it a record of the day-to-day progress of the work, it is often the only one that is kept in a consistent manner. The diary is important as a record and as an aid to the memory of the inspector during meetings and conferences. It also constitutes documented evidence that is admissible in court proceedings should the coating fail prematurely. Detailed diaries should therefore be kept by the inspector on a daily basis, and should include such information as the weather, temperature, humidity, surface conditions, material used, drying or curing conditions, general appearance of each coat, any repairs that were necessary (including their extent and location), an evaluation of the quality of work being done, and the general appearance of the coating. Any particular difficulties during the application also should be recorded.

As evidenced by this discussion, an inspector's job is not only important, but is often difficult as well. As stated by Tator and Trimber,

"A few instruments, some knowledge, and good common sense are all that is required for good coatings inspection."[11] Sometimes the difference between a good coating job and one that is plagued with trouble can be attributed to the inspector's temperament and personality. A good inspector helps to ensure good quality control of the coating application, which should result in the satisfaction of the owner, general contractor, coating contractor, and all other parties involved.

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19 Typical Uses of High-Performance Coatings

The uses of high-performance coatings have grown almost in an exponential fashion since they were first introduced in the early 1930s. Hundreds of useful applications have been developed and hundreds more have been tried. For example, inorganic zinc (IOZ)-coated washing machine tubs were once made with reasonably successful results. IOZ has also been used to coat the fan in a wind tunnel. A five-coat vinyl lining was once tried on 55-gal steel drums used to transport wine, and on small metal battery boxes. Several thousand feet of small-diameter oilfield piping was also once lined with a five-coat vinyl system to prevent corrosion and paraffin buildup and actually remained in service for several years. Epoxy coatings have been used to coat toilet seats and vinyl coatings have been used on airline food trays. While most of these minor applications were successful, they did not represent the type of application for which the high-performance, corrosion-resistant coatings were designed.

The typical high-performance coating is used for large corrosive industrial applications where no other type of material will provide the service or the life that is both required and expected. They are primarily applied on large, in-place structures and are not designed as product finishes (e.g., for appliances, automobiles, etc.). They are used worldwide in most of the industries where corrosion is a factor. Of necessity, the uses described in this chapter will be quite general, since the variety of applications in most industries is too extensive to cover the details of each one. Therefore, coating uses, as outlined in this chapter, will be typical of the industry being discussed.

The Chemical Industry

In this case, the chemical industry will be discussed in very general terms, since it is difficult to find an appropriate division between chemical, petrochemical, refining, or heavy chemical plants. This is because the processes they involve overlap and much of the general equipment used (e.g., piping, pipe racks, tanks, etc.) is common to all of them.

The chemical industry is extremely complicated and involves many different kinds of processes and plants. The extent of the corrosion encountered ranges from none to catastrophic, with no two plants having identical problems. This is due to the variety of processes that are used for producing the same product, as well as the variety of maintenance philosophies employed by the production companies.

For example, salt, or plain sodium chloride (NaCl), constitutes the greatest tonnage of all chemicals and is produced in three different ways. It is produced from brine wells, where the salt water is actually pumped from underground structures. It is mined in large quantities as a solid in much the same manner as any underground mine is operated. It is also obtained through evaporation of seawater. Each one of these methods involves different corrosive processes; however, there is one corrosive chemical that is common throughout all three, that is, saturated NaCl solutions that are recrystallized for purification.

While operations for the production of salt exist in isolated areas, salt itself is an intricate part of the entire chemical industry. For example, 45% of the salt produced is used to produce caustic soda and chlorine. In turn, caustic soda and chlorine are used throughout the entire chemical industry to produce both organic and inorganic products such as ethylene dichloride and calcium chloride ($CaCl_2$). Wherever salt is part of a chemical process, high-performance coatings are necessary. IOZ topcoated with epoxies and polyurethanes is the most common coating system used.

One factor that is common throughout the chemical industry is the environment. For the most part, chemical plants are open work structures

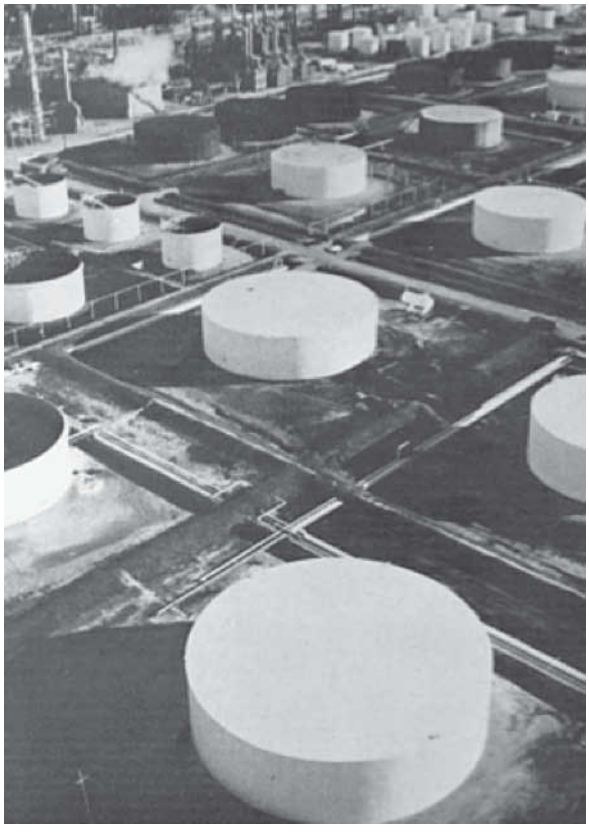


FIGURE 19.1: Tanks and structures coated with inorganic zinc base coats and high-performance topcoats. Source: Ameron Corp., Monterey Park, California.

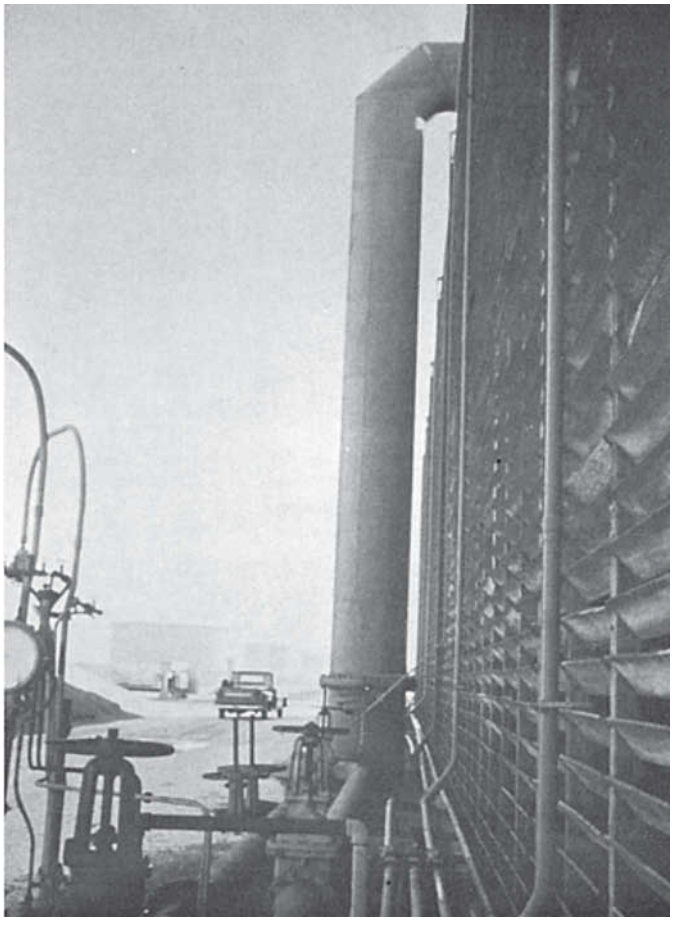


FIGURE 19.2: Excellent coating protection of a cooling tower pipe riser by a single coat of inorganic zinc.

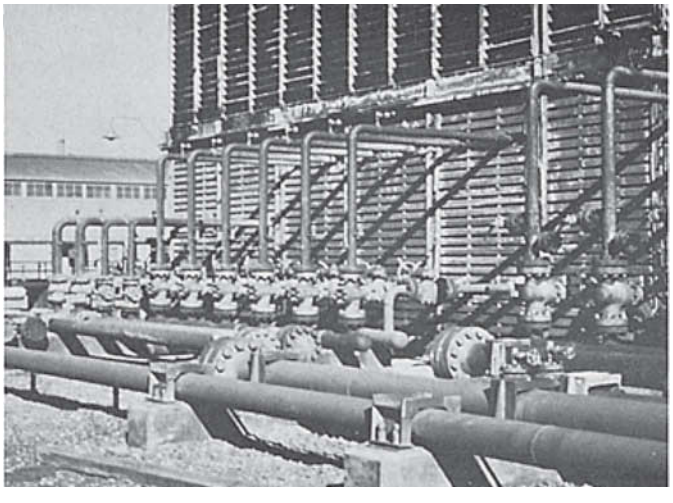


FIGURE 19.3: Structures and piping adjacent to a cooling tower coated with one coat of post-cured IOZ after seven years of service. The surface discoloration is due to cooling tower fallout.

and are exposed to the weather and whatever fumes or contaminants are in the area as byproducts from their own plant. Thus, the largest overall use of coatings is for the protection of these exterior structural steel units, including piping and tankage (Figure 19.1). The actual square footage involved in such steel surfaces cannot be calculated. It may run in to several million square feet in any one chemical plant.

Corrosive conditions vary primarily according to the atmospheric conditions that are present. These range from coastal areas (where marine conditions prevail), to the dry plains, as well as to areas of extremely high humidity and high temperature. Chemical plants adjacent to the coast and in highly humid areas generally will have the most corrosive conditions, irrespective of what they produce. Therefore, all exterior surfaces must be protected against such conditions by coatings.

The actual fumes and contaminating conditions that make up the environment of a chemical plant have been greatly reduced by emissions regulations in the environmental cleanup programs dictated by federal, state, and local laws. Thus, undoubtedly, there will be less corrosion from atmospheric fumes than has existed in the past. However, to offset this decline, the rising cost of maintenance is an economic factor in the use of better, more sophisticated, and long-lasting coatings. It is no longer practical for a chemical company to maintain a large painting staff that is continually cleaning and coating structural steel throughout the plant.

A secondary economic factor is the rising cost of steel and steel installation, which makes the cost of protecting steel structures a smaller percentage of the overall cost than ever before. The high-performance coatings, as compared with alkyds and other paints, are so similar in applied cost that the small difference is an insurance premium, which the operating company cannot afford to do without.

Certain areas are common to all chemical plants where corrosion is a serious problem. One of these is the cooling tower. Almost all chemical plants, from refineries to the production of fertilizers, have extensive cooling tower facilities. Serious corrosion problems exist not only within the tower area, but also in adjacent areas that are subject to high humidity and spray, salt that accumulates in the cooling tower water, and condensation of moisture and fallout from atmospheric pollution. In fact, one well-known chemical plant uses the area adjacent to a cooling tower as a coating testing area, since it represents the most corrosive conditions in the plant.

Figure 19.2 shows a cooling tower riser that has been coated with IOZ for several years. In this case, the single coat of zinc provided excellent protection. Most areas adjacent to the cooling towers (Figure 19.3), for example, piping, pipe racks, and similar structures, are coated with IOZ and often topcoated with an intermediate coat of high-build epoxy and a finish coat of aliphatic polyurethane, since weather resistance in the cooling tower area must be the best.

Probably the most common structure in the chemical industry is the pipe rack with the pipe that it carries. They are usually made of structural shapes that are welded or bolted together, therefore creating a myriad of edges, corners, and other sharp protrusions. In addition, the pipelines may be placed close together and joined with flanges and bolts. Raised face flanges leave a space between the flanges so that from a coating standpoint, the pipe rack and pipe represent a substantial coating problem. The IOZ coatings have vastly improved the protection provided to these structures. In many cases, IOZ has given adequate protection in a single coat and has provided many years of good corrosion protection (Figure 19.4).

On pipe racks that are in more difficult chemical areas, the addition of vinyl or epoxy topcoats has given excellent protection for many years without appreciable maintenance (Figure 19.5). It is, however, the inorganic base coat that has increased the life of coatings on pipe racks by several times that provided by ordinary organic coatings. The protection of edges, corners, and damaged areas and the elimination of undercutting and underfilm corrosion are the great advantages of the IOZ base coat.

Another area common to all chemical plants is stacks. There usually are all types of stacks from different reactors throughout the

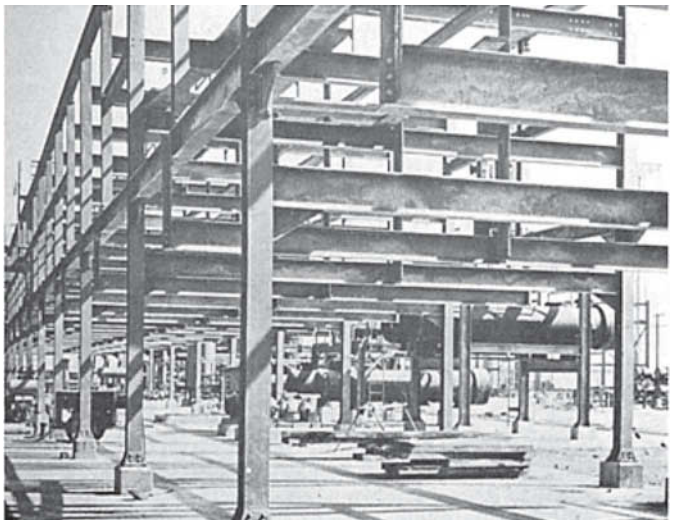


FIGURE 19.4: Typical pipe rack during installation coated with IOZ without a topcoat.

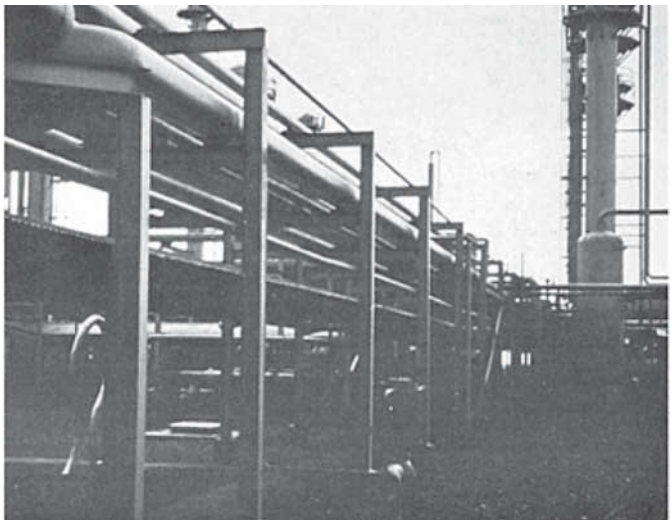


FIGURE 19.5: Refinery pipe and pipe rack coated with inorganic base coat and vinyl topcoats.



FIGURE 19.6: Refinery stacks coated with IOZ and silicone aluminum that is an excellent high-temperature system.

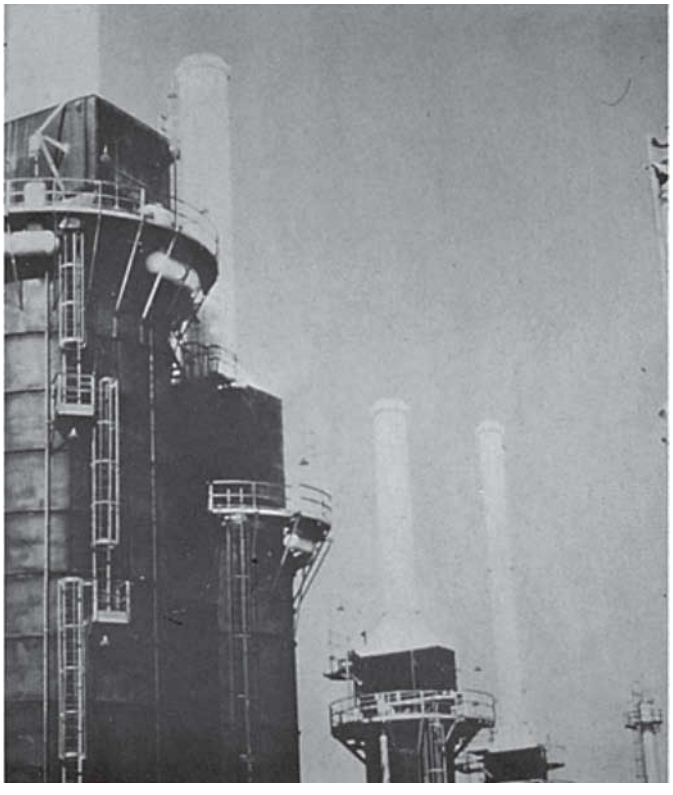


FIGURE 19.7: Chemical reactor stacks coated with IOZ base coat and white inorganic topcoat after several years of exposure and a stack fire that caused no coating failure.

plant; some may be hot, some may be cold, but usually they are both. IOZ has proven an excellent coating for stacks, particularly at the difficult operating temperatures of 200 to 500 or 600 °F. Where the IOZ is followed by silicone aluminum; excellent long-lasting appearance has been provided at higher temperatures (Figure 19.6). In the late 1990s products such as polysiloxanes have provided very good protection for stacks.

In at least one case, an IOZ base coat and an inorganic white topcoat were applied both to the interior and exterior of a series of reactor stacks. This combination, entirely inorganic, provided excellent protection to the stacks, both on the interior and the exterior, over a period of several years. This was in spite of a fire that burned one of two towers during the life of the coating. Even after being exposed to the fire, both the inorganic base and topcoat were in excellent condition (Figure 19.7). The only drawback to this coating combination is the porosity of the inorganic white topcoat, which tends to collect dirt and dust along with humidity.

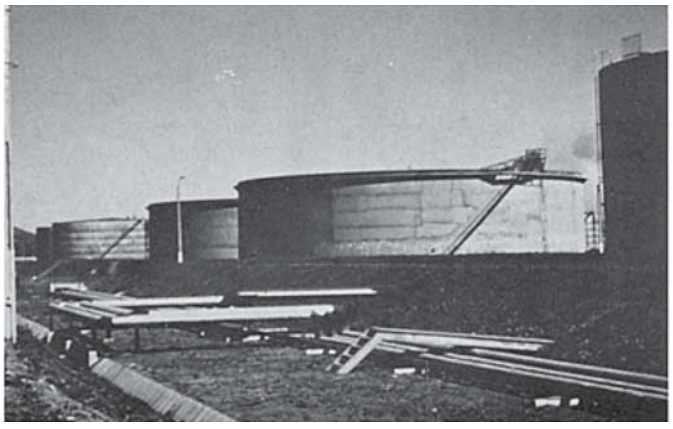


FIGURE 19.8: Floating roof refinery product tanks coated with one coat of post-cured IOZ after 10 years of service in a coastal marine atmosphere.

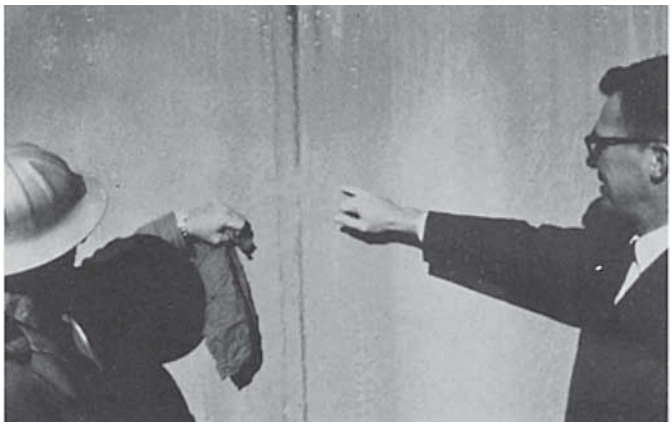


FIGURE 19.9: The interior of a floating roof refinery product tank coated with one coat of post-cured IOZ after 10 years of service. The small rust streak in the center is due to the rubbing of steel shoes on the vapor seal.



FIGURE 19.10: A tank farm newly coated with IOZ and white top coating so that any corrosion that may take place will be instantly evident.

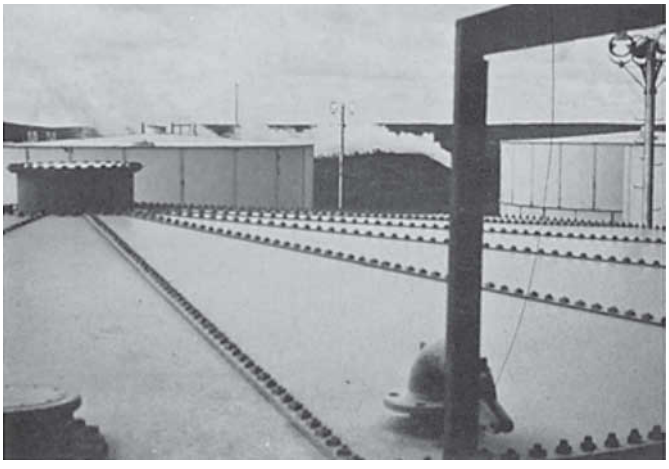


FIGURE 19.11: Bolted field storage tanks for crude petroleum coated with IOZ and white epoxy polyamide topcoats that provides excellent protection to the bolted joints.

Storage tanks pose a common problem throughout the chemical industry. The surfaces are all similar, that is, broad, flat, and relatively smooth. The atmospheric and weather conditions to which they are generally exposed are usually aggravated by chemical fallout from cooling towers, reactors, and adjacent industry. Therefore, any coating used must have excellent weather resistance as well as resistance to the local fallout conditions.

IOZ alone, preferably a post-cured or high-zinc water-based self-cured product, has given excellent and long-lasting service on both field collection tanks (petroleum production) and refinery tanks where chemical fallout is not severe. Figure 19.8 shows refinery tankage coated with water-based IOZ (one coat) after approximately 10 years in service. The interior of the floating roof tanks, which stored distilled petroleum products, were in a similar condition after the same period of service, as shown in Figure 19.9. Figure 19.10 shows a tank farm coated with IOZ and white vinyl topcoats, which is recommended for tank service to allow dirt wash-off. With the advent of stringent volatile organic compound (VOC) restrictions, polyurethanes and water-based acrylics have largely replaced vinyls as the finish coats of choice on exteriors of tankage and structural members.

Aliphatic polyurethane, polysiloxane, and water-based acrylic topcoats also provide excellent weather resistance and good service over IOZ base coats. Properly pigmented polyamide epoxy top coatings may also be used for such service. Alkyds or silicone alkyds, either alone or over a compatible organic intermediate coat, have been used extensively where the chemical fallout in the area is not severe. Figure 19.11 shows bolted field petroleum storage tanks with such systems.

Water treatment facilities are another area common to nearly all chemical plants. The corrosion problems in this case vary from plant to plant, depending on the chemical fume conditions. However, the coatings involved generally would be similar to those used on any water treatment facility throughout the country. Coal tar epoxies, as well as polyamide epoxies, have given good service under water conditions. Where white or light colors are required, the polyamide epoxy is recommended. Properly formulated chlorinated rubber coatings have also given good service. Both the polyamide epoxy and the chlorinated rubber can be used on underwater concrete surfaces. The coal tar epoxies are most practical for submerged steel equipment.

All chemical plants also have waste disposal facilities. In this case, however, corrosion problems are unique to each chemical plant and therefore do not carry any universal coating recommendation. Each plant must be considered individually. The coal tar epoxies have proven very effective in many wastewater facilities since they have good chemical as well as water resistance. Floating oil residue, especially aromatic hydrocarbon base, can cause many coating problems and thus should be carefully considered while selecting a coating for waste facilities. It is usually the minor waste products that cause both corrosion and coating problems. Figure 19.12 shows a small oil waste chamber in a refinery. All metal parts were coated with IOZ because of solvent contamination in the wastewater. The trend since the late 1990s has been toward very high solids epoxy systems wherever wastewater treatment equipment has to be protected. For concrete structures, 100% solid epoxy and polyurethane systems have performed very well. Beginning in the early 2000s elastomeric polyurethanes and polyureas made significant inroads into the wastewater industry.

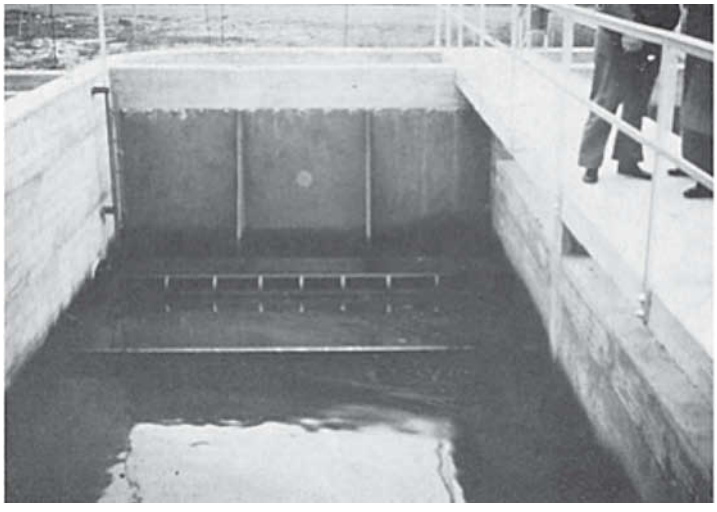


FIGURE 19.12: Concrete waste sump in a refinery where all metal surfaces are coated with IOZ to resist solvent attack from floating sludge.

The chemical industry can essentially be divided into two major categories. The first is the heavy chemical category, or the part of the chemical industry that deals primarily with inorganic material. This would include production of materials such as salts, sulfuric acid (H_2SO_4), soda-ash, caustic soda, and chlorine. The second category deals with organic materials. This area includes all organic chemical process plants, petrochemical plants, and refineries. There are many other facets to the chemical industry as well, such as pulp and paper, mining, plating, and soap manufacture. In fact, nearly all manufacturing plants use chemical processes in one way or another.



FIGURE 19.13: A typical conveyor for handling crystallized salt. In this case, IOZ is required for a base coat and may be used alone under certain conditions.

Inorganic Chemical Plants

Salt

The heavy chemical plants are usually based on a particular process or basic material. An example of this is the production of salt. Salt is the largest of the basic chemical materials produced from a tonnage standpoint, and it is the basic raw material for many other chemical products. As mentioned previously, it is derived in three ways (i.e., from wells, by mining, and from the evaporation of seawater).

The corrosion involved wherever salt is found is severe, as it easily pervades all processing equipment. The largest equipment involved is handling equipment (e.g., conveyors, pumps, piping, and transportation equipment). Figure 19.13 shows a salt conveyor coated with an IOZ coating. Such equipment accumulates salt dust and crystals in many inaccessible areas, so that without a thoroughly applied and fully resistant coating, corrosion would be severe.

Salt is usually handled in the form of rock salt, which invariably contains a high quantity of moisture so that wherever the salt accumulates, an area of serious corrosion results. Not only does corrosion take place rapidly, but when the surface is blasted for application of coatings, there is sufficient chloride remaining on the surface so that coating failure may be rapid as well.

A thorough surface preparation is important for any coating that is to be applied. Unless chloride levels on the contaminated steel are reduced to less than 50 $\mu g/cm^2$ atmospheric exposures and 7 $\mu g/cm^2$ for immersion exposures, failure of the newly applied coating can be predicted. However, the one material that has helped to overcome most of the salt and chloride corrosion problems is IOZ coatings, particularly the water-based IOZs that tolerate chlorides better than others. They have been used alone and in combination with topcoats to provide corrosion resistance to all types of conveyors and handling equipment, as well as an interior coating for salt barges. In the latter case, it must protect against abrasion from the crystalline salt as well as from corrosion.

One large salt operation is located at Gurerro-Negro in Baja, California and is an extensive seawater evaporation project. Most of the equipment involved has been coated with IOZ and high-build vinyls, all applied over a sandblasted surface. The weather there is warm and humid and the above coating combination has given excellent corrosion protection over a period of several years. Not only is there extensive salt handling equipment at the plant, there are several barges and additional handling and loading equipment on Cedros Island, which is a few miles at sea from the evaporation lagoon. This is the area where the very large salt-handling ships load and transport the salt to Japan. These ships are about the size of a medium-sized super tanker, with complex conveyors for loading and unloading salt. These are also protected with IOZ and vinyl or epoxy topcoats. Many salt barges are coated on the interior with zinc and polyamine epoxy topcoats that provide a tough, abrasion-resistant, as well as a corrosion-resistant, coating.

Caustic and Chlorine

The production of caustic soda and chlorine must be considered together since they are primarily produced in the same process by the electrolysis of salt or salt solutions. They are often produced in captive plants, although the majority is produced in relatively large production units that are close to either a source of salt or a low-cost power supply.

The process is a relatively simple one of breaking down the salt molecule into a two-component part, chlorine and sodium, by electrolysis. In one process, molten NaCl is used and the electrolysis produces chlorine gas and sodium as a metal. In another process, mercury is used as the cathode. Chlorine gas goes off at the anode and the metallic sodium dissolved in the mercury amalgam is reacted with pure water, and liquid sodium hydroxide (NaOH) is produced. When the sodium is dissolved out of the mercury, the mercury goes back into the process again. Approximately 45% of all of the salt produced in the United States is used for the manufacture of caustic soda and chlorine. Both products are produced worldwide by essentially the same process.

The chlorine, once produced, goes into a myriad of other industries and is used either as an intermediate or directly, as in the sanitation industry for the purification of water or sewage and in disinfecting swimming pools. Thus, it can be seen that the production of caustic and chloride involves a basic process on which many industries throughout the world depend.

Corrosion in caustic soda chlorine plants can be quite severe. The concentrated caustic soda disintegrates any oil-containing coating, while the chlorine gas is a difficult material from a corrosion standpoint, readily forming ferric chloride ($FeCl_3$). The corrosion problems are approximately the same, irrespective of the processes used to develop the two materials, and high-performance coatings are needed to provide adequate protection. All steel on the interior of such plants requires maximum protection, since even small quantities of chlorine will cause corrosion problems on any bare steel.

Floors, however, are the primary problem, due to the spillage and drip of chlorinated alkaline brine. Epoxy floor toppings have done a good job of protecting floor areas around and under the caustic–chlorine cells. Caustic–chlorine plants are often two-level structures, so that a high-performance floor topping is required to prevent seepage and corrosion from the second level. Coating systems used for structural steel must have excellent resistance to the highly reactive chlorine gas.

One of the most serious corrosion problems, particularly with the flowing mercury cells, involves the spent NaCl solution, which goes through the cells, and from which some of the NaCl has been removed by the electrolysis process. As the NaCl solution flows across the mercury, some chlorine is dissolved in the salt solution with the formation of hypochlorite (ClO). This waste NaCl solution is an extremely corrosive product, and it may be recycled in the process by the addition of more NaCl, so that the solution circulates continually through the plant. The storage tanks containing this material require the best lining material available, usually a heavy inert sheet lining such as plasticized vinyl chloride or oxidation-resistant synthetic rubber.

Fertilizer

The production of fertilizer is another extensive segment of the industry. One of the primary processes involved is the formation of useable phosphates from the natural phosphate rock. Phosphoric acid (H_3PO_4) is generally the first byproduct and is produced from phosphate rock in two ways: (1) the wet process, which uses H_2SO_4 to dissolve the rock, and (2) the dry process, which produces the elemental phosphorous through the use of an electric furnace. Very pure H_3PO_4 is produced by the latter method. Agricultural grade acid is produced by the wet process, which accounts for approximately 80% of all the H_3PO_4 produced. Fifty percent of the H_2SO_4 that is produced is used in the production of H_3PO_4. This combination of acids creates highly corrosive conditions, so that all areas of these plants require high-performance coatings.

The primary use for H_3PO_4 is in fertilizer. This may be in the form of calcium phosphate [$Ca_3(PO_4)_2$] (which is the super phosphate in fertilizer terms), ammonium phosphate [$(NH_4)_3PO_4$] (which is a crystalline chemical), or as crude H_3PO_4.

Even the warehouses storing phosphate fertilizers require good coatings. Super phosphate is made merely by the use of hot H_3PO_4 on limestone or similar rock, which is then allowed to digest in large buildings. The super phosphate dust is corrosive and all of the structural steel, including the large conveyors, require good protection. A base coat of IOZ followed by high-build vinyl or epoxy coatings has given good results.

All of the high-performance coatings have been used in connection with the production of phosphate fertilizers. There are many plants located in the phosphate sand country of Florida as well as large installations in Mexico where high-performance coatings have been used for five to 10 years.

Another fertilizer process is one that oxidizes the nitrogen in air to form ammonia (NH_3) and nitric acid (HNO_3). This is generally a high-temperature operation using steam, natural gas, and air. The majority of such plants are similar to any other chemical plant, with the structural steel surfaces subject to weather and local industrial conditions. There may be some HNO_3 and nitrous oxide (N_2O) fumes present, which can aggravate corrosion.

Ammonium nitrate [$(NH_4)(NO_3)$] is one of the end products of such plants. This is a crystalline material, with some tendency to absorb moisture, and it can break down to NH_3 and HNO_3. Another end product is calcium nitrate [$Ca(NO_3)_2$], which is also hygroscopic. Dusts or other accumulations of these products can create corrosive conditions. High-performance coatings have proven entirely satisfactory for many areas in such plants.

Sulfur

Sulfur is produced in several ways: mining natural sulfur, oxidation of hydrogen sulfide (H_2S), and the Frasch process. Seventy-four percent of the native sulfur is produced by the Frasch process, which consists of drilling a well into a sulfur dome and injecting steam and compressed air into the structure. The steam melts the sulfur, with the compressed air blowing the molten sulfur to the surface through a pipe, which is inside of the steam injection pipe. Sulfur arrives at the surface in a molten state and is piped into cooling areas where it solidifies. The combination of sulfur, compressed air, and steam results in a highly corrosive operation. However, the corrosion is primarily internal, and therefore does not involve exterior coatings.

Sulfur as an element is not necessarily corrosive; however, when oxidized, it becomes extremely corrosive. Many of the sulfur operations are also located in high humidity and marine areas, so that most of the structures require high-performance coatings. IOZ, followed by either vinyls or epoxies, does very well in this instance. However, the process piping is usually at temperatures above the capability of organic coatings. One of the best-known natural sulfur areas is the Freeport sulfur structure off Grand Isle, Louisiana. Post-cured IOZ was originally used on the structure and has provided many years of good protection in the marine exposure (Figure 19.14).

The other primary method of sulfur production is by the oxidation of H_2S, primarily extracted from natural gas. In this case, the sulfur must be removed for the gas to be useable so that sulfur becomes a byproduct of natural gas production. There are a number of units throughout the United States, as well as in other areas of the world, where H_2S is a part of the natural gas produced. Mex-

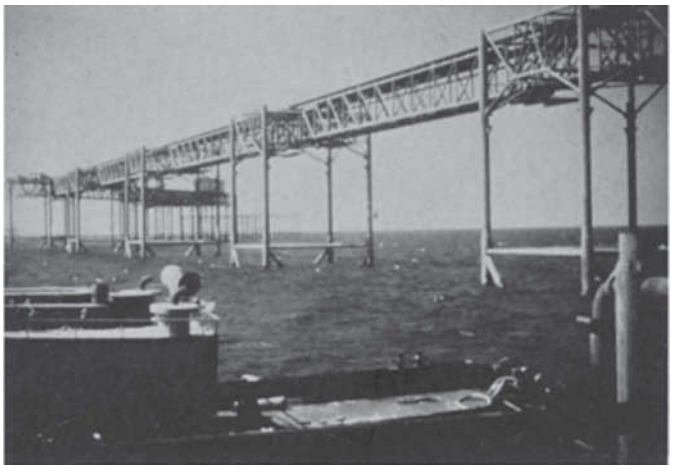


FIGURE 19.14: A section of an offshore sulfur structure that acts as a production working platform as well as a base for steam, air, and sulfur piping.

ico has several large units in the fields located in southeastern Mexico. Since H_2S is a difficult and corrosive material, all of the equipment and piping involved in the production and separation of H_2S from natural gas can be seriously corroded. Figure 19.15 shows the type of corrosion that is possible even on the exterior of unprotected equipment where H_2S is involved.

The production of H_2SO_4 is a process that varies from plant to plant. However, much of the acid is produced either from H_2S extracted from natural gas or from elemental sulfur, which is burned to sulfur dioxide (SO_2). Since either of these processes is corrosive, most plants are protected by high-performance coatings wherever temperatures allow their use. While much of the processing equipment is subjected to high temperatures, high-performance coatings protect most of the structural steel surrounding such equipment.

Leaks and spills are always a problem in acid plants. The production of H_2SO_4 is particularly difficult because of the highly oxidizing character of the concentrated acid. Where spills or leaks are possible, such as in the areas of pumps, acid-proof brick floors are installed, using either furan or silicate cements as a mortar for the brick. These are used on pump bases, floors, trenches, and similar areas throughout the plant (Figure 19.16). Extreme corrosion is possible in many areas, and the best possible protection is required for both steel and concrete surfaces.

The production of hydrochloric acid (HCl) creates extremely corrosive conditions, since chloride is in acid form. Much of the HCl is produced as a byproduct from other chemical reactions and is therefore part of another chemical system. Sixty five percent of the HCl plants are captive, where the acid is used in the formation of other chemicals. About 30% of the HCl is used in steel pickling.

HCl is a volatile acid, which means that it vaporizes easily. The vapor or fumes are extremely corrosive, forming iron chlorides wherever steel is exposed to the fumes. Because of the volatility, coatings must be highly resistant to the acid and to the fumes, preventing their penetration to the steel substrate. This not only means that the coating must be resistant, but it must be applied in the best possible manner as well. Both heavy-bodied vinyl and epoxy coatings have provided good protection to structural steel in fume areas. Lesser coatings would not be suggested for this service.



FIGURE 19.15: H_2S corrosion of the exterior of a crude oil production tank. Corrosion of the interior is often even more severe.

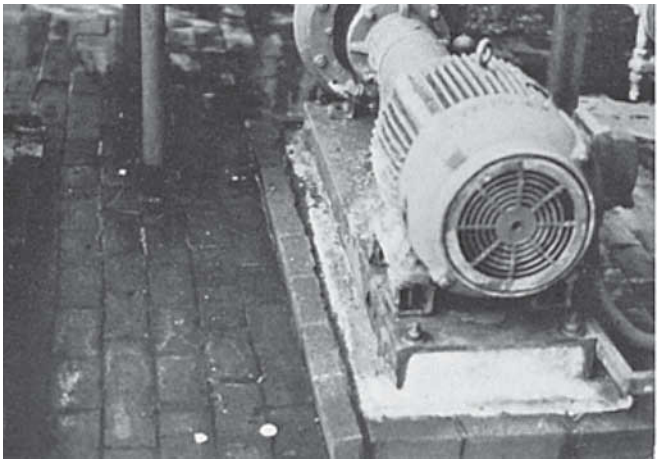


FIGURE 19.16: A typical pump installation handling acid solutions, showing the use of acid proof brick and dark furan mortar.

There are several industries where HCl corrosion is a serious problem. The production of titanium dioxide (TiO_2) is one of these. HCl is used to extract the titanium from the ore, titanium tetrachloride ($TiCl_4$) being one of the intermediate products. This reacts very readily with any moisture, recreating HCl, so that these processing plants require the best in high-performance coatings in order to provide the protection required for structural steel in the immediate process area, as well as wherever HCl fumes may contact equipment or structures. These are primarily fume conditions and are very similar to those existing in a HCl plant.

The HCl pickling of steel is another critical area from a coating standpoint. All areas in and around such a process require high-performance coatings for proper protection of the substrate. Heavy-bodied vinyl and epoxy coatings have provided good service in these areas when properly applied.

The production of silicones is also a potentially corrosive process, since silicone tetrachloride ($SiCl_4$) is one of the intermediate chemicals. This decomposes into silica and HCl, creating conditions within the plant and surrounding area similar to those of a HCl



FIGURE 19.17: A typical organic chemical plant, showing structural steel reactors, stacks, piping, tanks, and similar surfaces that require good protection.



FIGURE 19.18: A typical oil refinery unit with distillation towers and stack coated with post-cured IOZ.

plant. Heavy-bodied vinyl and epoxy coatings have provided good service in plants of this type.

The production of chlorine bleach is also a corrosive process, which involves the reaction of NaOH with gaseous chlorine. The resulting sodium hypochlorite (NaClO) solution or calcium hypochlorite [$Ca(ClO)_2$], if the chlorine is reacted with calcium hydroxide [$Ca(OH)_2$], is an extremely corrosive material in itself. The reason for its effectiveness as a bleaching agent is that it breaks down into oxygen and NaCl. The corrosive elements then are chloride, oxygen, and NaCl. The solution is unstable and tends to disintegrate into oxygen and NaCl with time and when in contact with many oxidizable materials.

Bleach plants are subject to heavy corrosion, both from fumes and wherever the liquid may be in contact with metal. High-performance coatings have been used in bleach plants for many years and, where they have been properly applied, have effectively protected the structural steel, tank exteriors, and equipment from corrosion. Many of these plants are relatively small and much of the bleach is produced on a local basis. Plants that use bleach in their processes, such as paper plants, may produce their own as a captive operation.

All of the previously discussed plants are candidates for chemical-resistant coatings. The ones that are most critical and have the most corrosion are those that involve halogen compounds. These are fluorine and fluorides, chlorine, HCl, hypochlorites, chlorides, bromine and bromides, and iodine and iodides. Wherever these materials are found, either in inorganic or organic processes, high-performance coatings are required for the protection of steel and concrete surfaces.

Organic Chemical Plants

Organic chemical plants are usually larger than most of the inorganic chemical plants and the processes they involve are quite different (Figure 19.17). The corrosion conditions in organic chemical plants range from innocuous to extremely severe, depending on the products produced. Acetic acid and derivative products can be highly corrosive. Plants which use acetic anhydride and other anhydrides can be difficult from a coating standpoint, since acetic acid is both a strong organic acid as well as a good solvent for many other organic materials. Thus, many coatings are penetrated by the solvent action and the acid initiates corrosion as it contacts the substrate. Strongly cross-linked coatings are best for the above circumstances.

On the other hand, the production of other solvent materials (e.g., alcohols) can be relatively noncorrosive. Once they are distilled and in their final form, many solvents are essentially noncorrosive and are handled much like gasoline or other petroleum products. In this case, the protective coating required is determined by the local atmospheric conditions, with humid, marine, and industrial environments requiring the best protection, while rural environments are satisfactorily maintained with less protection. An IOZ base coat, followed by vinyl, acrylic, or polyurethane topcoats could provide years of corrosion protection under the most severe conditions. Any proposed coating system must be tested and proven under the specific set of chemical reactions required during production.

Refineries

Refineries are included in the organic category since they produce most of the feedstock for the other organic chemical plants. While a typical refinery unit (Figure 19.18) appears to be similar in structure to most other chemical plants, hot surfaces, some of which exceed the limits of organic protective coatings, are more characteristic of refineries.

Refineries begin with crude oil as it comes from the production fields and break it down in continuous operating plants (making use of high temperatures, high pressures, and catalysts) into many different organic, primarily liquid, products. These range from Bunker C oil to diesel oil, gasoline, jet fuel, solvents, waxes, and asphalt. Many of the processes are self-contained so that the only exposed product is the beginning liquid (crude oil) and the end products (gasoline, solvents). Thus, refinery equipment is primarily composed of tankage, pipelines, pumps, reactors, distillation towers, and structural supports, which require exterior coatings to protect the structure, piping, and equipment from the atmosphere of the particular refinery. Refineries that are located near the coast and those located in highly humid or industrial areas usually require high-performance coatings (i.e., IOZ, vinyls, epoxies, or urethanes).

Areas of high temperature are a problem for organic coatings. However, IOZ coatings have given excellent protection at temperatures of 600 °F (315 °C) or somewhat higher (Figure 19.19). Where combined with aluminum-pigmented silicone topcoats for 800 °F (426 °C) to 1,000 °F (538 °C) service, such coating systems have given good results. IOZs modified with polysiloxanes have increased the temperature resistance to more than 1,200 °F (649 °C). IOZ base coats and inorganic topcoats have given very good service at elevated temperatures.

Inorganic topcoats are often based on hydrolyzed ethyl silicate combined with nonmetallic but reactive pigments, which create a hard silicate base product with excellent weather and temperature resistance.

Refinery storage tank interiors, since they usually hold products that are at ambient temperatures and atmospheric pressure, may



FIGURE 19.19: A refinery stack coated with post-cured IOZ, showing no corrosion after several years of exposure to humid marine conditions.

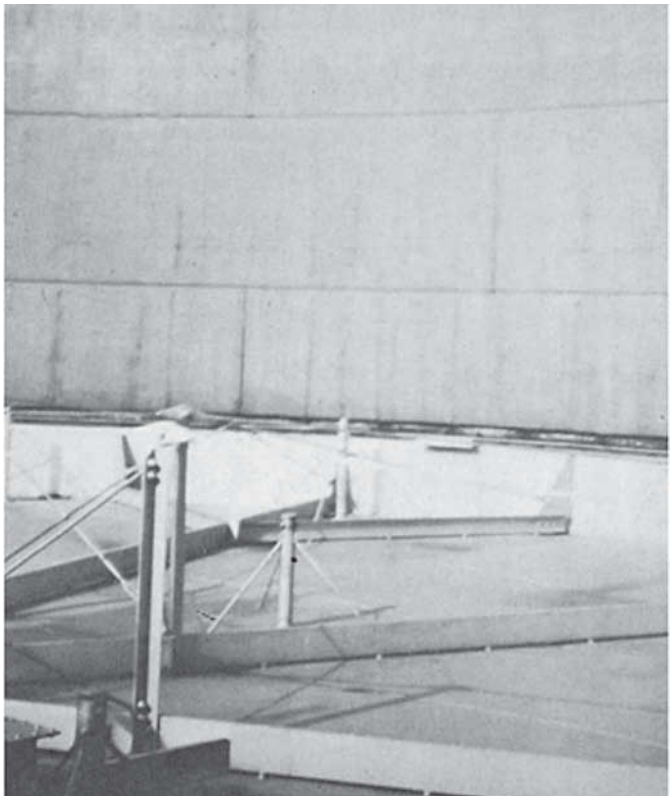


FIGURE 19.20: The interior of a typical floating roof tank coated with post-cured IOZ after storing gasoline for several years.

require coating both to prevent corrosion of the metal and protect the product from contamination. Severe corrosion can take place in closed roof as well as floating roof tanks, depending on the nature of the environment (Figure 19.20). One of the first applications of IOZ that was tried in the United States involved floating roof tank walls that were completely pitted with ¼-in (6.4-mm) pits. While the first trial was not perfect, it prevented additional corrosion for several years.

Refinery products such as gasoline, lubricating oil, and most fuel oils and jet fuels are noncorrosive in themselves. However, the combination of these materials with water, seawater, or marine or industrial atmospheres can be extremely corrosive. Thus, particularly where product contamination is also a factor, many refinery tanks are coated with IOZ by itself; overcoated with organic coatings such as vinyls, epoxies, or urethanes; or coated using a good solvent-resistant organic system without the IOZ base coat.



FIGURE 19.21: A petroleum production tank coated on the interior with coal tar epoxy (16 mils) and on the exterior with three coats of epoxy polyamide.

Tank bottoms usually pose a problem that requires use of heavy-duty materials such as glass-reinforced polyester or epoxy, and coal tar or coal tar epoxy. Tanks usually have a water layer in the bottom, which contains dissolved product materials. They also may contain a heavy layer of basic sediment, particularly in crude storage tanks. If H_2S is present, scale from the tank top can fall to the bottom and create a severe pitting problem. The heavy-duty linings (e.g., reinforced polyesters and epoxies) are required not only because of the corrosion, but also due to the abrasion inherent in flow areas of tank bottoms, particularly when basic sediment and other deposits must be removed.

The production of petroleum, while it differs from the refining process, creates similar problems, particularly in the area of tankage. While tank bottom problems are similar, they may be even more severe due to the salt water that is mixed with the produced oil. The accumulation of basic sediment also can be greater, and much of the oil comes directly from the well at elevated temperatures. Where H_2S is present, excessive corrosion of tank tops can occur, which in turn creates bottom corrosion as the iron sulfide (FeS) drops to the bottom. Petroleum wax and gypsum deposits can also aggravate the corrosion in oil production tanks.

Nevertheless, the same high-performance coatings have provided good protection. Coal tar epoxy coatings have given many years of good service on production tanks in the H2S crude areas of Mexico (Figure 19.21). Figure 19.22 shows the vent on a similar storage tank in the same production area completely corroded in two years from H_2S. The coal tar epoxy on the interior of the tank gave excellent protection over the same period of time.

The production of natural gas usually accompanies petroleum production. The gas must be separated from oil and water and com-

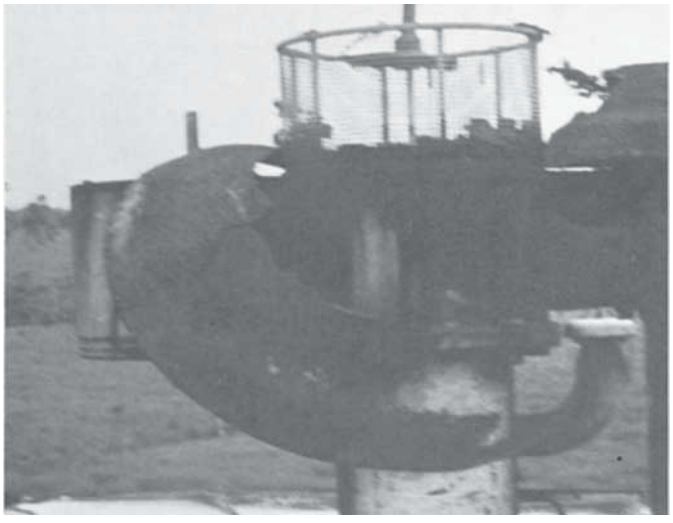


FIGURE 19.22: A production tank vent completely corroded from H_2S in two years.



FIGURE 19.23: Metal gas separators at the production site exposed to a tropical atmosphere and high quantities of H_2S protected by an IOZ base coat with epoxy topcoat.

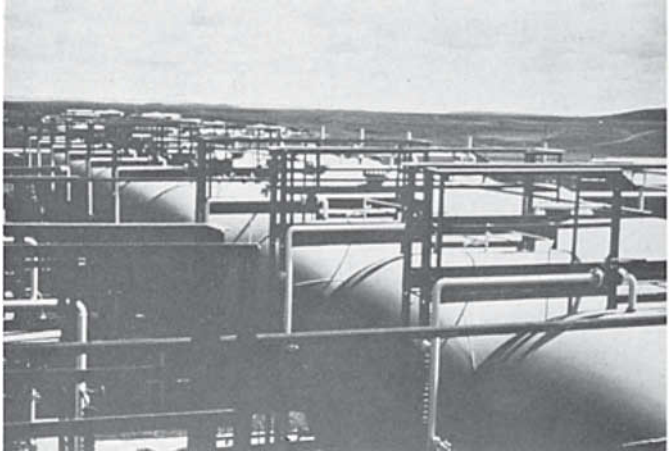


FIGURE 19.24: High-pressure gas holders at Tierra Del Fuego protected with one coat of IOZ.

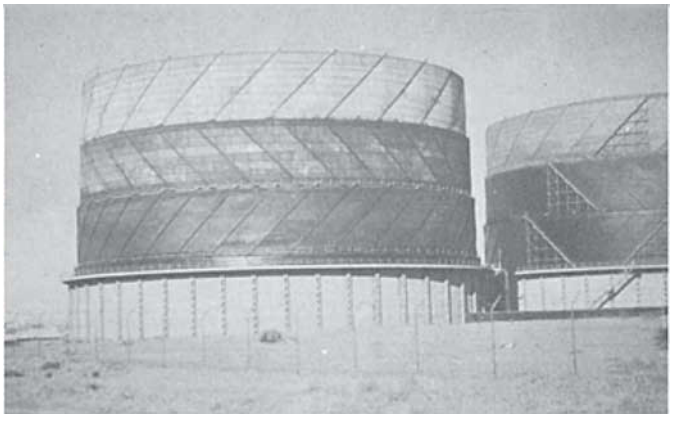


FIGURE 19.26: An expandable gas holder that usually is at a distribution point for natural gas protected by one coat of IOZ, even in the water seal.

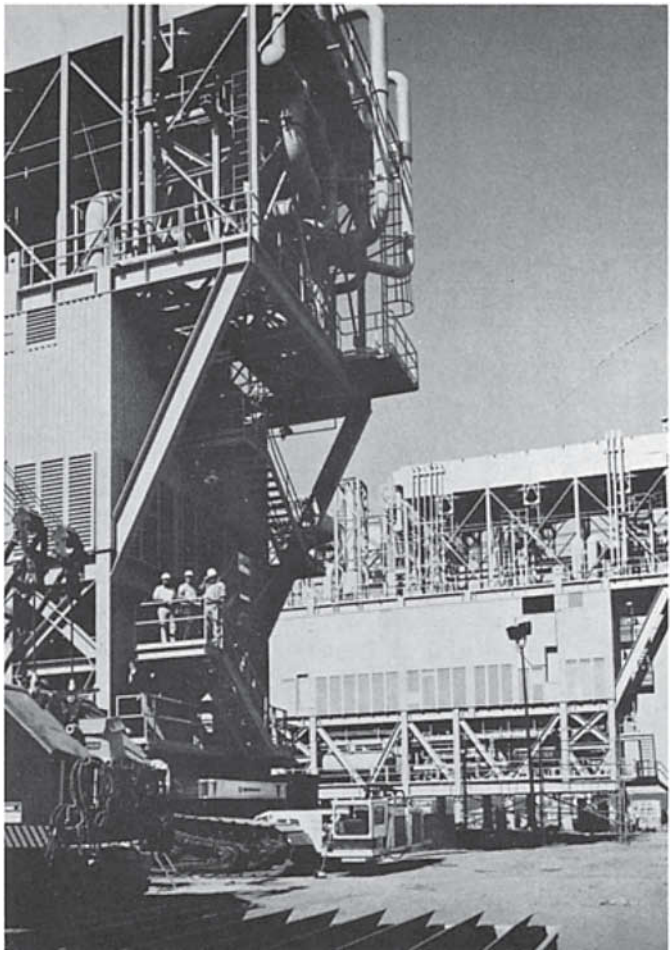


FIGURE 19.25: Gas compression units for use on offshore platforms in the Gulf of Mexico protected with an IOZ coating with epoxy topcoats.

pressed for pipeline transportation. H_2S and other gas impurities must be removed and the gas recompressed for long-line transportation. All of these operations require better than average coatings, depending on the location of the production field and the H_2S concentration in the natural gas.

The transportation of natural gas is most often handled by pipe, and high-quality coatings are required on the exterior to prevent corrosion and blowout due to the high-pressure gas. Hot-applied coal tar reinforced with fiberglass wraps, vinyl tape with a butyl rub-

ber adhesive, and fusion-bonded epoxy powder coatings have been used. The greatest mileage of gas piping has been coated with glass- reinforced coal tar in multiple layers. Figures 19.23 through 19.27 illustrate coatings uses in natural gas production and distribution.

The interior of gas transmission piping also must be lined with high-performance coatings. The problem in this case is one of friction from the flow of gas through the line. There is little corrosion on the pipe interior, unless the gas contains considerable H_2S, since the gas is "bone dry." Any water vapor is just that many more cubic feet of product to force through the pipe. The lining material is a specialized, thin film catalyzed amine epoxy applied in one coat, and it reduces the friction of the gas in the pipe to the degree that makes the lining both practical and economical.



FIGURE 19.27: Gas transmission piping coated with hot-applied coal tar pitch and glass reinforcing. The white color is whitewash for heat protection for the coal tar. Source: Ameron Corp., Monterey Park, CA.

Other Chemicals

In addition to petroleum and refinery products, there are at least 40 organic chemicals that are produced in excess of 1 billion lb/year. Ethylene is produced in by far the largest volume, and it reaches 20 billion lb/year. About 40th on the list is carbon tetrachloride (CCl_4) at 1 billion lb/year. Other large-volume materials are propane, benzene, ethylene dichloride, propylene, toluene, ethane, methanol, formaldehyde, vinyl chloride, butadiene, ethyl alcohol, and glycerine.

A characteristic of the organic chemical series, like the refinery products, is that many, in themselves, are not very corrosive, since many of them are produced and handled as gases in a completely closed atmosphere. Any fumes that exist come from leakage in valves or piping or from stacks. The high-volume products that can be most corrosive are those organic compounds containing halogen atoms (e.g., fluorine, chlorine, bromine, and iodine). The end products may be ethylene dichloride or any of the other organic chlorides, including vinyl chloride. There is also ethylene dibromide and other organic bromides. There are also a number of organic iodides. The production of all of these materials involves corrosive conditions. The organic chemical plants are primarily openwork structures where the structures, processing units, piping, and storage tanks are all subject to the atmosphere and weather. Many of these plants are located in areas of high humidity and are subject to atmospheric fumes from other processes and other plants in the area. These organic chemical plants usually have extensive tank farms and miles of piping and pipe racks. All of these installations are costly to maintain since, in many instances, millions of square feet of surface need to be coated. High-performance coatings are the only practical answer to the preservation and protection of these structures. The most successful coating systems, and the ones that have been used extensively throughout the world, are base coats of IOZ followed by topcoats such vinyls, epoxies, urethanes, chlorinated rubbers, or other chemical-resistant coatings that may best meet the local corrosive conditions.

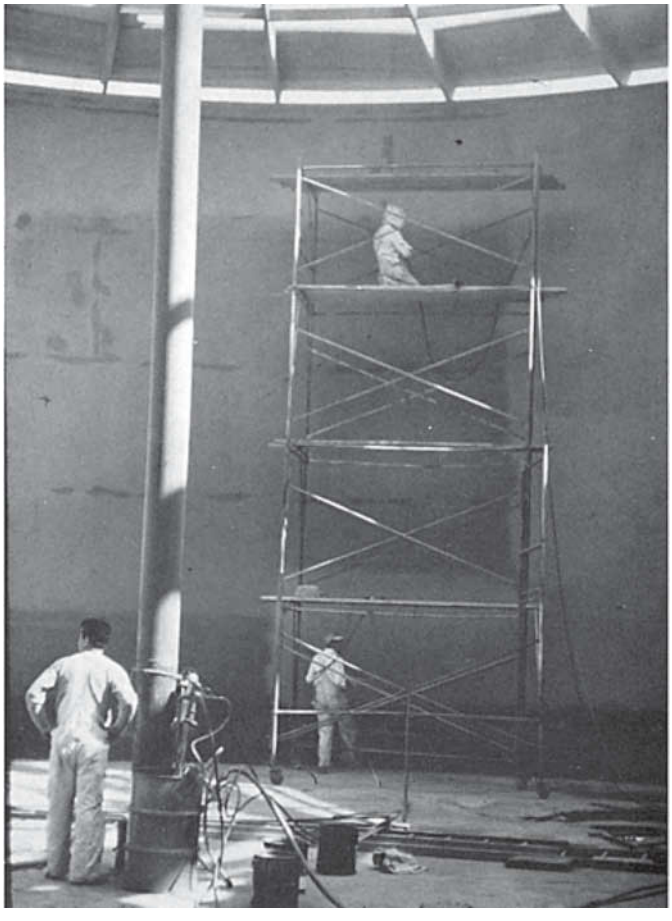


FIGURE 19.28: The interior of an industrial alcohol tank being lined with a vinyl coating.

Tankage is a critical area involved in the production of organic chemicals. While there are many solid organics, there are also many liquid products, such as ketones, various aromatic materials, alcohols, aldehydes, esters, and chlorinated solvents. Many of the containers for these materials require coating for the protection of the organic liquid or to prevent the tanks from deterioration. There are many products used for such purposes, including vinyls, amine-cured epoxies, polyurethanes, modified epoxies (e.g., phenolic epoxies, novolac epoxies, medium-temperature cured epoxies, and high-bake epoxies), phenolics, and IOZ coatings. The coating depends on the organic product and its use.

Figure 19.28 shows the interior of an industrial alcohol tank being lined with a vinyl coating system. Where ethyl alcohol is to be used as a food or is not contaminated or denatured with strong solvent, vinyl chloride-acetate copolymers make good linings, since they are insoluble as well as non-contaminating to alcohols.

Pulp and Paper

Pulp and paper production is considered part of the chemical industry because many of the problem areas are similar (e.g., structural steel, tank exteriors, weather exposure, quantities of water, chemical fumes, and fallout). It is a large industry represented by over 1,000 individual plants, and consists of an inherently very corrosive process. To illustrate this, consider that there was about 103 to 104 million tons of paper produced in the western world in 1971. The cost attributed to corrosion throughout the plants producing this amount of paper amounted to 320 million dollars for the same year. In other words, over $3/ton of paper produced in 1971 was directly attributed to corrosion.

There are basically two types of areas to consider in a paper plant. Atmospheric areas are areas of the plant where coatings are subject to atmospheric corrosion, humidity, and some slop and spillage of water, usually resulting in wet and dry conditions. Immersion areas consist of tank and equipment interiors, which are subject to continuous immersion in water, contaminated water, chemicals, and so on.

Atmospheric

The entire paper plant, including all structural steel, tank exteriors, and other areas, is subject to atmospheric corrosion. A paper plant is subject to more severe corrosion than many other plants due to the chemicals involved in the manufacture of paper and the extremely large quantities of water that are required to wash the chemicals out of the pulp.

The chemicals involved are generally aggressive ones, particularly those used in the bleach area (e.g., chlorine, sodium chlorate, chlorine dioxide [ClO_2], and NaClO). Many paper plants actually manufacture these materials for their own use so that essentially there is an internal chemical plant producing the extremely corrosive chlorine-containing oxidizing chemicals, as well as using the chemicals in the pulp bleaching operation. The bleach manufacture and the pulp bleaching operation create a fume problem, with chlorine, NaCl, and ClO_2 reacting with any exposed steel. Corrosion produced by chlorine extends into the pulp washing areas where extremely wet conditions exist. This compounds the severity of corrosion on equipment, piping, pumps, pump bases, and structural steel.

Because of the existence of chlorine, these areas require excellent surface preparation and well-applied high-performance coatings. For maximum protection, the coatings should be applied as the plant is built, using an IOZ base coat, followed by heavy-duty coatings such as heavy bodied vinyls, epoxies, urethanes, or the most resistant chlorinated rubbers. This area of a paper mill cannot tolerate poor surface preparation, poor application, or coatings that are less than the best.

The primary recovery area is another area where corrosion is a problem. It consists of large furnaces that burn the black liquor from the primary cooking operation in order to recover the basic chemicals involved (i.e., NaOH, sodium sulfide [Na_2S], and sodium sulfate [Na_2SO_4]). Much of the difficulty in this area comes from the fly ash from the burning process. This type of fallout can occur throughout the paper plant, but is heaviest in the local recovery area. The fly ash consists of dry corrosive dusts, usually quite alkaline, that contain all of the previously mentioned chemicals, including carbon and various chlorides. Wherever these dusts accumulate, and then collect moisture from rain or high humidity, corrosion is severe.

Slaked lime also is used as part of the recovery process, which results in large quantities of calcium carbonate ($CaCO_3$) and calcium sulfate ($CaSO_4$). These materials are recycled and are calcined in the recovery area, creating large quantities of calcium oxide (CaO) dust that is highly alkaline. Wherever this accumulates and collects moisture, corrosive conditions exist.

The third area that creates a serious atmospheric problem is the blow down area. This is where the pulp from the primary cooker is blown down into either a blow pit or blow tank, with the resulting steam spreading throughout that area of the plant. Steam carries many different types of organic solids, but also contains NaOH and Na_2S. NaOH is extremely alkaline, while the Na_2S creates conditions of sulfide corrosion throughout the plant. Sulfides and iron react rapidly, followed by oxidation from moist air, with regeneration of the sulfide as H_2S. Thus, high-performance coatings are essential in these primary chemical areas. IOZ base coats, followed by vinyl, epoxy, or possibly urethane topcoats, have been proven under these conditions. In the actual paper-making area, water and humidity are the primary corrosive agents. The large amount of water and steam coming from the machines can create serious corrosion problems, which cannot be tolerated because of the possible contamination of the paper. A drop of rusty condensation or a bit of scale from a rusty beam will cause the paper to be rejected. With the plants on 24-hour, seven-day operation, rejects and stoppages are costly. Therefore, tightly adherent water-resistant coatings (e.g., vinyls and epoxies) are required. Coating these areas once the plant has been in use is extremely difficult.

The above conditions primarily exist in kraft or sulfate-type paper mills. In the sulfite-type paper mill, the corrosive conditions are similar, but generally even worse due to the acidic type of digesting liquor they use. The sulfide cooking liquor is made in the paper mill by burning sulfur to form SO_2. This is then reacted with calcium and magnesium carbonate, and calcium or magnesium bisulfite [$Mg(HSO_3)_2$] is obtained. The fumes from the sulfite manufacture and from the blow pits create corrosive conditions wherever they are in contact with steel. The sulfite liquors are also corrosive to concrete.

Under almost any atmospheric condition, the use of an IOZ coating underneath an organic coating will extend the life of the topcoat by several times. This is true even when the atmospheric corrosion is caused by an acidic or alkaline condition. This is because the IOZ coating ties chemically to the steel surface so that there is no undercutting of the organic film, as there would be if it were applied directly to the steel surface. This is particularly true where sulfides are present, since they are particularly insidious from a corrosion standpoint. Inorganic base coats have more than proven their worth in paper mills.

One of the more recent problems encountered in paper mills involves environmental controls, which have necessitated additional ducts, scrubbers, and both air and water treatment equipment. Many of these ducts and scrubbers are made from reinforced plastics, as is the pipe used for water, chemical, and pulp transfer. Reinforced plastics aid in overcoming the corrosion problem. On the other hand, all structural supports for the reinforced plastic equipment and all adjacent buildings require the best corrosion protection that coatings can provide.

A paper plant that is properly coated during its initial construction has taken a major step in reducing corrosion and maintenance. In many areas of a paper mill, particularly from a maintenance standpoint, abrasive blasting or an equivalent type of surface preparation may not be possible, since abrasive media contamination in any of the machine areas or pulping processes could be extremely damaging. Therefore, much of the maintenance in a paper mill must be done by power sanding, power brushing, or the use of needle

guns and similar means. Also, much of this work must be done during an annual overhaul period when the entire plant is down. Thus, equipment and constraints, plus continually damp conditions, make coating repair difficult in a paper mill. Because of these conditions, surface-tolerant epoxies have become the coating of choice, at least for prime coats due to their unique ability to penetrate and bond to less than perfectly cleaned surfaces.

During maintenance, where relatively small areas of bare metal are involved, it is recommended that these areas be primed using a surface-tolerant epoxy primer over the bare steel areas and feathering it out over the old coating. While not as effective from an undercutting standpoint as inorganic or organic zinc coatings, the ability to penetrate residual corrosion and cure in moist conditions is more important. The proper topcoats can then be applied.

Where coatings must be applied under difficult maintenance conditions, there is an important step in the application process, following surface preparation, which can make the difference between success and failure. Once the surface has been thoroughly ground or prepared with a power tool or other nonabrasive media to remove all of the old coating and as much of the corrosion product as possible, it is recommended that, if possible, these surfaces be heated by the use of large propane torches to a temperature well above ambient. The temperature should not be so great as to damage the existing coating, but should be sufficiently high to drive all moisture out of the crevices, pits, corners, and similar areas. At the same time that the moisture is being driven out, any sulfides that may be present are also oxidized and the resulting H_2S driven off. If this is not possible, the use of 100% solids, non-pigmented penetrating epoxy sealer is recommended to isolate the residual corrosion and contaminants from the following coating system.

Once the heating is carried out and the surface is dry and hot to the touch, the primer should be brushed on the surface. It should be thoroughly brushed into all pits, crevices, and similar areas to ensure full coverage. The heat from the substrate will lower the viscosity of the primer, so that with brushing, it will wet-out and penetrate much more thoroughly and quickly than on a cold application. Heat also has the effect of drying the primer rapidly so that topcoats can be applied rapidly as well. This, again, is insurance against intercoat contamination, which is a constant problem in paper mill applications.

Immersion

Use of coatings in immersion areas in a paper mill should be approached with caution. These areas combine strong chemicals with relatively high temperatures, so that, for most of these areas, spray-applied, relatively thin coatings are not adequate.

Many types of linings have been tried under these conditions, and most of them have met with little success. Thus, wherever linings are required, the problem should be thoroughly studied, analyzing all corrosive conditions, temperatures, concentrations, and times involved before attempting any solution. Most paper plants use ducts and vessels of stainless steel (SS) where internal corrosion is a problem. Where even these are not practical, as in digesters, blow-down pits, and bleaching operations, the most successful and longest lasting answer is found in the use of membranes and brick or tile linings using furan or polyester-type cements. The primary materials involved are hard-burned red shale brick or tile, or carbon brick laid up with either furan or polyester cement. The furan may be used for most areas, except where oxidizing conditions are involved. Polyester cements are used where oxidizing bleaches are found. Such systems have been used for years in paper plants, and, where properly installed, have provided excellent resistance and service.

There are some areas where thin lining materials can be used. These are primarily for water, water treatment, and water reclamation clarifiers; settling basins; aeration tanks; and other standard water processing equipment. Vinyls, epoxies, and coal tar epoxies have provided the required protection.

The Mining Industry

The mining industry generally has not used high-performance coatings in the past. This is because copper, zinc, nickel, and other metals have been roasted or smelted and converted to metals by hot molten reduction processes. These smelters were similar to those used for steel production (i.e., massive steel or cast iron units that generally received no coating whatsoever). The mining of more complex and lower-grade ores has now become essential, and much of the dry processing of the ores is neither economical nor practical. This has resulted in the chemical processing of the lower-grade ores, often by acid leaching. In the case of nickel, it is also leached by an ammoniacal ammonium carbonate process. The refining may then be by precipitation or electrolysis. Of course, the wet processing of ores is much more corrosive than the dry process, and therefore high-performance coatings are needed in the plants to protect them against serious corrosion.

Copper, zinc, and uranium generally use a H_2SO_4 leach to extract the metal from the gangue or waste rock. This acid is relatively dilute, in the 5% to 15% range. In the case of copper, it is generally at ambient temperature. In the case of uranium, the temperature often is raised to 150 °F (65 °C), or slightly more during the processing. These acid solutions are extremely corrosive, and wherever they come in contact with either metal or concrete, rapid corrosion takes place. The solutions of copper and nickel are even more corrosive, since even a neutral solution of these salts will displace iron wherever the solution comes in contact with it.

There are also a number of other methods of leaching these ores. $FeCl_3$ is one method used for copper, as well as HNO_3 leaching. Ammoniacal ammonium carbonate is another leach that is used. The copper may be recovered from the pregnant solutions by electrowinning and solvent extraction. Irrespective of the leaching method used, the process involves corrosive solutions.

One quick test for copper in an ore is to dissolve it in almost any acid and then place a shiny nail in the liquid. If there is any copper in the solution, it will immediately precipitate out on the iron surface, creating a copper-red surface. In order for this to take place, an equivalent amount of iron goes into the solution. Therefore, any solution of copper or nickel can be quite corrosive to iron or steel.

This process is used in a practical way at most copper mines. The waste water from the mine is passed over a bed of scrap iron or steel, the copper precipitates, and the steel goes into solution. Thus, even small traces of copper can be removed. This is called cement copper, since it is a very fine paste. Many of the salts of copper, zinc, uranium, and nickel are acid salts. This means that when the copper, zinc, or other metal salts are put in solution, the solution is automatically on the acid side because these salts are a reaction of a relatively weak base, which would be the metal oxide and a strong acid such as sulfuric.

Taking this into consideration, wherever there is a liquid processed or wherever liquid exists in the refining of these metals, corrosion is inherently present. All concrete and steel surfaces thus require high-performance coatings to protect them against rapid disintegration.

One of the largest and most critical areas to be protected in all of the extraction processes is the leaching tanks. The early copper

leach tanks were lined with heavy asphalt linings. These were blocks of asphalt laid like tile or brick and fused together to form a lining. The lining on the bottom of the tanks was often several inches thick. Abrasion is one of the key factors here, because of both the dumping of the ore into the tanks and, more importantly, the removal of the insoluble gangue after all of the metal has been extracted.

In some of the uranium extraction processes, large rubber-lined steel tanks have been used. More recently, some of the larger copper-leaching facilities have been lined with plasticized vinyl sheet placed into the concrete structure as it was poured. The sheets of vinyl plastic are then heat welded to together to form a continuous membrane throughout the leaching tank. The physical attachment of the plastic sheet to the concrete through the use of tee extensions into the poured concrete structure is a decided ad- vantage over coatings or sheet applied with adhesive alone. Good service has resulted from the use of linings of this type.

In addition to the leach tanks, numerous flotation units, precipitators, concentrators, washers, clarifiers, and similar equipment are used, many of which combine both concrete and steel construction. Each requires a heavy-duty lining or coating. Throughout the processing of the solutions, all coatings and linings must be applied with extreme care, since any pinholes or holidays will cause rapid failure of the metal or concrete. In general, multiple-coat, heavy, thick coatings such as high-build epoxies are required, except in areas where rubber or plastic sheet linings are necessary.

Many pipelines for metal solutions or leaching liquid are lined using vinyl plastisol. This is due to the continued abrasion throughout the process, as well as the need for a thick, heavy lining to fully protect the underlying surface. Thick, heavy coatings or linings provide the safety factor that is required. Wherever concrete tanks or structures are part of the process equipment, plastic sheet linings are a good recommendation, as they are continuous, pinhole free, tough, and abrasion-resistant. Most importantly, they have the strength and extensibility to bridge the checks and small cracks that are always present in concrete.

In the case of liquid processed nickel, copper, or zinc, the final refining process is usually electrolytic. This is done by plating out the metal from the solution onto large electrodes, which may then be melted and cast into ingots or re-refined by the electrolytic process to obtain high purity metal. The electrolytic refining area is highly corrosive inasmuch as acid solutions are again used and temperatures of the electrolytic solutions are elevated (120 to 160 °F [49 to 71 °C]). For the most part, these processes take place in an enclosed building, which creates fume problems. In this case, high-performance coatings are a must for protecting structural steel.

Sheet lead has been used as a lining material for electrolytic cells. This is extremely costly from a material standpoint, as well as from the standpoint of labor used in lead burning and placement of the lead in the cells. The danger of elevated blood lead levels for the workers requires careful personal protective equipment and regular medical checkups. Nevertheless, as it was one of the secondary metals refined from the basic ores, it was readily available and resistant to the acid solutions. It had a serious drawback in that during the electrolytic process, part of the crude copper or zinc electrodes could fall and hit the bottom as they were gradually dissolved. If electrical contact between the electrode and the fallen piece was maintained, a hole was immediately burned through the lead. The cells in more recent installations have been lined with plasticized vinyl sheet. In this case, the burn-through does not occur since the heavy plastic liner acts as an insulating membrane.

Many auxiliary areas also exist, such as floors underneath equipment, tanks, and adjacent structural steel, which also require coatings. Inasmuch as the floors are subject to leakage and spills, heavy-duty abrasion-resistant coatings must be used. Troweled epoxy floor toppings are recommended. On the structural steel, IOZ and a vinyl or epoxy maintenance coating has proven to be satisfactory. In processing areas in cold climates where all processes are enclosed, humidity, steam, and fumes concentrate so that a high-performance coating system is required for all surfaces.

In many cases, mining operations are considered temporary, since the equipment, tankage, and structures will only be used for a limited period of time. However, where the ore bodies are large and years of production contemplated, the proper coatings, linings, and floor toppings are merely good insurance for a trouble-free operation for a number of years. Again, the cost of protection is a small part of the replacement value of costly equipment and structures.

Coal Mining

Coal mining is probably one of the largest segments of the mining industry. A study of the coal industry from a corrosion standpoint reveals three areas of concern.

1. The coal mine, which is the area where the coal is actually removed from the ground. It may be either an underground or a strip mine.
2. Coal preparation plants, which take the raw coal or the mine-run coal from the mine and prepare it for shipment and use.
3. Transportation of the mined coal by railroad car, barge, or slurry pipeline to the point of use.

An important conclusion in the study of coal mining from a corrosion standpoint was the fact that the corrosion problems found in the coal industry are not particularly sulfur oriented. The problems from sulfur in coal do not exist during the mining operation, but rather occur during the actual burning of the coal and oxidizing the sulfur in the coal to SO_2, which creates an acid condition that is a cause of both corrosion and air pollution.

The corrosion problem from the coal itself is due to the salt that is contained within the coal, primarily NaCl. The salt is extracted during the preparation of the coal, which is the operation where the coal is sized, washed, dried, and classified for use. The main corrosion problem, then, is found in the coal preparation plants.

The coal preparation process is primarily one of washing and classifying the coal into two grades: metallurgical and steam coal. Classifying the coal into sizes, and washing or cleaning the coal of debris such as rock, slate, sand and so forth, all involve water, which is used throughout the entire preparation process. The water is collected and reused so that the salt or NaCl content builds up to a rather substantial point. In the dusty part of the preparation plant, the same wash water is used periodically to wash the accumulated coal dust from the structure, thus spreading the salt through all parts of the plant area. The lower areas of the structure are constantly wet due to the preparation process and the washing of the dust from the plant structure. The resulting corrosion is similar to marine corrosion, with tubercles of rust forming on the structural steel wherever moisture tends to accumulate. Coal dust and coal sludge also accumulate in all types of hidden areas. When these are wet, the coal aggravates the corrosion since it is cathodic to steel.

Coal preparation plants are usually large aboveground structures, although they are considered part of the actual mining operation. Most mines have their own coal preparation plant, although there are some cases where two or more mines may combine production

and process it through one preparation plant. Coal preparation plants consist of a structure from six to 10 stories high, with a long conveyor raising the coal from the mine or ground level up to the top of the preparation plant. The preparation plant is primarily a structural steel structure covered with aluminized or galvanized corrugated sheet. The principal equipment involved in the coal preparation plant is belt-conveyors. Other equipment includes numerous vibrating screens that grade the coal to size, heavy media separators (where the coal is separated from the rock and slate), coal crushers, magnetic separators, dicer tables (a specific gravity separation by vibration), froth or foam separators, dewatering screens, centrifugal dryers, cyclone water clarifiers, in-plant conveyors and chutes, silos for the finished coal, and loading equipment.

The flow of the coal through the preparation unit starts from the mine stockpile on a long conveyor to the top of the plant. As the coal enters the plants, it goes over primary screening units, which separate the coal into various sizes. The heavy media separator is primarily water. Coal passes through the plant primarily by gravity from one level to another. Since water is used even at the highest levels, the plant is damp or wet throughout the processing building. The amount of water and dampness increases as the coal goes down from the top to the bottom of the plant, and all corrosion within the plant is primarily caused by water. The water is reused, so that salts accumulate in the water, forming a highly conductive media that creates the extreme marine-like corrosion problem.

While in many small, temporary operations no protective coatings are used and corrosion continues with little or no maintenance, many of the larger units do protect against corrosion problems through use of high-performance coatings. The primary high-performance material used is IOZ, as either a primary coating or as a base coat. Since the corrosion is primarily chloride oriented and there is little actual immersion, a properly applied IOZ coating provides good protection to the structural steel used throughout the plant and on conveyor lines. However, there are areas where vinyl or epoxy topcoats are used over the IOZ, both of which have proven to be satisfactory.

One operation that is part of some of the larger coal preparation plants is a drying process where the fine coal is dried for use by electrical utilities. When drying is required, waste coal from the plant is burned to create hot air, and the coal is passed counter-current to the hot air for drying. This can be a very corrosive process because, due to the appreciable sulfur content of the coal, the primary sulfur compound (iron pyrite) is oxidized by the hot air, creating SO_2 or H_2SO_4. These gases must be scrubbed out of the hot air after the coal has passed through. Some of the pyrite remaining on or in the coal is also oxidized, so that any fallout of the coal dust is also extremely corrosive. Thus, the entire area around the coal drying sections of the preparation plant must be well protected by acid-resistant coatings. Fallout on either steel or concrete surfaces creates immediate corrosion, and these areas must be washed at frequent intervals to reduce the corrosion problem.

Except for the drying area in the preparation plant, there are no fumes involved in the preparation of coal. Concrete floors, which are used throughout the coal preparation plants, are not affected by either the coal or the wash water. On the other hand, areas where the concrete is tied into any metal structure are severely corroded due to the accumulation of corrosive salts.

The remaining operation in coal mining is the transportation of coal to the point of use by coal trains, hopper cars, slurry pipelines, or barges. In this case, corrosion is also primarily chloride oriented, with the coals high in NaCl being much more corrosive than the ones with the low chloride content. Abrasion is a substantial problem in the transportation of coal, although use of coatings to prevent this problem has been limited up to this point. Some protective coatings are now being used in barges, particularly to protect hidden areas where coal dust and chloride salts accumulate.

The Steel Industry

The steel industry differs significantly from the chemical industry, in which entire plants are coated for corrosion protection. Unless a steel plant is located in a marine atmosphere or a severe industrial area, many of the structures are subject only to mild atmospheric corrosion. On the other hand, some extremely corrosive conditions do exist in fully integrated steel mills. The primary areas of concern are the pickling facilities, the coke plants, the byproduct plant of the coke operation where ammonium sulfate $[(NH_4)_2SO_4]$ is collected, the smoke and fume scrubbers, the water treatment plant, and the acid regeneration area.



FIGURE 19.29: The inside of a batch-type pickling tank. In such tanks, the furan mortar between the brick may be more resistant to the hot acid than the brick itself.

The pickling area, of which there may be several within one integrated plant, is probably the most corrosive area within the steel mill. This is because H_2SO_4 is the primary product used to pickle steel. It generally exists in concentrations of 10 to 15%, and is kept as near the boiling point as possible by steam injection. There are two types of pickling, batch and continuous operation. First, and most important, is the continuous strip pickle lines where steel strip is continually passed through the acid bath prior to some other operation (e.g., cold rolling, galvanizing, tin plating, aluminizing, or some organic coating operations). The continuous strip pickle lines are for relatively light gauge metal and they pass through the bath at a rapid rate.

The pickling operation not only includes the H_2SO_4 bath, but hot water washing, hot water rinse, and a quick drying operation prior to the strip going on to be galvanized or tin or organic coated. With steam injection, hot pickling solution, and the rapid movement of the steel through the pickling bath, there are plenty of fumes that can condense on any surface in the area.

The second type of pickling operation, the batch type, involves heavy plates that are pickled free of mill scale. Pipe, bars, wire, fabricated beams, or even sheet are also pickled by the batch process. These operations primarily occur prior to galvanizing or some other coating process. The batch pickling operation is not only located in steel mills, but also may be found in galvanizing plants. This is the type of pickling operation used by steel fabricators for plates prior to making them into tanks and similar structures. All structural steel to be galvanized is passed through the batch-type pickling operation prior to hot dip galvanizing.

The primary corrosion problem in this process involves the pickle tank, which, in the case of a continuous process, may be several

hundred feet in length. In the case of the batch process, the tanks are usually 50 ft (15 m) or less in length. In each case, the protection for the interior of the tank against the hot acid is an acid proof brick lining system (Figure 19.29). One of the most important parts of this system is the membrane, which prevents acid contact with the steel or concrete tank proper. This may be rubber or vinyl chloride sheet 1/16 to 1/8in (1.6 to 3.2 mm) thick. The acid-proof cement and brick primarily are used for abrasion protection and heat insulation for the membrane itself.

In many cases, the exterior of the tank, as well as the surrounding floor area, must be covered with acid-proof brick and cement to provide protection against hot acid spills. The steel areas adjacent to the pickling tanks (i.e., the steel structure of the building) are subject to splash, spray, fumes, and moisture condensation. These areas require protection by high-performance coatings in order to prevent the steel structure from serious corrosion. They can be protected by heavy duty vinyl, epoxy, or coal tar epoxy coatings.

The acid-proof brick lining system has been used in this service for many years and is a standard of the industry. The acid-proof cement is made with a furan resin with a backing between the membrane and the brick of sulfur and silica cement. Such a system is fully resistant to the hot dilute acid. Tanks where the brick has been eaten away after several years of use have been seen with the furan cement extending ½ to 1 in (13 to 25 mm) beyond the brick.

The second area in the steel mill, and perhaps an even more important area from a coating standpoint, is the coke plant and its surrounding area. Coke is made in ovens by burning coal in an essentially reducing atmosphere, which removes all of the volatile material from the coal and leaves the coke, or essentially pure carbon, as an end product. Coke ovens are made in such a way that the volatile materials from the burning of the coal are carried over into a byproduct plant. One of the byproducts is NH_3, which is treated with relatively dilute H_2SO_4 to form $(NH_4)_2SO_4$. This material is used extensively as a fertilizer.

The primary corrosion problem around the coke plant is due to the quenching of the coke. Once the coking operation is complete, the hot coke is dumped from the furnace and must be quenched rapidly. This is done by the use of rather large quantities of water, which, in many cases, come from the waste water from the rest of the steel mill. During the quenching process, large volumes of steam are formed, which carry any volume of salt that the water may contain to all adjacent steel areas surrounding and downwind from the quenching area. This can amount to sizable area of a steel mill that needs to be coated. One large, multiple-story steel structure was completely coated with a vinyl primer and two heavy-body vinyl topcoats during the construction process. After several years of service, the coating was still providing excellent protection to the steel structure.

The coke oven byproduct plant is primarily for the processing of coal tar pitches and the extraction of various aromatic hydrocarbons from the coal gas. One is $(NH_4)_2SO_4$, which is the primary corrosive agent. The $(NH_4)_2SO_4$ itself is a white crystalline material, much like NaCl. It is hygroscopic and is corrosive due to the hydrolysis in contact with water to form NH_3 and H_2SO_4. Concrete and structural steel areas therefore require coatings to prevent disintegration. Vinyl coatings and heavy-duty epoxy coatings have been used successfully. Concrete floor areas can be protected with epoxy floor toppings.

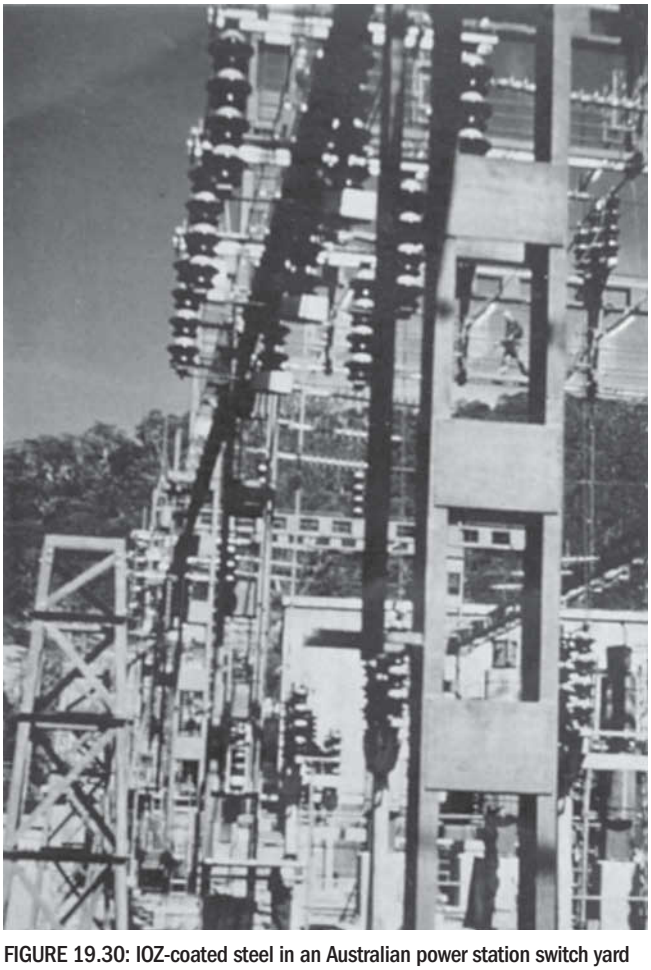


FIGURE 19.30: IOZ-coated steel in an Australian power station switch yard after many years of trouble-free service from the use of the single-coat system.

The water treatment areas in the steel mill are an important part of the overall operation to prevent contamination of water sources. The water must be neutralized, the dissolved solids (e.g., soluble iron compounds) precipitated, and the water clarified before it can be emptied into any other body of water. Much of the water is reclaimed and reused. While the primary effluent into the water treatment plant is acidic, the treating processes are similar to many water treatment plants. The same coatings would be used, that is, a coal tar epoxy or 100% solids epoxy, for the underwater areas of tanks and equipment, and either heavy-duty vinyls or epoxies above the water. In the primary influent areas where strong acid solutions come into the plant, acid brick and cement-lined tanks and processing equipment should be considered.

Acid regeneration plants are also becoming a part of the steel industry. This is particularly true of the HCl pickling facilities. The conditions in these plants are similar to the conditions where the acids are used for pickling. Similar coating and lining materials should be used.

Steel plants that manufacture SS also have pickling facilities where HNO_3 is used for both pickling and passivating the stainless to make it fully corrosion resistant. HNO_3 is both an oxidizing and a volatile acid and therefore, is a very corrosive one. Coating systems for structural steel should be heavy-duty vinyls or epoxies, while areas requiring acid-proof brick would require polyester cements.

Because of environmental restrictions, more and more is being invested in smoke and fume abatement, which requires large scrubbing facilities, many of which are subjected to extremely corrosive conditions. Where temperatures are sufficiently low, coatings are effectively used around and within the scrubbers.

The Power Industry

While each segment of the power industry has its own unique problems, they all have one particular concern in common, that is, the need to protect the structural steel, pipe racks, electrical

distribution towers, and similar steel structures located throughout the plant. The need to coat these areas with high-performance coatings depends to a considerable degree on the atmospheric conditions and the geographic area in which the power plant is located.

Figure 19.30 shows the structural steel in a power station switchyard coated with a single coat of IOZ. Many such stations as well as long load transmission towers have been coated in a similar way throughout Australia. In many cases, the IOZ has outlasted galvanized towers and equipment.

Many power plants are located adjacent to the ocean in order to use seawater as cooling water, and are thus subject to marine atmospheric corrosion. This indicates the need for an inorganic primer, followed by the most weather-resistant topcoats available. Today, a typical system used might be an inorganic base coat, epoxy intermediate, and a polyurethane topcoat. Another good system would be IOZ and water-based acrylic intermediate and topcoats. The power industry generally requires excellent appearances in a coating in addition to good corrosion resistance, for public relations reasons.

In most power plants, the need for coatings is on the exterior of equipment and structures, since most of the interiors (e.g., control and generator buildings) are enclosed and therefore not subject to weathering or severe corrosion. Many of the operating parts of plants are open structures where piping and structural steel is subject to all of the atmospheric conditions that exist in the area. In this respect, power plants are similar to chemical plants and refineries, and often utilize the same coatings for corrosion protection.

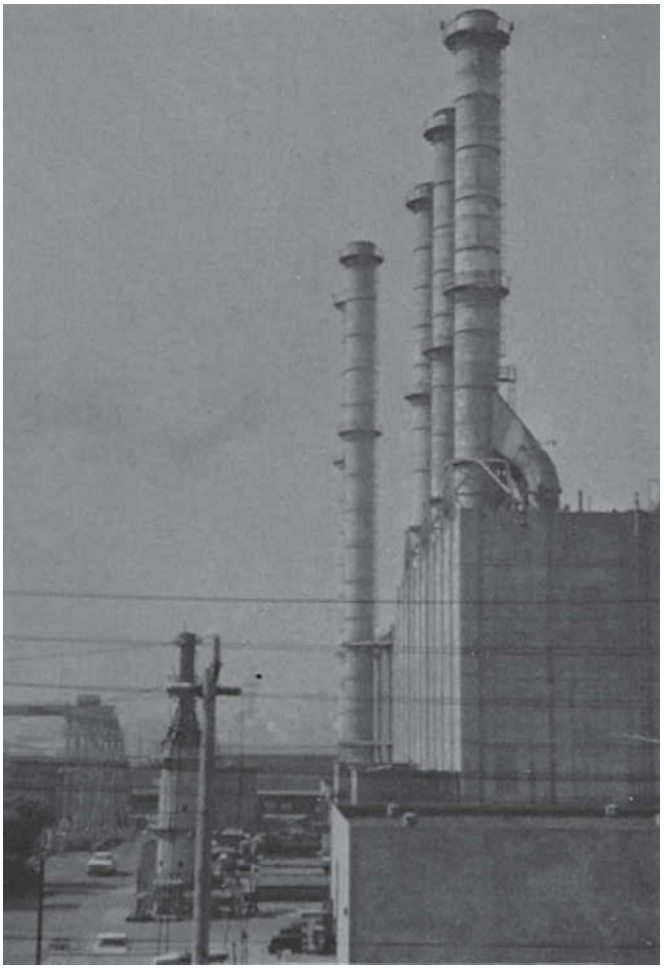


FIGURE 19.31: Oil-fired power plant stacks in a marine and industrial atmosphere after 15 years of exposure.

Oil- or Coal-Powered Steam Plants

The largest areas in the oil-fired plant are the oil storage tanks. Depending on the type of oil used, and to a certain extent the geographic area where the plant is located, the storage tanks require coating on the interior as well as the exterior. On the exterior, an IOZ primer base coat is recommended and has, in many cases, proven adequate without overcoating. However, it may be followed by weather-resistant topcoats. On the interior, a two- or three-coat epoxy system has given good service. In others, a single coat of IOZ also has performed well.

In coal-powered plants, there are usually extensive conveyor systems in place of storage tanks. These are subject to both salt and acidic conditions due to coal handling. Most coal will contain some sulfur in addition to salt. When subject to moisture, rain, or high humidity over a period of several months, the sulfides oxidize to create corrosion problems wherever the coal dust accumulates and absorbs water. In addition to being slightly acidic, the coal itself is cathodic to steel and will therefore, when in direct contact with steel, set up an electrolytic cell, causing the steel to pit and corrode in that area.

Heat exchangers, cooling towers, and cooling piping are common to both oil- and coal-fired plants. Most of this piping, and all of the cooling towers, are above ground, with all of the inherent corrosion problems that go along with a cooling tower area. If the oil or the coal contains some sulfur, this increases the problems. If either of these types of plants are located near the ocean and are using salt water for cooling, the problems are multiplied, so that any piping involved would require proper coating to prevent corrosion due to the seawater. Also, if the piping is steel, it has to be properly lined to provide long-term protection. Properly applied coal tar epoxies, as well as concrete linings, have been used on the interior.

Many of the new plants have extensive pollution control systems, including large scrubbers and reactors to remove the sulfur oxides from the air. This equipment generally represents an area of high corrosion and, depending on the temperature, requires high-performance coatings for corrosion free maintenance.

All of these plants also have extensive water treatment facilities. This is necessary in order to supply deionized and deoxidized water for boiler makeup. Again, high-performance coatings are recommended for both the interior and exterior of this equipment, and the coatings used are the same as for any water treatment facility (i.e., coal tar epoxy or 100% solids epoxy for immersion and vinyl or polyamide epoxy for the exterior).

Stacks are also common to both of these types of plants. Where steel stacks are used, IOZs have been used for exterior protection and have given excellent service over long periods. Figure 19.31 is an example of steel stacks in a power plant located in both a marine and industrial atmosphere. After 15 years of service, the post-cured IOZ coating was still providing full corrosion protection.

Hydroelectric Plants

Hydroelectric plants are generally located near large dams or similar structures. The exposed steel areas on the dams and powerhouses may be exposed to high humidity and water, thus requiring high-performance coatings. Such areas include rotary drum gates, floating drum gates, tainter gates, and simple lift gates as well as trash racks. Such mechanisms are subjected to highly oxygenated,

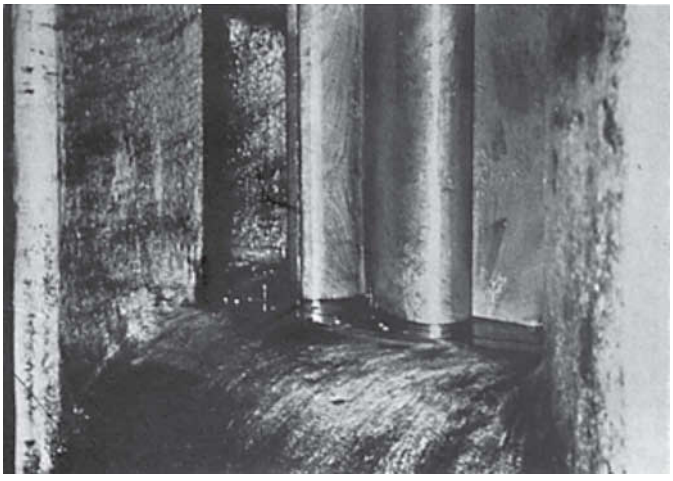


FIGURE 19.32: The scroll case of a large low-pressure, high-volume water turbine developing hydroelectric power after five years of service from the B. of R. VR6 vinyl coating (six coats).

rapidly flowing water, as well as to abrasion from floating debris and ice. Many such areas were coated with vinyl coatings (five to six coats) in the late 1930s and early 1940s. Some of the coatings are still intact and operating. Many other coating systems (e.g., epoxies, coal tar epoxy, chlorinated rubber, and IOZ) have been used since then, with much success.

Penstocks are a necessity for hydroelectric power. These have been coated on the interior as well as the exterior in many areas throughout the world. For example, Shasta Dam made some early tests where Bureau of Reclamation vinyl specifications VR-3 and VR-6 were tested against a large series of other coatings, including hot-applied coal tar. Both vinyl coatings gave excellent performance over this period of time compared with the other products. Today the Corps of Engineers enjoys an exemption from VOC regulations for immersion-grade vinyl coatings. Hot-applied coal tar enamel and coal tar epoxy also showed up well.

IOZ coatings have been used on the exterior of many penstocks, particularly in Australia. One example is the Snowy Mountain Scheme, which was put in service over 30 years ago. There is a large penstock in Central Mexico that is coated on the interior with coal tar epoxy and on the exterior with IOZ. Much of this penstock is in a rock tunnel so that the IOZ is exposed to extremely humid, wet conditions most of the time. This unit has been in service for approximately 25 years.

There are two types of hydroelectric plants. One uses the Pelton wheel, which is a very high-speed, high-pressure unit that can only be made of metal, except in the penstock. However, there also are many low-pressure penstocks, which use a very large impeller and scroll case to turn the generator. These may be 30 ft (9 m) or more in diameter. A large volume of water flows through the scroll case, but at relatively low pressure, and they usually are made up of heavy steel. Figure 19.32 shows the large baffles that direct the water into the impeller. The scroll case and the impeller were coated with Bureau of Reclamation VR6, and the photograph was taken after five years of service.

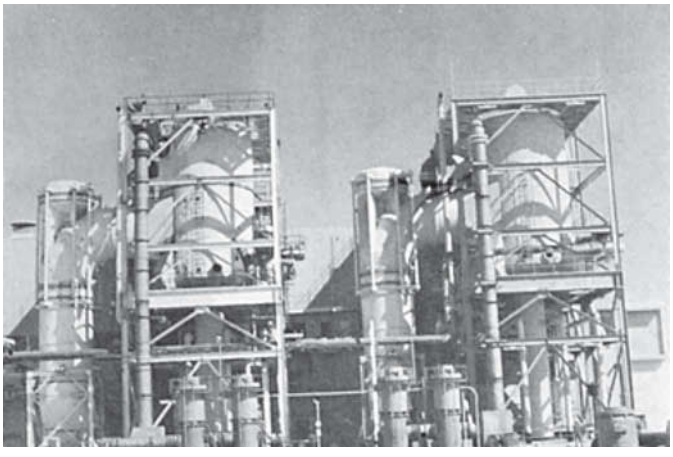


FIGURE 19.33: A geothermal generating plant with barometric condensers with a two-coat inorganic system. Any corrosion would badly stain the white inorganic topcoat.

Geothermal Plants

Only a few geothermal plants exist around the world. Their corrosion problems are undoubtedly unique in that there is considerable waste steam, which contains large amounts of salts and some H_2S. Therefore, all of the structural steel, piping, any tanks or water processing equipment, and often some concrete areas, require protection.

One of these plants has used high-performance coatings, and it is located just south of Mexicali in Baja, California. In this case, many of the hot areas of the plant were coated with IOZ and an inorganic topcoat. This plant had been in service for from 15 to 18 years and the coating had performed in an excellent fashion. An addition to the plant was completed, and the inorganic coating system was used on it as well. Less critical areas were coated with epoxy polyamide coatings. It is anticipated that additional geothermal plants will be located around the world, wherever heat from the earth's crust can be tapped.

Figure 19.33 shows two barometric condensers coated with the two-coat inorganic system, after approximately eight years of service.

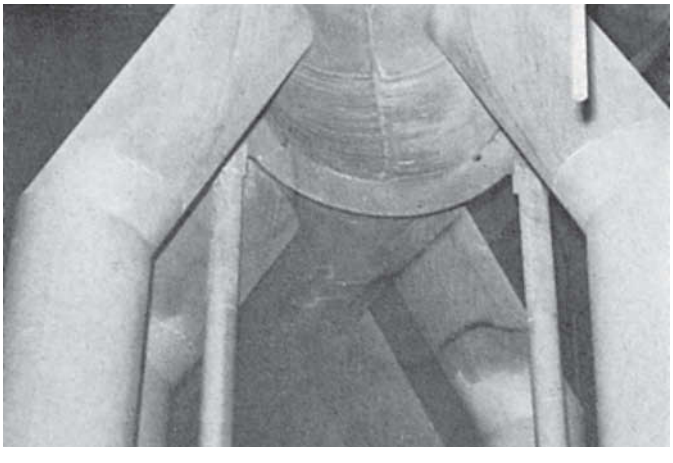


FIGURE 19.34: Nuclear power plant down comers coated with an IOZ and polyamide epoxy system.

Nuclear Plants

Coatings for nuclear plants, except for the exterior structural steel areas, are quite different from those used in other power industry segments. The general intent is to apply coatings that will last 40 years, which in itself requires high-performance coatings. For the most part, the coatings are for standby protection, except in the areas where the coating is exposed directly to water, for example, on the interior of the torus, quenching mechanisms, and fuel storage areas. The primary reason for the majority of the coating is to prevent penetration of any radioactive material into the concrete structure or onto any bare steel

area, which would be difficult to decontaminate. The coating provides the decontaminating surface, and, except in the reactor areas where it is subject to radioactivity, it acts as a standby protection. It is therefore subject primarily to atmospheric conditions or wear from ordinary use or foot traffic.

An example is shown in Figure 19.34 where IOZ and polyamide epoxy topcoats are applied to the exterior of the down comers of the fast-quenching mechanism. Here, the coating is subject to some moisture, but otherwise is protecting against standby corrosion until an emergency occurs.

Because of the standby protection required of the coatings, there are tests that the coatings must pass before they can be used in areas where there is a possibility of radioactive contamination. Design basic accident (DBA) and loss of coolant accident (LOCA) conditions are two pertinent ones. These tests simulate conditions as they might be if a power reactor went critical, with a failure of some of the mechanical components. These and other required tests are critical when it is realized that a relatively thin coating film must stand up to the accident conditions and still provide a surface that will decontaminate well enough to allow repair and early resumption of power production. The inorganic silicates, epoxy amine, epoxy polyamide, epoxy phenolics, specially cured epoxy coatings, or combinations of these products are the coatings that provide the essential protection to the critical areas of nuclear power plants.

Since the beginning of the Manhattan Project, concrete has been the principal building material for all nuclear plants and facilities. These include the original plants for the development and extraction of plutonium, experimental reactors, heavy water plants, nuclear fuel plants, as well as the present day nuclear power plants.

The concrete areas in these plants are massive, with millions of square feet and hundreds of thousands of tons of concrete used not only as a structural material, but as a basic shield against high-density radiation. The structures themselves range from concrete tanks to small experimental reactor houses, to concrete holding basins for hot uranium slugs from the original piles, storage areas for spent uranium fuel, massive underground chemical plants where all equipment is operated and maintained by remote control, and concrete containment areas around the primary nuclear power reactors.

Unfortunately, concrete has its problems, the principal one being porosity. Most of the radioactive materials, whether in the form of a solution, a solid, a powder, or, in some cases, a gas, if they accidentally come in contact with a bare concrete surface, are quickly absorbed by it. Once absorbed, they cannot be readily removed except by destruction of the concrete surface. The improvement of the concrete surface is therefore essential, and this is where coatings enter the picture.

The magnitude of the problem can be better understood when it is realized that there are two to five times the area of concrete to be coated in a typical nuclear plant compared with steel areas. There are hundreds of thousands of square feet of complex surface to be coated in each plant. These may range from very critical to relatively noncritical areas. Nevertheless, the concrete surface must be coated to eliminate any porosity that would retain radioactive materials. In order to provide a surface that would readily decontaminate if exposed to radioactive materials, special coatings were developed to eliminate the basic porosity of concrete and that would pass the tests for nuclear accidents. Fortunately, the epoxy resins have the necessary resistance to radiation so that epoxy surfacers were developed that would meet the other requirements. Epoxy surfacers and epoxy or epoxy phenolic topcoats are now standard for concrete surfaces that could become contaminated.



FIGURE 19.35: The spray application of an epoxy surfacer to a concrete surface in a nuclear power plant. The surfacer, when troweled, effectively fills the concrete surface to make a smooth, impervious base for the polyamide epoxy topcoats.

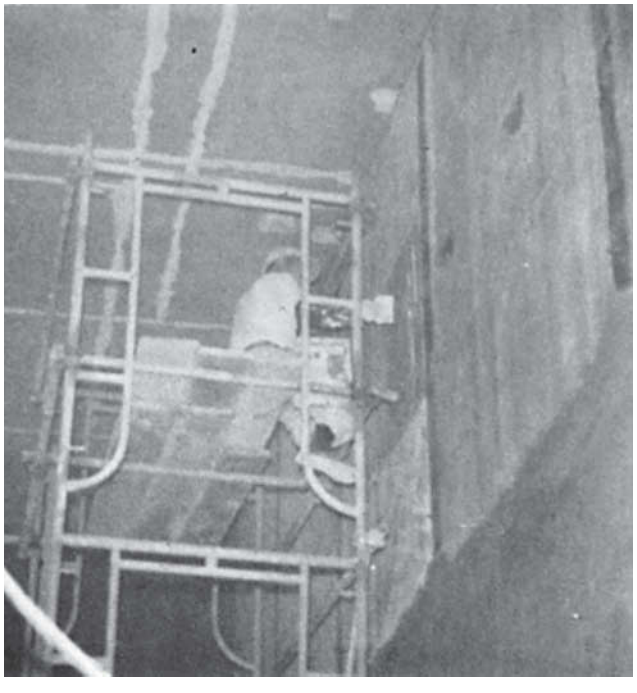


FIGURE 19.36: An epoxy surfacer being applied by trowel to a large expanse of concrete on the interior of a nuclear power plant.

Figure 19.35 shows the application of an epoxy surfacer by spray to a concrete surface in a nuclear power plant. In most areas, the surfacer was applied in this manner and then troweled for proper smoothness. Figure 19.36 illustrates the magnitude of the concrete surfacer in a nuclear power plant, as well as the application of the epoxy surfacer by trowel.

Steel surfaces, on the other hand, are smooth, dense, uniform, and present few of the coating application difficulties inherent in concrete surfaces. When abrasive blasted, mild steel presents an almost ideal surface over which to apply coatings. All of the principal types of coatings that have the required radiation resistance have been used. These include primarily vinyls, epoxies, and IOZ. Single



FIGURE 19.37: A steel reactor containment shell (under construction) is coated in IOZ without topcoats.

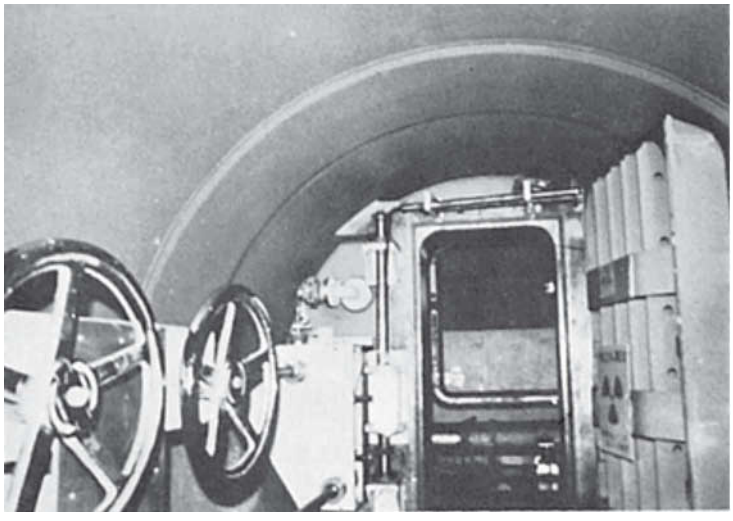


FIGURE 19.38: An epoxy surfacer being applied by trowel to a large expanse of concrete on the interior of a nuclear power plant.

coats of inorganics have been applied to many areas of the containment vessel, torus, and down corners. Other areas are coated with a combination of inorganic and epoxy coatings. Still others are coated with two or more coats of vinyl or epoxy. In the nuclear energy field, in order to permit proper decontamination, the same topcoating systems are required over both steel and concrete surfaces, which are expected to provide similar impervious surfaces and last for an equivalent period.

Figure 19.37 shows a steel reactor containment shell coated with IOZ alone. High resistance to radiation and good corrosion resistance are required in this case. Figure 19.38 is a critical area, an air lock into the primary containment area. This area is coated with in organic zinc and polyamide epoxies for the most effective decontamination.

The Food Industry

The food industry is a widespread, fragmented industry in which there are many small plants dispersed around the world in rural as well as in urban areas. There is one overriding corrosion problem inherent in the food processing industry: floors. They are a critical problem in every food plant for several reasons: (1) sanitation, (2) resistance to all types of food products, and (3) abrasion from foot traffic and mechanical handling equipment. There is no other single area in the food industry that is as important as a properly protected floor.

New floors are not difficult to lay or coat. Old floors, however, are among the most difficult of all areas to coat. This is because the concrete is dense and usually hard troweled and smooth. Where the coating is worn or broken, oils, grease, fatty acids, proteins, and sugars penetrate the surface and are difficult, if not impossible, to remove. Floor maintenance coatings or surfaces must be capable of penetrating and adhering to such surfaces without blistering, peeling, or other failure. It is not uncommon to use copious amounts of steam, detergents, and wet jetting equipment at high pressures to remove the contaminated concrete and reach sound, gray concrete for recoating. Specially formulated epoxy surfacers and 100% solids epoxy topcoats are often used to coat the repaired concrete. Where appearance is a factor, it is not unusual to see very expensive tile systems laid over membranes and grouted with acid-resistant cements.

There are several segments of the food industry, each with its own individual problems.

1. General food processing plants, which consist of meat packing plants, cheese and milk plants, fruit and vegetable packing plants, soft drink plants, aircraft service kitchens, chain restaurant kitchens, precooked and packaged food plants, candy companies, and bakeries. The galleys and kitchens aboard ships also are included in this segment.
2. Breweries
3. Wineries, which are more highly developed in the United States than in any other area of the world
4. Sugar mills
5. Corn product plants

General Food Processing

General food processing plants are located throughout the world in both rural and highly populated areas. The overriding problem throughout this segment of industry is sanitation. Equipment, floors, and wall areas (from the floor up to approximately 4 or 5 ft [1.2 or 1.5 m]) are subject to constant washing, dampness, steam, and contact with disinfectants or bactericides such as sodium or Ca(ClO)2. In addition, these areas are subject to various food acids such as acetic, lactic, citric, and phosphoric acid, as well as many kinds of sugars. Proteins, fatty acids, oils, and fats also may be present in these areas. Wherever there is an accumulation of these materials, bacteria, yeast (fermentation), and fungus are often found, which then create acidic conditions.

Other areas are subject to highly alkaline cleaners and detergents. This includes the equipment area where processing vessels, bottle washers, pumps, and bottling and canning equipment are used or are washed with alkaline materials.

The most critical area in food processing plants is the floor. Not only is it subject to all of the previously mentioned materials, but because it is usually wet, it is a prime source of contamination by bacteria and fungus. Plain concrete floors are unsatisfactory, and coatings are not practical, primarily from an abrasion and thickness standpoint. Thus, the standard in the industry is acid-proof brick

or cement or quarry-tiled floors grouted with chemical-resistant cements (e.g., furan or epoxy grouting materials). Floor surfacers of the same resinous materials are often used in less critical areas with good success.

Figure 19.39 shows a quarry-tiled floor using furan grouting in a large meat-packing house. The quarry tile is impervious to grease, water, steam, protein, and microorganisms, as is the furan grout.



FIGURE 19.39: Quarry tile floor subject to abrasion, chemical cleaning house. Floors such as this have given service for 10 to 20 years. Source: Ameron, Inc., Monterey Park, CA.

Breweries

Breweries are located throughout every country in the world and, in many cases, represent the largest plant in their area. The problems in some areas of the plant are similar to those in the food processing industry; that is, conveyors, bottle washers, and bottling and canning equipment. Again, the greatest problem involves floors, since these are the areas where abrasion and constant damp or wet conditions exist. The same products can be used here as in the food processing industry.

A large area to consider in any brewery is the cold-rooms where the refrigerated holding tanks for finished beer are located. When the tanks are washed, the effluent often goes onto the floor and is directed out through the floor drains. These floors are therefore subject to beer, detergents, bactericides, and continuing moist-damp conditions. That is why one of the large breweries in Mexico, which adds several aging tanks at least every two years, has used only quarry-tiled floors with furan grout dating back to at least 25 years ago.

Since the temperature in beer cellars is 35 to 40 °F (2 to 4 °C), there is constant condensation on the exterior of the steel tanks and, in many cases, on the walls and ceilings. The exterior of the tanks often has been coated with vinyls or epoxies with good results over a number of years. This has been true not only in various areas of the United States, but in other countries as well. It must be emphasized that since breweries often serve as a local showplace, all parts are maintained for both sanitation and appearance. Therefore, semi-gloss or glossy coatings are preferred throughout the brewery. Alkyds are often used on noncritical walls and ceilings.

The interior of the brewery tanks that are not made of SS may be glass lined or lined with high-bake phenolic coatings for maximum resistance to immersion and fermentation. The ones lined with phenolics require great care both in the application of the critical phenolic and in the curing process. Several thin coats are usually applied, with a mild bake in between each coat and a final high bake to cure all coats together. When properly done, many years of excellent service can be obtained from either the phenolic or glass lining.

Wineries

The segment of the industry that concerns wineries is quite different from either of the other two segments discussed because it essentially is a seasonal fermentation process. The plants are single-purpose and, except for the bottling rooms, most areas are relatively dry with no corrosion. However, where wooden storage and fermentation tanks are used, there often is some leakage that can damage concrete floors. This makes floor toppings in these areas an advantage.

The primary concern in wineries is contamination of the wine, which makes tank linings extremely important. If any wine is exposed to iron, it changes to a bluish ink color and develops a definite metallic taste. Wine, therefore, usually is stored and fermented in wood, SS, or specially lined steel containers.

The fermentation process is a difficult one from the standpoint of coatings, because it produces nascent carbon dioxide (CO_2) on the coating surface. Nascent CO_2 (i.e., single molecules of CO_2) is an extremely small molecule and can pass through most plastic materials in a manner similar to moisture vapor. Thus, the linings of fermentation tanks must be able to resist blistering and loss of adhesion due to the passage of CO_2 through the coating.

In the early days, multiple-coat vinyls were used in many wine tanks, primarily for finished wine after the fermentation process had been completed. However, vinyls were never very successful for service during the fermentation process. They were only successful for finished wine when the coating was heated for several days to eliminate the solvents. In fact, several of the champagne tanks that were lined at a California winery shortly after World War II were still in use and the vinyl was still providing full protection after 20 years of service.

However, a better type of lining is a tightly cross-linked thermoset coating. An epoxy urethane can provide excellent service as a fermentation tank lining for concrete tanks. In fact, there were several in California and a number in Mexico that were in service for over 10 years. Other highly cross-linked epoxy phenolics and high-bake phenolics have given equivalent service on steel. A strongly cross-linked epoxy amine coating should be satisfactory as a coating for concrete fermentation tanks.

The transportation of wine is an important part of the business. Most of the wine produced in California is shipped east. Thus, in order to be economical, it must be shipped in lined tank cars and bottled at the destination. Wine connoisseurs may shudder at the thought, but 10,000 or more cars are used in wine service in the United States, with even more being used for transportation to Europe. The original cars were lined with multiple-coat vinyl coatings. In fact, vinyl coatings provided the opportunity that was needed for the wine industry of California to become a major business. Before the time of vinyls and tank cars, wine had to be shipped across the United States in bottles. Presently, epoxy phenolic and high-baked phenolic coatings are used in this type of service.

Sugar Mills

Sugar mills process sugar cane or sugar beets. They are crushed, the juice is pumped into tanks, and it is concentrated, crystallized, passed through centrifuges, recrystallized, dried, and bagged. The sugar syrup or sugar juice is relatively corrosive in that it ferments rapidly, forming acetic acid. Sugar solutions themselves are slightly acidic and therefore, are quite damaging to concrete floors.

Epoxy concrete floor toppings in the crushing areas are an advantage. Vinyl or epoxy maintenance coatings have been used successfully on conveyors and other handling equipment, structural steel, and the exterior of equipment in various sugar plants throughout the world. Most plants now use SS for concentrators, crystallizers, centrifuges, and most storage tanks.

Corn Products Plants

In many ways, corn products plants are more characteristic of the chemical industry than the food industry. There are numerous products produced from corn; however, the principal ones are corn oil, starch, and dextrose. They are usually produced in large, multiple-story plants, enclosed with a large amount of structural steel and concrete floors, which must be protected.

The area that is most difficult from a corrosion standpoint in a corn products plant is the starch area. Once the starch is formed by a cooking and grinding process it is then treated in several different ways to develop the required properties. Starches may be reacted with HCl, NaOH, enzymes, sodium or calcium hypochlorites, peroxide, SO_2, or other chemicals. Some reaction equipment is rubber lined, and an oxidation-resistant coating is used for protection of both steel and concrete. The process using SO_2 in some plants has caused concrete ceilings and columns to spall due to the SO_2 reacting with the concrete. Vinyl coatings have given good protection in the oxidizing and acid areas. Epoxy coatings and floor toppings have been used successfully in other plant areas.

Sewage Treatment

With the increasing emphasis on a healthy environment in the last several years, there has been a substantial increase in the number of sewage plants put into operation. Many of these are located in rural atmospheres where, with the exception of some possible H_2S, there is little corrosion. Nevertheless, since these plants are permanent and therefore meant to operate with a minimum of maintenance, good long-lasting coatings should be used in all critical areas. Many of the larger plants in humid or coastal areas need the best protection possible on aboveground areas.

The influent in a sewage treatment plant is the primary source of corrosive conditions in the plant. The influent generally comes from a series of collection lines throughout a city or cities, which are concentrated into a central outfall that flows into the sewage treatment plant. The time involved in the flow of water from its entrance into the pipe from a plant or a home may vary greatly. However, under most conditions, transport through the pipeline has been sufficiently long so that the bacteria in the sewers have created a source of H_2S (which is corrosive).

The conditions to look for that create the proper atmosphere for corrosion in a sewer depend on several factors. The generation of H_2S is a bacteriologic action. Thus, all conditions for bacterial growth must be present in order for sulfides to be produced. If any one of the required conditions is absent, then it is unlikely that gas will be produced, since the growth of the bacteria will be prevented or seriously retarded.

There are four primary factors in sewer gas production and the resulting corrosion of concrete and exposed steel.

1. The average temperature of the geographic location is extremely important. Generally, the areas of the country where the average temperature is 60 °F (16 °C) or above are favorable for bacterial growth. The longer the high-temperature season, the more likely there will be H_2S produced under the sewage conditions. Even in areas where there are several months of cold temperatures, bacterial action can be rapid enough during the summer months to create a serious sulfide problem. Thus, sewer corrosion has been found even in southern Canada.
2. The sulfate content of the city water is an important factor in the life of the anaerobic sulfate-reducing bacteria. In cities where the water supply is extremely pure and where sulfates are almost nonexistent, the probability of sulfide production is reduced. The normal sulfate content of city water of average hardness is sufficient for these bacteria to generate H2S. Additional sulfates also may enter the sewer by groundwater infiltrating into the sewage system. The higher the sulfate content, the greater the quantity of sulfate bacteria that may be present and the greater the H_2S produced.
3. The age of the sewage in any system is extremely important. A sewer that flows rapidly and where retention is short ordinarily will not maintain conditions that will produce H_2S. If there are long outfalls or even long feeder lines into the outfalls, where the sewage becomes several hours old, then the formation of H_2S is usually rapid. The age of the sewage depends to a great extent on the slope of the sewer. In areas where the flow is slow, the pipe may act as a septic tank, producing large amounts of sewer gases. This is an important factor to look for in determining the possible corrosion of concrete. The older the sewage, the greater the chance of corrosion.
4. High concentrations of organic matter lead to sewer gas production. Low percentages of organic matter ordinarily prevent the rapid growth of the anaerobic bacteria, as these organisms require some organic compounds as part of their reduction of sulfates or organic sulfur compounds to H_2S. Food plants, fish canneries, meat packers, and plants of this type can materially increase the organic content of the sewage, as well as the H_2S development.

Two important terms that may be encountered in any study of a sewage system are biological oxygen demand (BOD) and oxidation-reduction (redox) potential. These terms often are used as a measure of the "strength" of sewage. The BOD is a measure of the amount of oxygen absorbed by a given amount of sewage in the laboratory over a five-day period. Ordinarily, where the BOD is high, the above four conditions for bacterial growth are all optimum. The oxidation-reduction potential of sewage is again a measurement of the condition of the sewage. If the sewage is on the reducing side, this condition is favorable toward H_2S production. If this potential is on the oxidizing side, then H_2S will not be present.

An important point to remember is that H_2S will not corrode concrete by itself. It is only when the H_2S reacts with the bacteria to form H_2SO_4 that there is any attack on the concrete. Any dissolved H_2S that may be in the sewer water is inert to the concrete. Generally, liquid sewage is no more corrosive to concrete than plain water. It is only the area above the liquid that becomes corroded. Steel is not like concrete in that H_2S can react directly with steel under almost any condition. Therefore, any steel that may be immersed in the sewage liquid must be effectively protected. This would include the bar screens, the scraper units in the grit chamber, and the scraper arms on the primary clarifier. Above the sewage, metal reacts with the H_2S and H_2SO and is seriously corroded in the same way as concrete.

In modern sewage plants, there is a great effort to decrease obnoxious odors. Therefore, many of the chambers in the initial stages of the sewage treatment are closed chambers, which create ideal conditions for the aerobic bacteria and, as a consequence, for severe corrosion of the concrete. Any concrete areas above the liquid level that are moist and enclosed can corrode at rates as rapid as 2 in

(51 mm)/year. Thus, most of these areas require the best in corrosion protection. Figure 19.40 shows a sewer chamber and the concrete corrosion that occurred even though the concrete was originally coated.

The majority of the surfaces that are in contact with the sewage are concrete. Concrete is difficult to coat because of its porous surface. In many ways, the concrete surfaces in a sewage treatment plant are similar to those in a nuclear energy plant. The surface must be completely impervious or the concrete underneath the coating will disintegrate. It must be remembered that the H_2S is converted into H_2SO by the bacteria. The bacteria will find any imperfection in the coating and will create H_2SO in that area, which will react with the concrete. The $CaSO_4$ that results has five times the volume of the original cement. Thus, in addition to the acid-cement reaction, there is a strong mechanical force involved that tends to break the coating away from the surface.

For instance, one coated surface showed no signs of any pinholes; however, after several months of service, the coating was covered with carbuncle-like areas where the acid had penetrated the coating and the sulfated concrete had pushed the coating out into a barnacle-like mound.



FIGURE 19.40: A sewer chamber showing the original coating and heavy concrete corrosion.

Although many coatings have been tried, only the best and most impervious ones with the highest adhesion have any chance of protecting these areas effectively. Even where operating areas (i.e., the bar screen pit, grit chamber, primary clarifier, and even drum filters, which are included in some plants) are left open, the area directly above the liquid level will remain damp and bacteria will feed on the H_2S at that point to create a corrosive condition. These waterline areas are often badly corroded and must be effectively protected.

In many sewage treatment plants, these damp areas just above the liquid are protected by flexible vinyl plastic sheet, which is designed to be cast into the concrete surface. All joints are heat welded. This is the most effective method of protecting concrete. The original application of this material in a sewage pump chamber in 1947 was still in service and effectively protecting the concrete in 1982. Millions of square feet of this material have since been applied to some of the largest sewage systems and treatment plants in existence. Newer versions of vinyl and polypropylene sheeting are being secured through the use of either mastic epoxy gels or epoxy/urethane/vinyl primers. While initial applications have been successful, they do not have the long-term track record of sheet vinyl embedded into the concrete during the casting process.

Where such materials cannot be used or are impractical, the most effective way to prepare a concrete surface for use under sewage conditions is to use an aromatic amine-cured epoxy surfacer, followed by epoxy amine (preferable 100% solids versions) or coal tar epoxy amine topcoats. Using a system such as this to prepare the surface, the concrete itself need not be anything other than as left by the forms. If it is dirty, a light blast will clean it up. However, the heavy-bodied materials will fill the surface, after which they are smoothed by rolling or troweling, so that an impervious, heavy topcoating can be applied over the surfacer.

These types of materials should be used wherever there are wet areas in a sewage treatment plant, including the covered grit chambers or any other covered areas throughout the plant (e.g., wet-walls, sedimentation basins, bar screen pits, etc.). It must be noted that only amine-cured epoxy surfacers and seal coats are recommended. Polyamide-cured epoxies are not effective under sewage conditions. The polyamide portion of the epoxy is consumed by various bacteria and soon turns to a slimy mush.

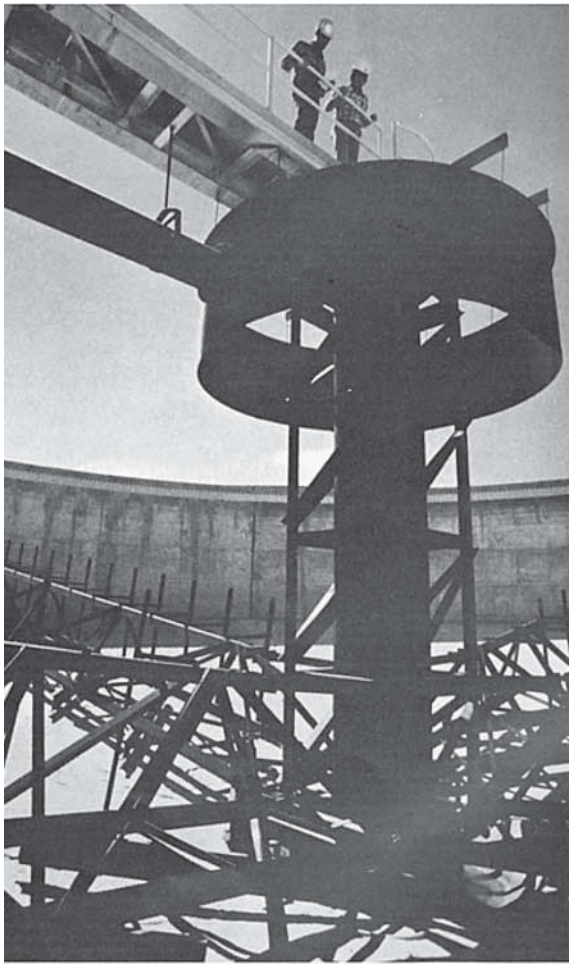


FIGURE 19.41: A typical clarifier mechanism coated with amine-cured coal tar epoxy for use in sewer service. Source: Ameron Corp., Monterey Park, CA.

Heavily loaded, thick, amine-cured surfacers and topcoats are the only types of coatings that can be sufficiently well applied to concrete to seal it against the above-water corrosion in sewage treatment plants. Hundreds of other thinly applied materials from microcrystalline wax to chlorinated rubbers and vinyls have been tried, but generally have not proven satisfactory. Many are resistant to dilute H_2SO on a smooth surface, but fail quickly when applied to concrete and exposed to severe sewage treatment plant conditions.

Coal tar epoxy coatings (amine-cured) have been very effective topcoats over epoxy surfacers. Such coal tar epoxies have shown excellent resistance to H_2S conditions. Steel, under these same conditions and particularly if it is immersed, can be effectively protected by a thorough blasting and the application of an amine-cured coal tar epoxy system. Steel areas, such as bar screens and clarifier rake arms have been effectively protected by properly applied coal tar epoxy coatings (Figure 19.41).

The single most critical factor in protecting both concrete and steel services in immersion or high humidity areas of sewage treat-

ment facilities is the requirement for pinhole and holiday-free application of the coating system. Any pinhole is an access point for acid attack, which then undercuts and expands the failure of the coating system very rapidly. Failures of coal tar epoxy and amine epoxy systems with less than 100% solids have been common due to solvent entrapment, blistering, and thin films on edges, nuts, and bolts. Many products have failed, not because they were deficient, but because of improper application and inspection, which allowed them to go into service with pinholes, holidays, or thin spots in the coating.

As with most plants, sewage treatment plants have a large aboveground area that needs coating. While there usually is only a minor amount of sulfide in the air, it is still necessary to provide for a minimum of maintenance. Thus, the maximum coating should be applied in the beginning. Whenever the sewage treatment plant is located in a highly humid area or an area along the coast, IOZ is suggested for all above-water areas. This will provide the primary protection, and any organic coating (usually an epoxy-polyurethane system or water based acrylics) applied in addition will provide the decoration and weather protection. If concrete areas above ground level (either poured concrete structures or concrete block) require protection, a number of coatings may be used. Except for the severe areas described previously, water-based vinyl acrylic coatings have given good service.

The Transportation Industry

The transportation of bulk chemicals may be one of the most difficult areas of all for protective coatings. While SS and specialty steels and alloys are used extensively for transportation containers, mild steel is also used for the transportation of many commodities, due to cost constraints. Most means of transport (e.g., trucks, tank cars, hopper cars, both dry and liquid barges, and ships) use linings primarily to protect the commodity being transported from any contamination. Bulk terminals, with their large number of storage tanks, should also be considered part of this overall industry, and involve the same types of linings.

The problem of container linings in the transportation industry is twofold. The principal problem is one of protecting the contained product from any contamination by iron or any other foreign material. For the most part, corrosion of the interior of the containers is secondary, except for specialty products that may be highly corrosive. Most of these are transported in special SS or alloy cars or hoppers, with these cars being dedicated to that particular corrosive material.

There are two ways in which the transportation industry handles products. The first is by a dedicated container. This would be a tank car, a hopper car, a barge, or special compartments aboard ship that are dedicated to an individual product and are never used for anything other than that product. For example, there are hundreds of tank cars and barges that are lined specifically for the transportation of caustic soda. Very seldom are these cars or barges used for any other purpose. Similar transportation equipment may be dedicated to corn sugar, ammonia nitrate fertilizers, formaldehyde, molasses, and similar products. This type of equipment, which is dedicated to one product, represents a relatively easy type of service, since the coating that is used on such transportation equipment can be specialized for that particular service.

The second type of transport, however, is much more difficult. This is where the containers, whether they be tank trucks, tank cars, barges, or ships, are used for any number of different commodities. In this case, a coating with a broad resistance must be used in order to withstand the change in commodities as well as the cleaning required between commodities. For example, many different solvents may be transported in an IOZ-lined tank. These include most of the petroleum products, acetone, other ketones, aromatic hydrocarbons, and even chlorinated hydrocarbons (which must be kept dry). Other products, such as molasses, glycols, corn oil, various vegetable oils, lards, and crude fats, are transported in epoxy-lined containers.

Epoxy coatings usually are specially developed for this purpose and may require force-curing at elevated temperatures in order to develop full resistance to the wide range of products. The interiors of tank cars, barges, and ship tanks are usually designed for easy coating application. There usually are no baffles in tank cars, very few in large tank barges, and the tanks aboard ship are large and completely smooth on the interior, except for girders and stiffeners. The interior is prepared for coating, with all of the welds ground smooth and edges or corners radiused to decrease difficulties in the coatings operation.

In addition, because the linings are specialized, the work is usually done by specialty lining contractors who have the necessary equipment for the application of coatings to tank cars and barges, or portable equipment that can be used for lining large ocean-going cargo carriers. Specialized blasting, heating, and dehumidification equipment is necessary for linings of this type. Application conditions are controlled so as to make the application of any coating used the best possible.



FIGURE 19.42: The interior of a refined oil tank in marine service lined with one coat of post-cured IOZ showing no corrosion or rust stain after several years of service.

Many of the products used (e.g., the IOZ coatings for solvents and specialty epoxies for caustic soda or for a variety of chemical products) have been in service for as many as 10 years and have provided excellent service over that period of time.

The lining of large ocean-going vessels for the transportation of petroleum products (ranging from crudes to lubricating oil) also should be considered in this category. Refined petroleum products such as diesel oil and gasolines have been transported in lined ships since the middle 1950s, primarily using IOZ coatings. There are many instances where ships have transported these products for over 20 years without corrosion or metal loss when coated with merely a single coat of the IOZ. Figure 19.42 is an example of a refined oil (i.e., gasoline diesel, lube oil, etc.) tank aboard an ocean-going tanker after several years of service in these commodities. Prior to high-performance coatings, the bulkhead steel in this type of service was corroded to one half its thickness in seven years. In this case, however, the tank lining was one coat of post-cured IOZ coating applied as a retrofit lining after the steel was severely corroded.



FIGURE 19.43: Typical marine exposures such as ships, docks, loading facilities, bulk storage, and miscellaneous onshore equipment require better than ordinary protection against the salt atmosphere.

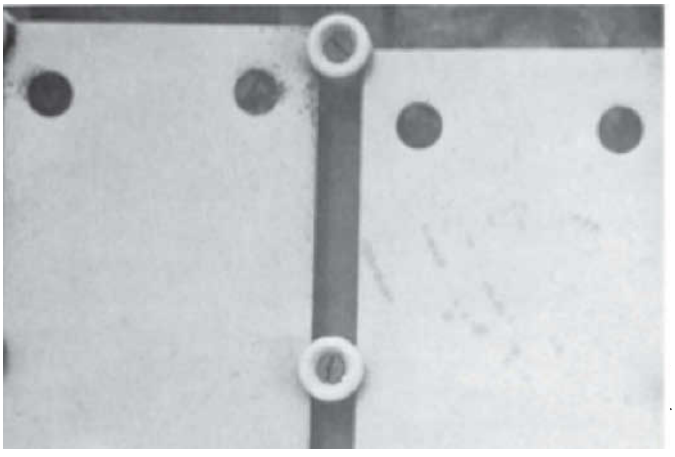


FIGURE 19.44: A sodium silicate-base IOZ coating after 25 years exposure on the 80-ft (24-m) lot at Kure Beach, North Carolina. Note the clean panel edges and the lack of corrosion around the holes.

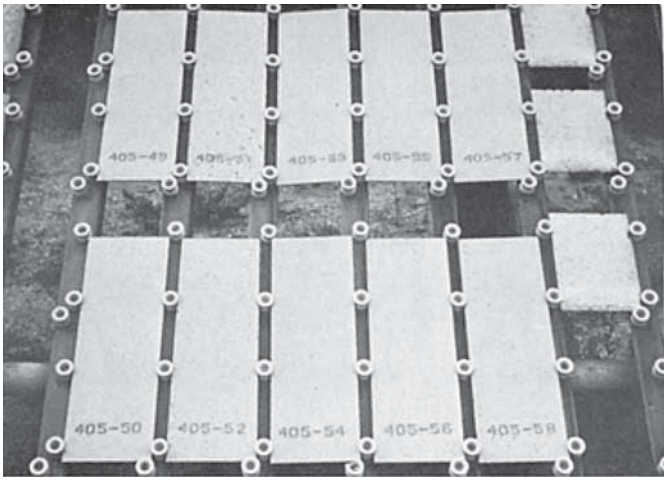


FIGURE 19.45: A series of zinc phosphate-base IOZ panels after 16 years of exposure on the 80-ft lot at Kure Beach, North Carolina. Note the lack of rust on the panel edges.

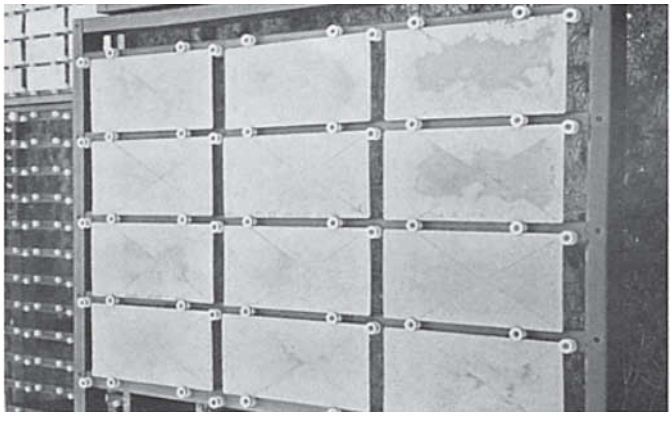


FIGURE 19.46: Panels coated with a lithium silicate-based IOZ coating after 15 years of exposure to a marine atmosphere. Note the absence of corrosion on both edges and scribes.

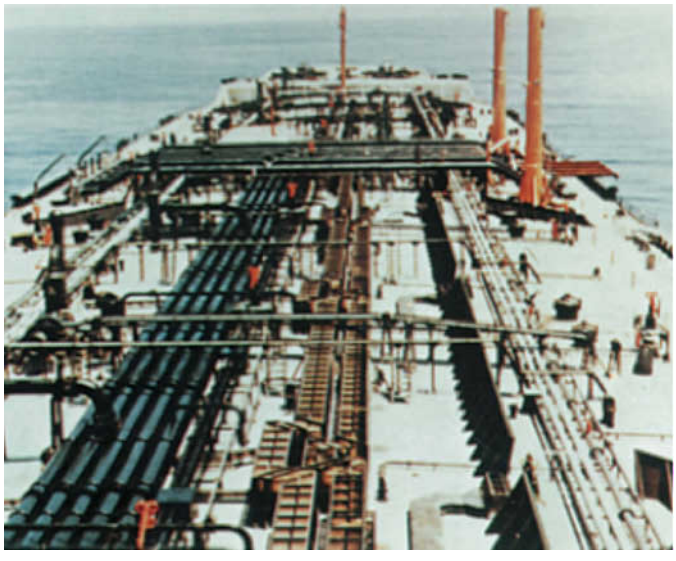


FIGURE 19.47: Deck of a large supertanker with one coat of an IOZ coating after five years of service.

the uses of protective coatings in this segment of the industry. It not only includes ships, docks, and their facilities, but also all inshore facilities within a reasonable distance of the seawater, since they are subject to increased corrosion problems due to the marine atmosphere. The one significant area not shown is that of offshore platforms and structures. However, the problems with offshore installations are similar to those for ocean-going vessels.

There are literally hundreds of different uses for high-performance coatings in the marine area. A complete presentation on contemporary marine coatings may be seen in Chapter 22, "Coatings for Marine Vessels." It has often been said that the IOZ coatings led to a revolution in the protection of marine structures. These coatings have been the one great breakthrough in protection of steel in a marine atmosphere in the last century.

As an example of the type of protection offered by the IOZ coatings, Figures 19.44, 19.45, and 19.46 show three distinct types of IOZ coatings that have been tested at the International Nickel 80-ft (24-m) Test Station at Kure Beach, North Carolina. The first is a sodium silicate-base material, showing panels exposed for over 25 years. The panels show no corrosion over this period of time, even along the edges and around the holes in the panels. Figure 19.45 shows a zinc phosphate-type coating that has been exposed to the same atmosphere for 16 years. Again, there has been no corrosion over this time period. Figure 19.46 shows a lithium silicate coating after 15 years, again in the same exposure. As can be seen, even the scribes have been well protected. While a panel with an equivalent exposure of ethyl silicate-based IOZs is not shown, there is no reason to doubt that ethyl silicate-based materials, using equivalent zinc content and coating thickness, would perform in

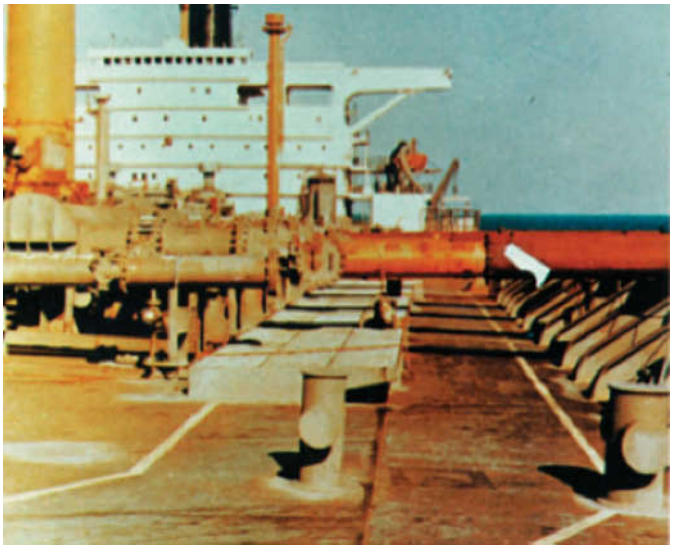


FIGURE 19.48: Coated ship deck near loading lines after five years of service shows rust stain from uncoated pipe, but no active corrosion of the deck itself.



FIGURE 19.49: Ship deck with one coat of an IOZ coating and vinyl topcoats after five years of service. Vinyl topcoat is used to protect against acid soot from boiler blow down.

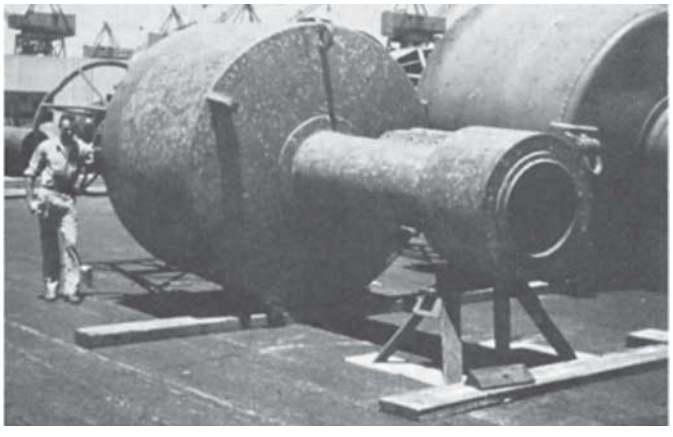


FIGURE 19.50: A large Coast Guard buoy coated with a vinyl primer and vinyl topcoats. Note the lack of corrosion or blistering after several years of exposure. White spots on the surface are barnacle bases.

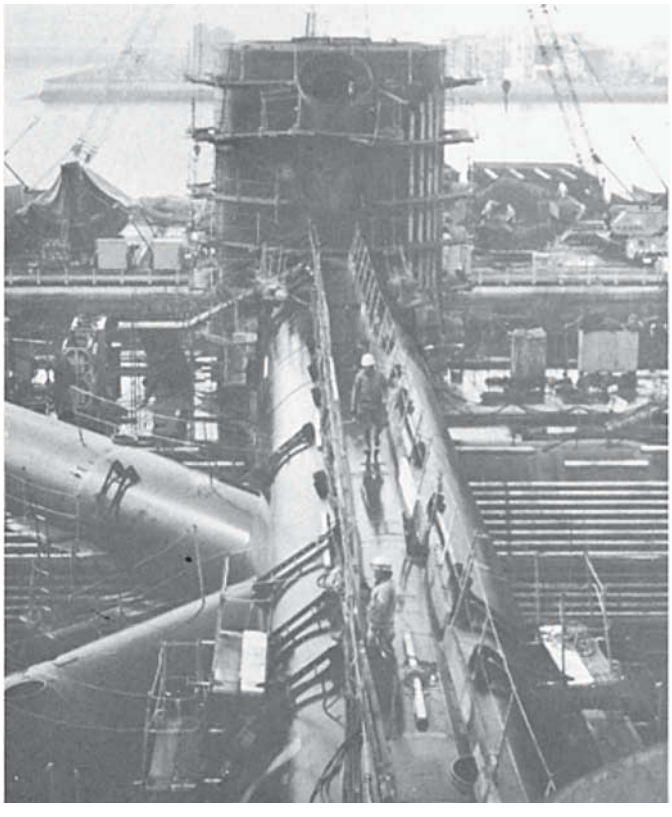


FIGURE 19.51: An underwater area of a very large semi-submersible drilling rig coated with an ethyl silicate IOZ base coat, epoxy polyamide primer, and two topcoats of coal tar epoxy.

an equivalent manner.

IOZ coatings have become the standard base for marine exposure protection and, while overcoated with organic materials in many cases, still provide the basic protection needed for the steel surface. The zinc base coat also eliminates the problem of undercutting of organic coatings when they are applied directly to steel surfaces under similar conditions.

Ships of all types have been one of the major users of high-performance coatings. Figure 19.47 shows the deck of a large supertanker protected with one coat of post-cured IOZ coating after five years of service. Note even the lack of rust stain on this deck.

Figure 19.48 shows a closer view of a similar tanker deck. In this case, the coated area is close to the loading lines, which is one of the most corrosive areas on the decks of these ships. This is due to the abrasion caused by the large flanges connecting the loading and unloading hoses to the ship's piping. This coating is also a single coat of in organic zinc, exposed for a period of five years. While in this case there is some rust stain on the coating, there is no active corrosion on any coated area.

Figure 19.49 is another example of a larger tanker deck, in this case protected with a base coat of IOZ, followed by vinyl topcoats. Again, after five years of service there was no evidence of coating failure on the entire deck. (The glossy appearance of the deck is due to a rainstorm that had just passed.) In this case, one of the reasons for the vinyl topcoats was to prevent contact of the IOZ coating with highly acid soot from the boilers, which precipitates on the deck during the boiler blow down. Use of high-sulfur crudes for steam production creates the highly acidic soot that, if allowed to contact IOZ, dissolves some of the zinc at the point of contact, creating a focal point for corrosion. The vinyl topcoats prevented this contact, and the coating system, provided excellent protection to the deck in spite of the acid soot precipitation.

There are also examples of excellent service from high-performance coatings without the use of IOZ. Such applications are becoming



FIGURE 19.52: A large jack-up drilling platform coated with IOZ and epoxy polyamide topcoats. Source: Ameron Corp., Monterey Park, California.

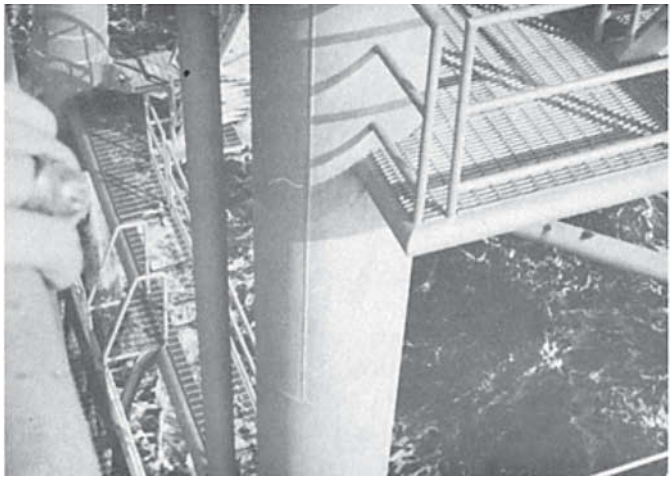


FIGURE 19.53: An offshore platform coated with IOZ and epoxy polyamide topcoats, showing excellent protection of the welds after 14 years of service in the Gulf of Mexico.

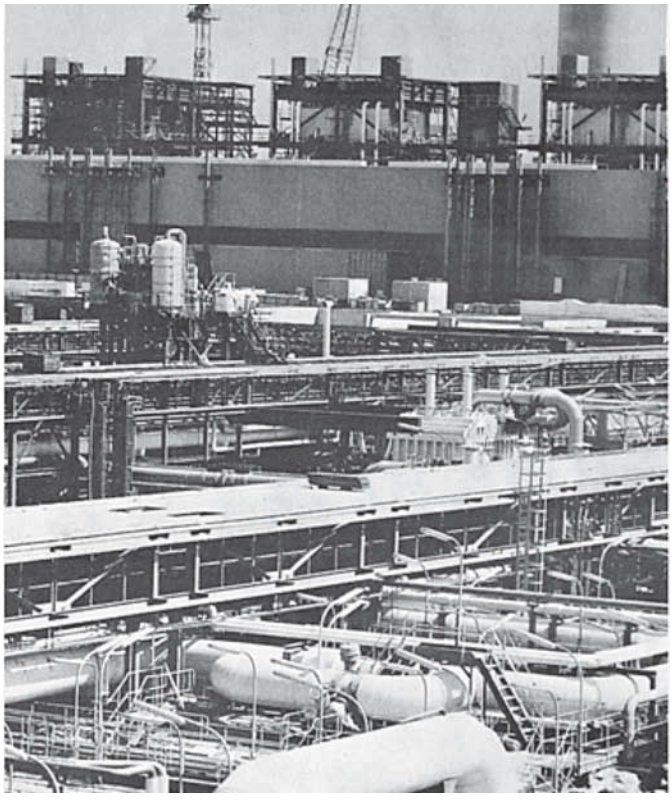


FIGURE 19.54: A saltwater desalinization plant along the Red Sea coated with IOZ and various high-performance topcoats. Source: Ameron Corp., Monterey Park, CA.

less frequent, however, due to the outstanding performance of the IOZs. Nevertheless, Figure 19.50 shows a large Coast Guard buoy that was coated with vinyl primer and three coats of vinyl topcoat. The buoy was removed for fouling removal after several years of service, at which time this photograph was taken. There was no corrosion, blistering, or other coating failure on the buoy at the time of its removal, and it was expected to be replaced in service without appreciable coating repair, except to add a coat of anti-foulant.

Figure 19.51 shows one of the largest offshore drilling platforms during construction. The coating used on all underwater portions of this semi-submersible drilling platform was a base coat of ethyl silicate-base IOZ, followed by an epoxy polyamide primer, and two or more coats of coal tar epoxy to provide the best possible corrosion protection.

Incidentally, corrosion tests for marine immersion that were conducted in Japan using coatings of different types from various areas of the world yielded similar results. Of all the coating systems tested, the one just described for use on the semi-submersible offshore drilling structure was the best of all systems tested with no corrosion, blistering, or other coating failure for the duration of the test.

Figure 19.52 shows the complex structure of an offshore jack-up drilling rig, all of which is protected by in organic zinc and epoxy polyamide topcoats. The proper protection of such a complex structure could not be obtained without the use of this type of high-performance coating system.

Figure 19.53 shows a close-up view of an offshore platform coated with IOZ, followed by polyamide epoxy topcoats. After 14 years of service in the Gulf of Mexico, the yellow color was high-visibility yellow included in the epoxy topcoat.

Seawater desalination plants are areas where marine corrosion can be concentrated. Several large desalination plants have been installed along the Red Sea coast of Saudi Arabia, all of which must be protected by high-performance coatings. Figure 19.54 illustrates the complexity of such plants, which must withstand not only the marine atmosphere, but also the high humidity in that area of the world. IOZ-base coats and various high-performance topcoats provide the basis for this protection.

All marine exposures are severe, whether they are full immersion, splash zone, or atmospheric. Marine structures of all types would be short-lived without the protection provided by the high-performance coating systems.



FIGURE 19.55: The Golden Gate Bridge across the mouth of San Francisco Bay coated with IOZ base coats and characteristic orange topcoats. Coating maintenance has been reduced to a minimum since the use of the IOZ base coat.

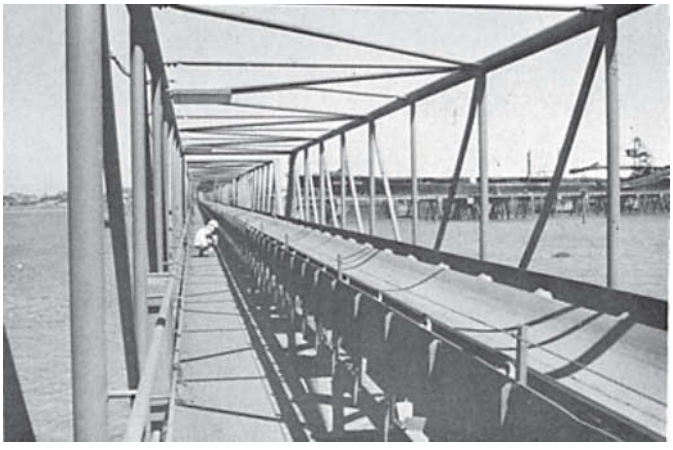


FIGURE 19.56: A bridge structure carrying an iron ore conveyor on the West Coast of Australia coated with one coat of inorganic zinc and showing no sign of corrosion.

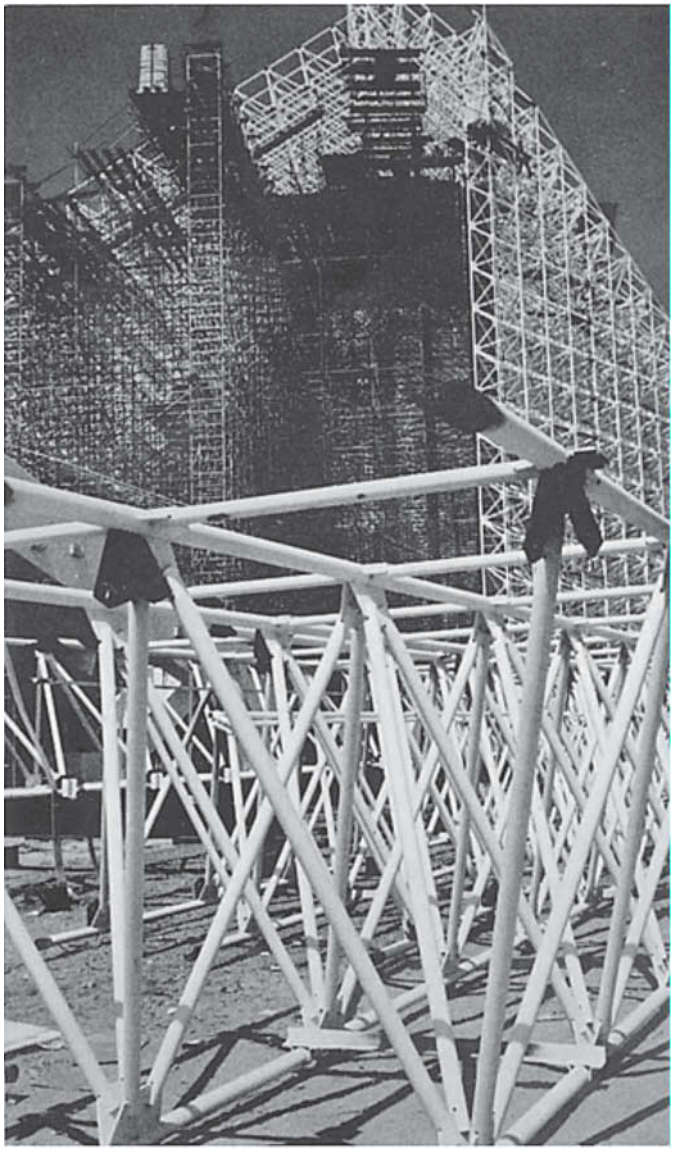


FIGURE 19.57: Structural steel for the "Glass Cathedral" in Southern California. Inorganic zinc was used as a base coat for all sections. Source: Ameron Corp., Monterey Park, CA.

Bridges

In some cases, bridges can be considered in the marine category, since many are located in marine areas, along coastal sections, or over saltwater waterways. There are also thousands of bridges, particularly railroad bridges, that are subject to salt conditions even though they are located inland, away from the coast. Salt conditions in this case are due to refrigeration brines, which have caused serious corrosion in years past.

Bridges are usually difficult structures to protect because of the many angles, corners, braces, rivets, bolts, high-tension cables, and similar methods of construction. Bridges have always been a problem to maintain, and the best possible type of coating system generally has been employed to maintain them in a safe condition. Even in the days prior to high-performance coatings, bridges were coated with red lead, linseed oil, and graphite coatings, which were the best available at the time.

IOZ also has made an impact on the protection of bridges inasmuch as it provides long-term protection and reduces the constant maintenance that is otherwise necessary. Hundreds of bridges around the world have been coated with IOZ and many coated with additional topcoats, ranging from alkyds to vinyls and epoxies. Many bridges have been in service for 10 or more years without appreciable maintenance when using the inorganic and high-performance topcoat system.

One of the most outstanding of these bridges is the Golden Gate Bridge across San Francisco Bay. This is an extremely difficult corrosion area, since it is in a marine atmosphere and there is constant fog in the area, although actual rainfall is relatively mild. Any salts

that build up on the bridge due to the prevailing wind across the entrance to the bay are kept in a continually moist condition, creating a highly corrosive situation.

For at least 15 years, the Golden Gate Bridge was coated with a base coat of IOZ, providing the needed corrosion protection. The application consists of abrasive blasting the steel to a thoroughly clean condition and applying the IOZ base coat, followed by two or more topcoats of the typical Golden Gate Bridge color. The bridge is an excellent example of the use of high-performance coating systems for maximum protection of steel structures. Figure 19.55 shows the Golden Gate Bridge under normal conditions (i.e., moist sea air with a constant breeze, usually a mid-day sun, with the fog bank off the coast waiting to blow in the early afternoon).

Figure 19.56 shows a bridge of an entirely different type. This is a bridge carrying a conveyor for loading iron ore aboard ship. The installation is located on the West Coast of Australia. The entire structure is coated with IOZ without topcoats, and the exposure is typical of a marine coastal atmosphere.

Specialized Uses

There are literally hundreds of specialized uses for high-performance coatings throughout the world. One of these is the use of IOZ as a base coat for all of the structural steel in the "glass cathedral" in Southern California, which is now considered a major showplace in the area. The IOZ in this particular case was used in order to reduce maintenance on a very complex structure to an absolute minimum. The entire structure is coated with white topcoats for maximum light and visibility (Figure 19.57).

Another unique application of high-performance coatings is the use of epoxy primer and polyurethane topcoats on aircraft. In this case, the coatings are subject not only to abrasion from sand, rain, and hail, but also to deicing fluids, hydraulic oils, and other similar chemicals. Use of this coating system, not only on private aircraft (Figure 19.58) but in many commercial aircraft as well, provides the best appearance along with high performance and protection.



FIGURE 19.58: A private jet aircraft coated with epoxy primer and aliphatic polyurethane topcoats. Maximum appearance and protection are obtained by using such a system. Source: Ameron Corp., Monterey Park, CA.

The use of high-performance coatings has been a major factor in reducing many different types of corrosion throughout the world. The applications for coatings range from exposures to rural atmospheres, industrial and marine conditions, splash, and fumes, to full immersion in many types of chemicals. This type of protection has only become available in the last 50 years, yet coatings have made many new plants and processes practical by allowing the use of low-cost materials through effective protection by coatings. Since steel and concrete are the most common building materials for industrial plants, ships, offshore structures, power plants, sewage and water works, and so forth, and with their costs escalating rapidly with inflation, the long-time protection of such structures is now a necessity. High-performance coatings over the last half-century have proven their effectiveness in providing this protection.

Coatings Under Thermal Insulation

One area that received scant attention in the industry prior to the 1950s is coatings under insulation (CUI).[1] Because of several catastrophic explosions and fires at plants prior to the year 2000, greater attention and research have been concentrated on developing new and better methods to protect the three main metals used in process that operate at elevated temperatures, namely carbon steel (CS), SS and duplex SS.

The culprit in corrosion under insulation is water. Two primary sources of water involved in CUI are:

(a) Infiltration from external sources
(b) Condensation

Water infiltrates from such external sources as:

- Rainfall
- Drift from cooling towers
- Condensate falling from cold service equipment
- Steam discharge
- Process liquids spillage
- Spray from fire sprinklers deluge systems, and washdowns
- Groundwater
- Condensation on cold surfaces after vapor barrier damage

External water enters an insulation system primarily through breaks in the weatherproofing. The weatherproofing breaks may be the

result of inadequate design, incorrect installation, mechanical abuse, or poor maintenance practices.

Condensation results when the temperature of the metal surface is lower than the atmospheric dew point. Although infiltration of external water can be reduced and sometimes prevented, insulation systems cannot be made vapor tight, so condensation as a water source must be recognized in the design of the insulation system.

Contaminants such as chlorides and sulfates are commonly found under insulation. Whether their source is external or internal, they are particularly detrimental because their respective metal salts are highly soluble in water, and these aqueous solutions have high electrical conductivity, thus accelerating the corrosion process.

The service temperature of equipment, vessels, and piping often varies, and the corrosion rate of CS under insulation is affected by:

(a) Intermittent or variable (cyclic service) operation of equipment
(b) Temperature variations along the height or length of the equipment
(c) Temperature at which attachments to equipment operate
(d) Idle or mothballed conditions

Attempts to prevent water from entering insulated systems are not sufficiently reliable to prevent CUI, and corrosion protection techniques such as inhibitors and cathodic protection have been less effective than protective coatings in mitigating corrosion under insulation.

Protective coatings remain the most reliable defense against CUI or all metal substrates. The following tables have been adapted from NACE SP0198-2010.[1]

TABLE 19.1: Typical Protective Coating Systems for Austenitic and Duplex SS under Thermal Insulation

System No.	Temperature Range	Prime Coat µm (mils)	Finish Coat(A) µm (mils)
SS-1	-45 to 60 °C (-50 to 140 °F)	High build epoxy 125-175 (6-7)	N.A.
SS-2	-45 to 150 °C (-50 to 300 °F)	Epoxy phenolic 100-150 (4-6)	Epoxy phenolic 100-150 (4-6)
SS-3	-45 to 205 °C (-50 to 400 °F)	Epoxy novolac 100-200 (4-8)	Epoxy novolac 100-200 (4-8)
SS-4	-45 to 540 °C (-50 to 1,000 °F)	Air-dried silicone or Modified silicone 37-50 (1.5-20)	Air-dried silicone or Modified silicone 37-50 (1.5-20)
SS-5	-45 to 650 °C (-50 to 1,200 °F)	Inorganic copolymer or coatings with an inert multi-polymeric matrix 100-150 (4-6)	Inorganic copolymer or coatings with an inert multi-polymeric matrix 100-150 (4-6)
SS-6	-45 to 595 °C (-50 to 1,100 °F)	Thermal sprayed aluminum (TSA) with minimum of 99% alumi-num. 250-375 (10-15)	Optional: sealer with either thinned epoxy or silicone coating at approximately 40 (1.5)
SS-7	-45 to 540 °C (-50 to 1,000 °F)	Aluminum foil wrap with min. thickness of 64 (2.5)	N.A.

Note: If IOZ-rich coating is applied in a shop and topcoat is applied in the field, proper cleaning of the IOZ-rich coating is required. The used of IOZ-rich coating under insulation is not a preferred system for service temperatures in the CUI range up to approximately 175 °C (350 °F). However, bulk piping is often coated with IOZ-rich coating in the shop and some owners purchase this piping for use under insulation. In these cases, the IOZ-rich coating should be topcoated to extend its life.

TABLE 19.2: Typical Protective Coating Systems for Carbon Steels under Thermal Insulation and Fireproofing

System No.	Temperature Range	Prime Coat µm (mils)	Finish Coat µm (mils)
CS-1	-45 to 60 °C (-50 to 140 °F)	High build epoxy 130 (5)	High-build epoxy 130 (5)
CS-2 (shop application only)	-45 to 60 °C (-50 to 140 °F)	N.A.	Fusion-bonded epoxy (FBE) 300 (12)
CS-3	-45 to 150 °C (-50 to 300 °F)	Epoxy phenolic 100-150 (4-6)	Epoxy phenolic 100-150 (4-6)
CS-4	-45 to 205 °C (-50 to 400 °F)	Epoxy novolac or silicone hybrid 100-200 (4-8)	Epoxy novolac or silicone hybrid 100-200 (4-8)
CS-5	-45 to 595 °C (-50 to 1,100 °F)	Thermal spray aluminum (TSA) with minimum of 99% aluminum. 250-375 (10-15)	Optional: sealer with either thinned epoxy or silicone coating at approximately 40 (1.5)
CS-6	Optional: sealer with either thinned epoxy or silicone coating at approximately 40 (1.5)	Inorganic copolymer or coatings with an inert multi-polymeric matrix 100-150 (4-6)	Inorganic copolymer or coatings with an inert multi-polymeric matrix 100-150 (4-6)
CS-7	60 °C (140 °F) maximum	Thin film of petrolatum or petroleum wax primer	Petrolatum or petroleum wax tape 1-2 (40-80)
Bulk or shop-primed pipe, coated with IOZ	-45 to 400 °C (-50 to 750 °0F)	N.A.	Epoxy novolac, epoxy phenolic, modified silicone inorganic copolymer, or a coating with an inert multi-polymeric matrix. Consult manufacturer for thickness and temperature limits.
CS-9 CS under fireproofing	Ambient	Epoxy or epoxy phenolic 100-150 (4-6)	Epoxy or epoxy phenolic 100-150 (4-6)
CS-10 Galvanized steel under fireproofing	Ambient	Epoxy or epoxy phenolic 100-150 (4-6)	Epoxy or epoxy phenolic 100-150 (4-6)

Reference

1. NACE SP0198-2010, "Control of Corrosion Under Thermal Insulation and Fireproofing Materials—A Systems Approach" (Houston, TX: NACE International, 2010).

20 Elastomeric (Rubber) Linings

Despite the tremendous advances in technology over the course of the 1990s and early 2000s, there are still some aggressive services that cannot be served by any liquid or powder applied organic protective coatings or lining. Natural and synthetic rubber compounds have been used for many years as linings for process and storage equipment in these severe services. Most often the problem of severe chemical and abrasive exposures require this type of lining. Thin film solution coatings, even those that are truly 100% solids, are generally unable to withstand such severe service conditions.

In their crude state, natural and synthetic rubbers possess physical properties that must be modified to obtain rubber linings capable of withstanding the aggressive services to which they are exposed. This is accomplished by compounding crude rubbers, and vulcanizing them into products that fit specific functions.

Curatives and Vulcanizing

After the addition of curing or vulcanizing agents, or accelerators, the application of heat causes cross-linking, yielding a durable product by binding the long polymer chains together. Sulfur, the first successful curing ingredient, is the basis of vulcanization. Other oxidizing agents such as selenium, telerium, organic peroxides, and nitro compounds, and also generators of free radicals, such as organic peroxides, azo compounds, and certain organic sulfur compounds such as alkyl thiruram disulfides, are also capable of vulcanizing rubber.

Pigments

Vulcanization improves the elasticity and aging properties of rubber, but in most cases it is necessary to further enhance such properties as tensile strength, abrasion resistance, and tear resistance by the incorporation of fillers. The most universally used reinforcing filler is carbon black, including furnace and thermal blacks. Inorganic reinforcing pigments such as zinc oxide (ZnO) and silica are used for reinforcement of light-colored linings. Inert fillers, such as whiting and various types of clays, serve merely as extenders and facilitate the processing of the compound.

Types of Rubber Linings

The materials in the rubber lining industry generally fall into one of three groups: rubber, synthetic, or combinations of both. The blend is designed to modify either one for a particular exposure by taking advantage of specific chemical and physical capabilities in the combination. The formula or recipe for the various combinations as well as the basic materials is specific for each manufacturer; there are no truly generic rubber linings. The generic term “rubber” does not mean that all manufactured stock is the same formula.

Natural rubber stock can be divided into a number of different systems. These are:

- Soft Rubber
- Semi-Hard Rubber
- Hard Rubber (Ebonite)
- Three-Ply Rubber

Synthetic rubber stock can also be divided into a number of different systems.

- Butyl
- Chlorobutyl
- Neoprene
- Hypalon
- Ethylene Propylene Diene Mix (EPDM)
- Nitrite

With these basic materials, one major manufacturer has 82 different compounds and combinations listed in their catalog. There are several special materials available.

- Chemically Cured Stock
- Pre-Cured Stock
- Self-Vulcanizing Stock

When preparing for a lining project, it is critical that the exposure anticipated be carefully defined in very accurate detail, including but not limited to:

- Type and Design of Equipment
- Solution in Detail
- Temperature of Service
- Abrasiveness of Solution
- Contaminants
- Pressure or Vacuum in Vessel to be Lined

Elastomeric lining materials are generally applied in 3/16 or ¼ in (4.8 or 6.4 mm) thickness. Based upon the service conditions defined, the manufacturer will recommend the type of stock and the thickness.

Most of the uncured materials are temperature sensitive. High temperature over time will cause the cure cycle to progress. Normal shop inventory and materials stored on site for a major project must be kept under tightly controlled conditions to prevent deterioration of its properties. Cements and adhesives will also have a temperature dependent shelf life.

Vessel Design

All surfaces must be accessible and open enough to accept sheet stock. All structural supports and fittings should be on the exterior. All penetrations should be large enough to accept sheet stock and preferably, should be flanged openings. Other attachments or piping can be introduced through the flange cover. All internal welds should be butt seams with no overlap seams. When all fabrication and welding is complete, the welds should be inspected for the following defects.

- Incomplete Joint Penetration
- Undercutting
- Overlapping
- Weld Spatter
- Weld Slag
- Excessive Weld Profile
- Excessive Weld Face Reinforcement
- Excessive Weld Face Concavity
- Sharp Edges and/or Projections

The steel surfaces should be inspected for the following defects.

- Laminations
- Hackles
- Needles
- Gouges
- Deep Pits
- Stamp Marks
- Center Punch Marks
- Arc Strikes
- Rogue Welds

When grinding is required to correct any weld or plate defects, the responsible engineer must establish the allowable reduction in plate or weld thickness after the grinding is complete.

Fillet welds should be ground to a minimum of ¼ in radius. Edges should be ground to a minimum ⅛ in (3.2 mm) radius. All grinding should be performed so that surfaces are faired into adjacent areas at a minimum 10-degree angle.

All the preceding conditions and corrective actions are designed to eliminate any possibility of trapping air under the sheet stock during application. The requirements for sheet lining are more strict than those for liquid organic coatings and linings.

Surface Preparation

Metal Surfaces

Industry practice is to abrasive blast all surfaces to NACE 1/SSPC-SP 5, "White Metal Cleanliness," with a profile of 1.5 to 3 mils (38 to 63 µm) All surfaces must be vacuum cleaned to remove the maximum possible dust and abrasive residue from the surface.

Concrete Surfaces

Although not often specified, rubber can be applied to concrete surfaces. The surface must be cured and dry. The surface must be prepared by abrasive blast or scabbler to open all air pockets and remove all surface contamination. Water-soluble contaminants must be removed by proper detergent and power washing, followed by thorough drying. The surface should then have a trowel-applied vertical or overhead concrete repair mortar to strike the surface evenly. After proper cure, the adhesive system should include a saturant type primer compatible with the cement system.

Adhesives

The adhesive will be manufacturer and material specific and should never be mixed with one another. The type of material and number of coats will vary. Some will require a tack coat applied to the stock prior to application. Mixing, application, and time between coats must be strictly observed, even more so than in the application of any organic coating.

Ventilation must be maintained during the cementing process. The solvents are heavier than air and will settle to the bottom of the unit being lined. Air volume and velocity across the surface must be sufficient to remove the vapors from the vessel. Vapor must also be below the lower explosive limit (LEL) and toxic level value (TLV).

Application of Sheet Stock

The sheet stock will be rolled with plastic sheet to prevent sticking together. This sheet will have a diamond pattern. The pattern left on the adhesive surface of the rubber stock must be the convex pattern. The ridges of the concave pattern represent about 18% of the surface and the diamond pockets will trap air. The convex diamond represents about 82% of the surface and the depressions form continuous lines for the air to be rolled (stitched) out in process of application.

When lining vertical surfaces, it is customary to start at the bottom so that the sheet overlap faces down. Each level of sheet should be shifted. No areas of lining shall have more than two layers of sheet stock. When the sheet corners come together, the overlay shall be cut down before applying the third layer. When rolling the rubber stock, 100% of the surface shall be covered uniformly, forcing any air from the rubber–steel interfaces. Welds, corners, and other such areas shall be stitched in the same manner to remove air and force the rubber into the existing configuration. Qualified applicators are critical at this point to ensure that air pockets are removed at the interface and sufficient contact pressure is exerted to assure uniform adhesion to the substrate.

The applicator will normally furnish and line several covers that are fabricated to fit over the manhole and/or pipe flanged opening into the vessel. The plates are processed during the project by the same individuals applying the lining. They are installed on the exterior flanges so that the exposure is the same as all areas of the tank, rubber ex- posed to steam, and steel exposed to atmosphere.

Inspection Prior to Cure

All areas of the lining should be subject to a spark test at a voltage specified by the manufacturer. The voltage will vary depending on the type of material and the thickness of the stock. It is commonly accepted that 0.04 in (1 mm) will equal 1,700 V. Normal range of voltages would be as follows.

- 3/16-in stock: 15,000 V
- 1/4-in stock: 20,000 V
- 3/8-in stock: 30,000 V

These figures are based on 20% of the lower dielectric strength of most natural, butyl, and neoprene materials. If a higher percentage is acceptable to the manufacturer, considerably higher voltages can be used. Inspectors must make a thorough visual inspection of the lining system and edges of the lap or cap seams.

Cure

In a shop with an autoclave or a larger pressure vessel, steam pressure will be used and time-and- temperature will be specified by the manufacturer.

In field operations, the atmospheric steam or boil cure will be used and again, the time-and- temperature will be specified by the manufacturer.

The primary problem with atmospheric steam cure is maintaining uniform outside steel temperature. Thermocouples (preferably recording types) should be installed at various elevations and quadrants of the vessel. Heat will tend to rise inside the vessel, creating considerable difference in top to bottom plate temperature. Control of bottom temperature is most important for complete cure.

The possibility always exists when atmospherically curing a field storage tank that the steam source will fail. With all openings covered with plastic or other material, the tank internal can very quickly go to vacuum conditions when the steam condenses. The tank will collapse! It is recommended that a vacuum breaker designed to split the plastic be attached to at least one opening for protection against the vacuum.

Condensation on the tank bottom is also a normal problem in atmospheric cures. A properly designed and constructed tank will have a solid crown bottom so that moisture will go to the ring wall and into a condensate sump. Provisions must be made to remove the condensate to the outside of the tank.

When two surfaces of uncured rubber are bolted together, the surfaces or surface of the uncured stock must be treated to prevent adhesion.

Method 1 Mix powdered graphite and water to a smooth paste and spread evenly over the uncured rubber.

Method 2 Use zinc sterite and soapstone the same way as Method 1.

Method 3 Use aluminum foil to separate the two materials.

It is not uncommon to stop the cure when the condensate leaving the tank reaches 170 °F (77 °C). When cooled down, the tank can be inspected and repairs made. The tank is then put through the full cure cycle.

Inspection Post Cure

A full visual inspection must be performed with particular attention to blisters and edges of seams. A full spark test should be completed on all areas of the vessel. The test panels will be removed and pull tests made for adhesion in accordance with ASTM D429, "Standard Test Methods for Rubber Property—Adhesion to Rigid Substrates, Method B." The minimum pull test value must be 25 lb/in (4.5 kg/cm) and apply to both the substrate and ply adhesion on calendered stock. If the test panels fail to meet the minimum, tests should be made on the tank itself.

Surface hardness should be tested with a Durometer gauge and compared to levels specified by the manufacturer. It is important to note that the surface hardness does not indicate the cure of the steel-rubber interface and consequently, the adhesion quality of level.

Repairs

Repairs required at this point in time, and after future inspections, must be agreed to by the owner and applicator based on the recommendations of the manufacturer. Repair materials can be:

1. The Original Material
2. Pre-Cured Material
3. Chemically Cured Material
4. Self-Vulcanizing Material

The manufacturer will furnish written procedure for the various systems. These will include:

- Surface Preparation
- Cementing
- Rubber Application by Type
- Cure Cycle—Time, Temperature, and Method Repairs may occur before and after curing. Repairs made before vulcanization are called "overlays." The overlay is vulcanized with the remainder of the lining and becomes as one with all the seams, sealer strips, or any other part of the lining. For purposes of this book, we shall consider only the repair of sheet applied rubber linings that have already been cured and/or placed into service, which generally goes as follows.

The first step is to find the area that needs attention and must be repaired. The usual method of determining the continuity of the rubber lining is by conducting a spark test of the entire lining with a high voltage detector set at the voltage recommended by the lining manufacturer, marking the pinholes or discontinuities as they are found so that none of the problems can be overlooked. In the severe service that rubber linings are expected to resist, only one pinhole can create a catastrophic failure.

1. Remove the lining around the damaged area back to an area of good adhesion. This may require grinding the rubber lining around the damaged area.
2. Prepare the substrate surface in the best manner possible (e.g., abrasive blasting, vacuum blasting, etc.). It is absolutely essential that abrasive blasting be done to NACE No. 1/SSPC-SP 5 "White Metal Cleanliness." If metal loss through pitting is extensive, it must be repaired by adding weld metal to small indentations or totally replacing with a metal patch inlaid to fit the area removed and welding inside and outside. If the rubber-lined tank is a pressure vessel, it must be hydrostatically tested to one and one-half its normal working pressure. All edges of the remaining rubber around the repair should be feathered (ground to a bevel) or skived. The sound, firmly adhered rubber lining should be roughened to at least 4 in (102 mm) beyond the exposed metal. The cleaned surface must be immaculately vacuumed to remove all cleaning residue.
3. Apply primer and/or adhesive. If the lining being repaired is a soft rubber lining, the primer and all other adhesives must be applied to the exposed metal only. If the lining being repaired is a semi-hard or hard rubber lining, the primer and all other adhesives must be applied to the metal as well as the roughened area of the rubber to be overlapped. Patches smaller than 12 in2 (0.09 m2) have an uncured rubber panel the size of the exposed metal inlaid to bring the surface flush to the existing lining. Trim the edges of the inlay even with the parent lining and re-cement to top of the inlay and an area approximately 4 in all around its perimeter. After proper drying time, apply an overlaid patch to cover the inlay. Spark test the area to ensure continuity of the lining and patch area. It is absolutely critical that all air bubbles are physically removed from beneath the new patch with a rubber roller, sticher, or goose-neck sticher, depending on the slope of the repair area, or a failure will reoccur.
4. Cure the patch in place by heating (in many cases steam is used) or by curing chemicals. The cure must be equivalent to the original lining. Retest with high voltage spark tester to assure full continuity of the entire lining system. (Worker's shoes or tools can easily damage a good lining while repairing a bad spot.)

Curing is the critical part of the process, and every care must be taken to cure the repair area so that the end result is equivalent to the original lining. Since there are many grades of rubber lining, and each has its own idiosyncrasies, manufacturer's instructions should be carefully followed.

Safety

Most rubber linings will be installed in a confined space. The adhesive materials are flammable (explosive) and toxic. Proper ventilation, electrical equipment, and tools must be selected based on the conditions in the work area. Personal clothing and breathing apparatus must also be selected to be compatible with the work atmosphere.

Reference Documents and Standards

Any corrosion engineer, maintenance manager, inspector, or other person involved in either the installation or repair of rubber linings would do well to familiarize himself or herself with the following documents and standards.

- ASTM D1566 (Latest Revision), "Standard Terminology Relating to Rubber"
- ASTM D1418 (Latest Revision), "Standard Practices for Rubber and Rubber Lattices—Nomenclature"
- ASTM D3486 (Latest Revision), "Standard Practices for Installation of Vulcanizable Rubber Tank Linings and Pipe Linings"
- ASTM D429 (Latest Revision), "Standard Test Methods for Rubber Property—Adhesion to Rigid Substrates, Method B"
- ASTM D4276 (Latest Revision), "Confined Space Entry, Practice"
- ASTM D-2240 (Latest Revision), Rubber Property—Durometer Hardness"
- British Standard Code of Practice CP 3003: Part 1 (Latest Revision), "Lining of Vessels and Equipment for Chemical Processes—Rubber"
- NACE SP0178 (Latest Revision), "Fabrication Details, Surface Finish Requirements, and Proper Design Consideration for Tanks and Vessels to be Lined for Immersion Service"
- NACE Draft T-6A-62/1996, "Rubber Lining for Abrasion and Corrosion Service"

The Author is particularly indebted to Sixtus J. (Jack) Oechsle for contributing his years of experience in all types of organic solution and sheet linings for industrial and marine vessels to the drafting and completion of this chapter.

22 Coatings for Marine Vessels

Introduction

A review of the trends in newbuilding and maintenance activities in the marine industry could easily make a strong case for the statement that there has been more new technology (particularly coatings technology) introduced into the marine industry than any other worldwide industry. While many of the products used in the marine environments are technically the same as those used in the industrial environments, there is a great deal of modifications used to adapt the technology to the specific demands of the marine industry. Specific areas where tremendous improvements in technology have taken place are as follows:

1. The most significant changes in marine coatings technology have been in the protection of the underwater hull, particularly in the protection against fouling of the hull by marine organisms. While older rosin-based technology is still used on smaller-sized shallow-water boats, barges, etc., that are relatively easy to bring into a drydock or inclined slipway for repairs and refurbishing of the anti-fouling, the huge expense of drydocking a large ocean-going vessel makes it imperative to constantly seek new coating systems that extend the drydock intervals to 60 months and beyond. Perhaps the greatest leap in technology for the marine industry has been the development of foul-release coatings as an alternative to antifouling coatings. This entire subject will be explained in detail later in this chapter. Examples of these systems can be seen in Tables 22.1, 22.2, and 22.3.

TABLE 22.1: Premium Performance Four-Coat Self-Polishing Antifouling System

Coat No.	Low to medium speed vessels with frequent calls in port. Service intervals up to 90 months.	DFT (µm)	Total DFT
1	Self-priming polyamide/amine anticorrosive	175	
2	Self-priming polyamide/amine anticorrosive	175	
3	Polyamide amine adduct tie coat	125	
4	Nano-capsule silyl acrylate (fiber-reinforced)	175	650

TABLE 22.1a: Patented Premium Performance Four-Coat Linear Polishing Antifouling System

Coat No.	Low to medium speed vessels with frequent calls in port. Service intervals up to 90 months.	DFT (µm)	Total DFT
1	Self-priming epoxy anticorrosive	125	
2	Self-priming epoxy anticorrosive	125	
3	Modified silicone tie-coat	100	
4	Linear-polishing antifouling	150	500

TABLE 22.2: Typical Premium Performance Four-Coat Foul Release System

Coat No.	Silicone hydro-gel polymer coating for deep-sea vessels with service speeds above 8 knots. Service intervals up to 90 months.	DFT (µm)	Total DFT
1	Self-priming polyamide/amine anticorrosive	175	
2	Self-priming polyamide/amine anticorrosive	175	
3	Silicone-based tie coat	125	
4	Silicone hydrogel polymer coating	150	625

TABLE 22.2a: Patented Premium Performance Slime Release System

Coat No.	Fluoropolymer coating for deep-sea vessels, even those in warm waters, and slow steaming. Service intervals up to 90 months.	DFT (µm)	Total DFT
1	Self-priming epoxy anticorrosive	150	
2	Modified epoxy tie coat	100	
3	Linear polishing fluoropolymer coating	125	
4	Linear polishing fluoropolymer coating	125	500

TABLE 22.3: Typical Premium Performance Four-Coat Foul Release System

Coat No.	Fluoropolymer foul release coating system for all types of vessels. Service intervals up to 120 months.	DFT (µm)	Total DFT
1	Pure epoxy abrasion-resistant aluminum coating	150	
2	Pure epoxy abrasion-resistant bronze coating	150	
3	Silicone elastomer tie coat	150	
4	Fluoropolymer foul release coating	180	630

TABLE 22.4: Typical Film Loss in ASTM D4060 Taber Abrasion Tests

Generic Description	Type of Curing Agent	Lowest Film Loss (mg)	Highest Film Loss (mg)
IOZ primer	Potassium/lithium silicates	40	Unavailable
	Ethyl silicate	100	326
Zinc-rich epoxy	Polyamide	100	300
	Amine adduct	67	385
Solvent-free epoxy	Cycloaliphatic amine	100	221
	Amine adduct	107	200
	Polyamine	41	200
	Polyamide	84	259
	Novolac	100	287
Multi-purpose epoxy	Polyamide/polyamine blend	102	250
	Polyamide	94	210
	Phenalkamine	65	120
Tank lining	Phenolic	41	88
	Novolac	90	260
Surface-tolerant epoxy	Phenalkamine	30	120
Pure epoxy	Polyamine	30	95
Glass flake epoxy	Polyamide	90	120

TABLE 22.5: Premium Performance Abrasion and Corrosion-Resistant System for a Cargo Hold Area

Coat No.	Product Description	DFT Range (µm)	Recoat Min. @ 25 °C	Recoat Max @ 25 °C
1	Ethyl silicate inorganic zinc	50-75	18 h	Unlimited
Stripe Coat	High solids amine epoxy red oxide	25-75	4 h	5 days
2	High solids epoxy buff	100-150	4 h	5 days
3	High solids epoxy gray	100-150	4 h	N.A.

TABLE 22.5a: Alternative High-Performance Abrasion and Corrosion-Resistant System

Coat No.	Product Description	DFT Range (µm)	Recoat Min. @ 25 °C	Recoat Max @ 25 °C
1	High solids glass flake epoxy	750-1,000	N.A.	N.A.
NOTE	Epoxy holding primer may be used	25-75	2 h	24 h

2. Another significant change has been in the development of "universal primers." There is no primer that is truly universal in the technical sense, but new formulations have broadened their potential use to all but the most critical or most specific marine protective or tank lining environments. Newer epoxy formulations have been developed that allow for application over a broad range of substrates and existing coating layers, both as a means of getting greater productivity in newbuilding operations and as a means of extending the recoat window between application of primers and intermediate or finish coats in a coating system.
3. New technology abrasion-resistant coatings for dry cargo holds, working decks, and helicopter decks are now commonly produced with all the abrasion-resistant pigment incorporated into the coating during the manufacturing process, compared to the previous systems that required application of pigments such as sand, quartz, slag, etc., into the freshly applied epoxy intermediate or finish coat. The relative abrasion resistance of different organic and inorganic coatings can be seen in Table 22.4. An example of these abrasion-resistant coating systems can be seen in Table 22.5.

It is appropriate for the marine coatings engineer or project manager to differentiate between the newbuilding situations vs. the maintenance situations. In international shipyard newbuilding situations, the following are often standard:

- New steel grit blasted to Sa 2.5,1 "Very Thorough Blast-Cleaning," for most parts of the vessel
- Build for anticipated 20-25 years of service
- Production process designed for fast speed/throughput of blocks
- Painting is often considered the main drawback to on-time delivery of the vessel.

In maintenance situations the following can often be recognized:

- Surface to be painted is primarily previously painted structural areas
- Lower surface preparation standards are used (i.e., water jetting to NACE WJ-3,2 "Waterjet Cleaning of Metals—Thorough Cleaning," tool cleaning to St 3,3 manual abrasive blasting to Sa 2,4 "Thorough Blast-Cleaning," for dry dock situations)
- Expected service life of coating work varies according to age of the vessel
- Application conditions are varied, often less than required by coating manufacturer
- Time for both surface preparation and application reduced according dry dock schedule

Following are the typical use areas onboard ship and the most common coating systems used in each area. The tables showing these products from seven global-scale manufacturers have been verified by the manufacturers' technical departments involved. Typical systems commonly recommended by marine coatings manufacturers are also shown for each use area. These systems are assumed to be applied over either an intact or a secondary surface prepared inorganic zinc (IOZ) shop primer. The areas are considered in alphabetical order rather than an attempt to portray any degree of importance.

Traditionally the marine industry has focused on protecting different areas of the vessel with protective coating systems tailored for each particular area. With the advent of universal epoxy primers, the number of different products involved in these coating systems continues to diminish. This is potentially a good change, but it has potential drawbacks from a service life standpoint. While a universal epoxy primer provides good abrasion resistance and long-term recoatability, they do not have corrosion resistance equal to either the IOZ primers or the zinc-rich epoxy primers. Degradation or impact damage of the topcoats occurs frequently in normal marine service. As a result, the owner/specification engineer has a critical decision to make when selecting coating systems for the newbuild of a cruise ship, cargo ship, floating production storage and offloading vessel, floating production unit, offshore supply/crew boat, or any other type of marine vessel.

Marine coatings are normally grouped into the following service areas:

- Topsides and superstructures
- Decks
- Cargo holds
- Cargo tanks
- Ballast tanks
- Portable water tanks
- Underwater hull

Service areas are further defined by the types of products commonly used in these areas:

- Abrasion-resistant coatings
- Antifouling and foul-release coatings
- Cargo tank linings
- Cofferdam and voids coatings
- Cosmetic finishes
- Foul release coatings
- Heat-resistant coatings
- High-performance deck coatings
- Potable water tank linings
- Primers and tie coats
- Shop primers
- Universal primers

Abrasion-Resistant Coatings

Dry cargo holds are subject to constant abrasion both from the loading of products from conveyor belts, palletized products that are loaded into the holds with cranes, and impact damage from prefabricated steel structural components and piping that are loaded by cranes. Granular products such as iron ore and coal can cause damage by both impact and gouging. The gouging normally occurs on the cargo hold bottoms from movement of the load during the voyage. Impact damage can occur to both the cargo hold bottom and the bulkheads when the loading conveyer is fitted with an adjustable elbow attachment to project the coal or iron ore at right angles to the bulkheads in order to speed up the loading process. This impact damage is referred to as "shooting damage" since the granular cargo is being projected around the cargo hold at fairly high velocity.

Prior to the introduction of universal epoxy primers, the first coat of coating systems for dry cargo holds typically involved either permanent IOZ primers or zinc-rich epoxy primers in order to limit the undercreep corrosion where bare metal was exposed by the impact of the load. Beginning in the decade from 2000 to 2010, there has been a gradual change to the use of universal primers in dry cargo holds due to both the higher cost and longer minimum and maximum recoat times of any primer that contains zinc vs. the universal epoxy primers that reduce both the material cost and the labor cost in the shipyard production process. While these holds are considered dry holds, it is not unusual to find that the portable (McGregor) hatch covers lose their close fitting tolerances from handling damage and begin to leak water during heavy seas. There is also a potential for condensation inside the holds when the high relative humidity encountered in ocean voyages reaches the dew point inside the hold. Corrosion can become so severe that a number of ships were lost at sea in the past due to loss of structural stability from severe pitting-type corrosion.

There is also severe degradation and impact damage from the unloading process, which typically involves bucket loaders of various types that are lowered into the cargo hold to lift the cargo onto either conveyor belts or crane lifts. The marine project engineer would be wise to consider the abrasion resistance of the coating systems (both primer and topcoats). Table 22.4 is a compilation from a review

of product data from various manufacturers that shows loss of coatings film thickness in accordance with ASTM D40605 Taber Abraser Method using a CS17 wheel with a 1-kilogram load for 1,000 cycles.

Antifoulings and Foul Release Coatings

The following history was compiled from news releases from International, Jotun, and Wikipedia.

412 BC: Arsenic and sulfur mixed with chian oil reported in Aramaic papyrus writings

3rd century: Greeks used tar and wax to coat ships bottoms.

13th to 15th centuries: Pitch, oil, and tallow used on wooden ship bottoms by the Chinese to discourage barnacles and toredo. Every few months the vessel had to be hoved over and graved on some convenient beach.

16th century onward: The main form of protection for wooden ships was copper sheathing or the use of a mixture containing sulfur and arsenic. It was not until the development of iron hulls that copper sheathing was abandoned.

17th century: In 1625 William Beale was the first to file a patent for a paint composition containing iron powder, copper, and cement. In 1670, Philip Howard and Frances Watson patented a tar, resin, and beeswax paint.

1761: The HMS Alarm was sheathed with copper plates on the bottom, sides, and false keels. By 1770 the Royal Navy was installing copper bottoms on its entire fleet.

1791: William Murdock patented a varnish mixed with iron sulfide and zinc powder, using arsenic as an antifoulant.

19th century: By 1870, more than 300 antifouling patents had been registered. Then as now, the basic principle of the majority of antifouling paints is to use biocide(s) to deter the settlement of fouling organisms through a leaching mechanism.

1847: The inventor of the antifouling paint was Captain Ferdinand Gravert, who sold his chemical formula in 1913 in Taltal, Chile.

1854: James McInnes patented the first practical composition to come into widespread general use. It used copper sulfate ($CuSO_4$) as the biocide in a metallic soap composition, which was applied hot over a quick-drying priming paint of rosin varnish and iron oxide pigment. This was soon followed by a similar product known as "Italian Moravian," which was used well into the 20th century.

1863: James Tarr and Augustus Wonson were awarded a U.S. patent for antifouling paint using copper oxide (CuO) and tar.

1881: Holzapfels antifouling compositions were introduced. The Holzapfel brothers were the founding fathers of International Coatings, Ltd.

1885: Zuisho Hotta was given the first Japanese patent for an antifouling paint made of lacquer, powdered iron, red lead, persimmon tannin, and other ingredients.

1906: The U.S. Navy began to manufacture its own antifouling coatings and tested shellac and "hot plastic paints."

1926: The U.S. Navy developed a hot plastic paint using coal tar or rosin as binder and copper or mercuric oxides as toxins. This was followed later by cold plastic paints, which were easier to apply.

1960s: Contact leaching antifoulings were introduced, designed to increase antifouling lifetimes by increasing the biocide content.

1974: International introduced the first self-polishing copolymer (SPC) antifouling.

1987: The first tributyltin (TBT)-free controlled depletion polymer (CDP) polishing antifoulings were introduced globally.

1996: International introduced the first commercially available biocide-free foul release technology for fast craft. Self-polishing copolymer antifouling using patented copper acrylate technology.

1999: The first foul release system for deep sea scheduled ships was introduced. The revolutionary low surface energy coating technology controls fouling without the use of biocides.

2000: Jotun introduced the first self-smoothing and self-polishing antifoulant. International introduced Linkcoat, allowing direct conversion of biocidal SPC antifoulings to foul release systems.

2002: Jotun introduced silyl acrylate antifouling technology. International introduced the first self-polishing antifouling system blending SPC and CDP technologies.

2008: Jotun introduced hydrolyzing silyl acrylate self-smoothing and self-polishing technology for vessels sailing between 12-26 knots speed.

2010: Jotun introduced nano-repellant silicone technology featuring both repellant and foul release properties.

2007: International introduced exceptionally smooth fluoropolymer technology with very low levels of average hull roughness for increased fuel efficiency.

2012: International introduced fluoropolymer foul release coating with slime control, allowing operators to maintain performance through entire docking schedule.

2012: International introduced patented Lubyon technology, a linear polishing antifouling designed for 90-month service intervals on deep-sea vessels.

2013: Sigma introduced patented binder self-polishing technology antifouling for extreme and aggressive fouling conditions with potential service life of 60 months.

From the moment a vessel enters service, the condition of its hull and propeller surfaces begins to deteriorate. Through a combination of mechanical damage and the onset of biological fouling, these surfaces are constantly under attack. At each dry docking, work is done to restore the hull and propeller surfaces to a good condition. However, with increased focus on lowering fuel costs and reducing emissions, owners are increasingly focused on what happens between dry dockings.

A comprehensive study based on actual vessel performance data collected from 32 vessels over 48 dry-docking intervals concluded that average energy efficiency loss attributable to hull and propeller performance for a typical vessel in a typical trade was between 11 and 18%, depending on the length of its dry-docking interval (typically between 36 and 60 months). A typical vessel trading over a 60-month interval, for example, was found to use 36% more power at the end of the dry-docking interval, as compared to the beginning, in order to maintain the desired speed.

Antifoulings can be classified by the two dominant technologies: CDP and SPC. However, some manufacturers market special blends of CDP and SPC technologies for special service conditions.

Controlled Depletion Polymers

The soluble rosin blend CDP types typically react with seawater to gradually release their toxic components that are intended to either kill the sea life or discourage its attachment in its early stages of exposure to the hulls. Rosin-based antifoulings may have low or high quantities of rosin. Those with a low level are known as contact leaching antifoulings. They are mechanically tough, have no polishing characteristics, and commonly have a maximum in-service lifetime of 24 months.

The high rosin level products are softer, dissolve slowly in seawater, and are known as CDP antifoulings As the rosin blend is degraded by the seawater reaction and the passage of the ship through the water, the film achieves a smoother surface, so there is a certain amount of self polishing going on, but the main purpose is to expose new layers of the toxicant material, often a copper-based blend with other toxicants. Depending on the formula and whether the vessel is in regular service or in interrupted periods of service and stagnant dockage, these antifoulings will provide effective performance for periods from 36 to 60 months. However, the use of rotating brushes or rotating waterjet nozzles are necessary to remove firmly attached sea life such as barnacles after the 24-month period.

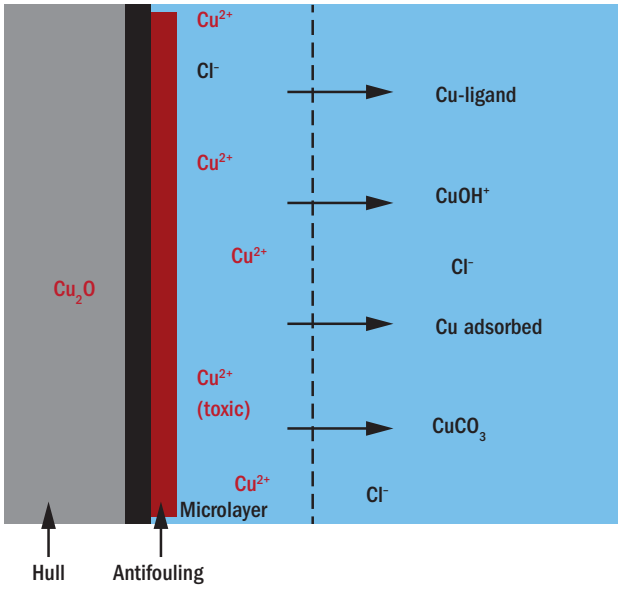


FIGURE 22.1: Copper anti-fouling schematic. Source: Jotun Marine Coatings.

Prior to 2003, many antifouling coatings contained TBT compounds as the most effective biocide. TBT was banned by the International Maritime Organization (IMO) because the residual TBT compounds found in the mud layers of harbors and rivers were poisoning shellfish such as oysters. The IMO ban on TBT that was fully enforced in January 2008 resulted in increased use of copper in various forms along with co-biocides in order to maintain 36 to 60 month drydock schedules for oceangoing vessels.

The beauty of copper as an antifouling biocide is its rapid loss of bioavailability, and hence detoxification. In the almost static micro-layer of water on the underwater hull of a ship, copper exists as highly potent cupric ions (Cu^{2+}) leaching out from the antifouling paint. Here, on the hull surface, these active ions effectively prevent settling and growth of fouling organisms. As these unstable ions reach the water column they rapidly become complexed, adsorbed, or in other ways deactivated by organic and inorganic matter. Copper is effective in the water microlayer on the hull surface (Figure 22.1).

Self Polishing Copolymers

The SPC types are typically either copper acrylate or silyl acrylate technologies. Available since 1974, SPC antifouling coatings are capable of delivering 4% fuel and emission savings with up to 90 months of service between drydockings. The self-polishing characteristic is the result of a hydrolysis reaction. The release of biocides is sustained throughout the coatings' lifetime by chemical control of the leached layer size and composition. On immersion, SPC antifoulings react with the sodium ions in seawater to produce a soluble layer on the surface of the coating. This layer dissolves at a predetermined rate, consistently exposing fresh antifouling and maintaining a continuous, controlled release of biocides. Volume solids range from 40 to 54% with concurrent reductions in volatile organic compound (VOC) emissions during application.

Marine coating manufacturers have constantly expanded the technology involved in antifouling coatings, such as nano-scale engineering of either nano capsules or nano springs (Hempel) to improve the release and repellant properties of the outer layer of their foul control systems (Figure 22.2).



FIGURE 22.2: Self-polishing copolymer after several months in service. Courtesy Hempel Coatings.

SPC and CDP Blends

These are standard performing self-polishing copolymer antifoulings, based on a blend of SPC and CDP technologies. The careful combination of these two technologies produces antifoulings that have the controlled depletion polymer benefits of surface tolerance, high volume solids, and an attractive cost base, together with the SPC attributes of polishing rate control, reduced leached layer size, and control of biocide release.

Foul Release Coatings

Foul release properties are particularly important when considering slower speed vessels (<15 knots). These vessels often trade on the spot market and may have static periods awaiting a charter or waiting to discharge/load cargo. The excellent foul release properties of silicone and fluoropolymer coatings means that even during exceptionally long periods of inactivity, fouling attachment can be

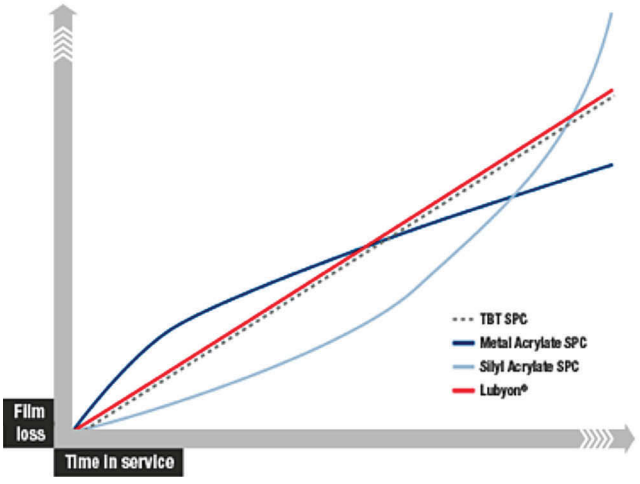


Figure 22.3: Film loss vs. time in service. International Lubyon patented technology.

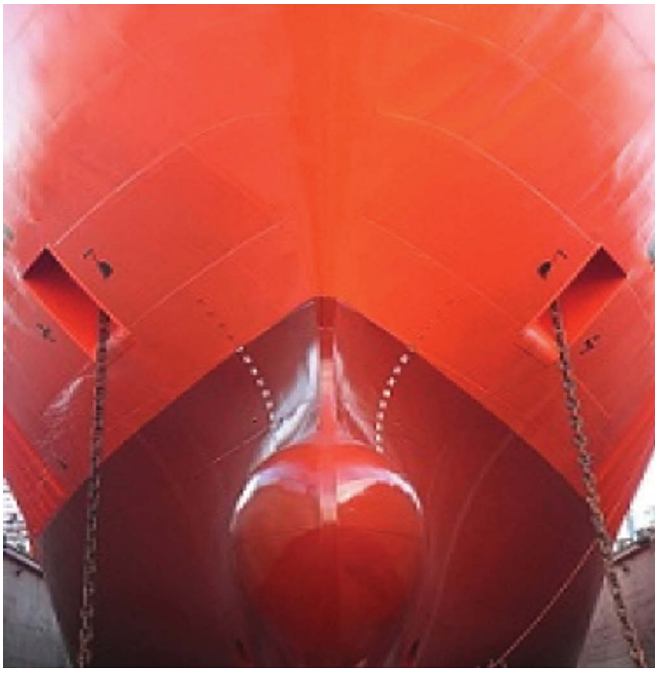


Figure 22.4: Epoxy siloxane foul Release coating. Source: Jotun Coatings.

either removed by the vessel getting under way, or if underwater cleaning is the option selected, then less force is required to remove the fouling growth so less damage may result. The better static resistance and improved foul release properties of these coatings means the product is suitable for use on newbuildings during fitting out periods.

Silicone elastomer foul release coatings provide an ultra smooth, slippery, hydrophobic surface and are chemically durable. There is no film degradation, polishing, or other chemical changes, so extended drydocking intervals are possible. The smooth surface means fouling organisms are typically unable to attach, or have difficulty settling onto the surface. Typically the entire system consists of an abrasion-resistant epoxy primer, a special three-component silicone elastomer tie coat, and a three-component silicone elastomer finish coat.

Fluoropolymer chemistry represents the very latest advances in foul release technology formulated to make it very difficult for fouling organisms to adhere to the coated surface. It is understood that marine fouling organisms secrete an adhesive, either of a hydrophobic or hydrophilic nature depending on the fouling species. Having a balanced amphiphilic surface (both hydrophobic and hydrophilic) can minimize the chemical and electrostatic adhesion between the surface and a wide range of fouling organisms (Figure 22.3).

In early 2013, two significant advancements in foul release coatings were announced by two of the leading marine coatings manufacturers. International Paint introduced a new fluoropolymer-based foul release coating with a unique slime release action. The tailored surface chemistry of this new biocide-free technology specifically influences and resists the adhesion and settlement of organisms that make up slime colonization. This is claimed to be the first ever slime release coating for all vessels, even in warm waters and slow steaming.

Jotun introduced the marine industry's first epoxy-polysiloxane-based antifouling coating (Figure 22.4). Combined with Jotun's foul release technology, this new system produces a smooth, glossy surface optimized for owners seeking to reduce costs related to dry-docking and maintenance. Requiring only two coats, this biocide-free system results in significant drydock and application cost savings.

Cargo Tank Linings

Some of the most critical service conditions that marine coatings users encounter require the use of coatings as linings. In rare cases they may be the same coatings used in atmospheric service, but they are usually specially formulated for three specific purposes:

1. To protect the substrate (carbon steel, aluminum, alloys, or other materials) from attack by the liquid being transported inside the tank
2. To protect the liquid being transported from contamination by the substrate
3. To restore structural integrity to an old tank, while meeting the requirements for protection of the substrate from corrosion and the liquid in storage from contamination

All coatings are permeable to some degree. The choice of coatings for use as tank linings requires a much greater knowledge of the properties of the liquid being stored, and the ability of the coating to withstand permeation by that liquid than any coating being applied in atmospheric service. For that reason, this chapter deals specifically with a narrow range of coatings with proven marine service in some very aggressive liquids.

Choosing a Tank Lining

Few project managers have an in-depth knowledge of the suitability of various tank linings when placed in immersion of aggressive, penetrating liquids. It is possible to review the product data sheets of several global scope coating manufacturers to get a general idea of which linings might work in a given situation. However, this approach is risky in that the product data sheets, of necessity, have to be quite general in nature. Following are three recommended alternatives that will provide choices with better chances of being successful in a ship's tank transporting a specific liquid cargo.

1. Conduct comparative side-by-side testing of candidate systems in a laboratory program that simulates to the best extent possible the service conditions expected in that particular tank. This takes time, but can give very good indications of a tank lining's ability to resist permeation by a particular liquid for a given period of time at a stated storage temperature. The shortcoming of these

tests is that ship tanks are not static like ground storage tanks—they are in constant movement as they cross the seas. A static test in a laboratory can give misleading results about the ability of a tank lining to withstand the wave action that develops in ship tanks during heavy seas. There are a few dynamic wave action test tanks in the Far East but these are more expensive to construct and maintain than some laboratories can afford.

2. If time does not allow for comparative laboratory testing, the coating manufacturers can be requested to provide their cargo resistance guides, cargo protection guides, or tank coating resistance information service for the products that are being considered for a particular tank. Although this normally is a limited to specific testing for specific time frames such as 30 and 60 days (intended to simulate intended voyage times), it does give good guidelines about the performance characteristics of each product. In addition, these resistance guides normally come with some very valuable precautions regarding immersion of the chemicals depending on the pH, temperature, etc., of those chemicals. Some very valuable information is normally available about cleaning chemicals, procedures, and recovery times between different cargoes.
3. Review selected case histories of tank linings used in similar services. This can be very valuable as it gives longer-term results. However, when doing so, the project manager must be careful to confirm that the service conditions are truly similar to his or her expected service conditions. He or she must also be careful to confirm that the product shown in the case history is still formulated the same as when that case history was conducted. VOC and hazardous ingredient regulations have caused changes in products to achieve higher volume solids that can, and have, drastically altered the chemical resistance of those products.

Tank Lining Chemical Resistance

Choosing the right tank lining system for a given commodity can be quite simple or very difficult, depending on the amount of information that is readily available about the product that will be transported in a specific tank. Individual product data sheets from the manufacturer will usually make a broad statement in the product description section of the product data sheet, such as "a high-solids, two-coat chemical-resistant lining system with exceptional resistance to a wide range of chemicals and solvents." Although this sounds good and is reasonably accurate, it lacks sufficient detail to base a tank lining specification for aggressive media, such as methanol, acetone, methyl tertiary butyl ether (MTBE), acrylonitrile, sodium hydroxide (NaOH) solutions, etc.

Most global marine coatings manufacturers publish lists of products that have been tested and/or stored in tanks lined with some of their products. Four of the leading global scale marine coatings manufacturers are Hempel, International, Jotun, and Sigma. All four of these manufacturers restrict their recommendations to a short list of core products with long-term proven ability to carry aggressive cargoes with specific limits on the duration of the loading (Table 22.6).

TABLE 22.6 Typical Premium Performance Tank Lining System

Remove all fabrication defects, remove all weld spatters, grind edges to minimum 2-mm radius, abrasive blast entire surface to ISO Sa 2.5 with a surface profile of 50-75 µm.				
Coat No.	Product Description	DFT Range (µm)	Recoat Min. @ 25 °C	Recoat Max @ 25 °C
1	Amine adduct phenolic epoxy (Novolac)	100-150	36 h	28 days
Stripe Coat	Amine adduct phenolic epoxy (Novolac)	25-75	36 h	28 days
2	Amine adduct phenolic epoxy (Novolac)	100-150	36 h	28 days
3	Amine adduct phenolic epoxy (Novolac)	100-150	36 h	N.A.
Note: Stripe coat must be contrasting color and must be brush applied.				

Ballast Tank Linings

Ballast tanks are some of the most corrosive areas on a ship, particularly the fore peak and aft peak tanks where the compartments are so restricted by the horizontal and transverse stiffeners that it is very difficult to apply a pinhole or holiday-free coating. Figure 22.5 shows a typical ballast tank configuration. With the advent of the IMO PSPC MSC.215 (82) "Performance Standard for Protective Coatings"[6] effective December 2006, coating systems for ballast tanks for all ships and double skin hulls in cargo ships delivered after July 1, 2008 must be coated with a coating system designed to provide a service life of 15 years prior to significant maintenance. Typical coating systems for ballast tanks to meet PSPC requirements involve at least two coats of either polyamide or polyamine epoxy with a stripe coat on all edges and welds. Some owners are changing their systems to solvent-free epoxies with better edge retention properties to limit the edge corrosion problems commonly seen in all tank linings. The topcoat must be a light color such as blue, green, and white for visibility purposes during scheduled surveys of the vessel.



Figure 22.5: Typical ballast tank configuration. Source: "The Future of Ballast Tank Coatings," JPCL 6 (2008).

NACE Publication 38457,[7] "Guidelines for Ballast Tank Coatings Systems and Surface Preparation," contains extensively illustrated guidelines with information and advice on technical matters related to the design, building, operating, maintenance, and repair of the corrosion protection systems of ships ballast tanks. It gives options and information to designers, shipyards, and ship owners and is specific enough to be used as a reference document for shipbuilding, ship repair, and ship maintenance purposes. The marine project manager should not only inform himself/herself of the requirements in MSC 82/24/Add.1 Annex 3; he should insist that his coating inspectors know its requirements and he should monitor their activities to ensure that the requirements are met. A few examples of these requirements are:

1. Take one gauge reading per 5 m^2 of flat surface areas
2. Take one gauge reading at 2 to 3-m intervals and as close as possible to tank boundaries, but not further than 14 mm from edges of tank boundaries
3. On longitudinal and transverse stiffener members, take one set of gauge readings as shown in Figure 22.6, taken at 2 to 3-m intervals and not less than two sets between primary support members
4. Take three gauge readings for each set of primary support members and two gauge readings for each set of other members as indicated by the arrows in the diagram
5. Take one set of gauge readings for each 2 to 3-m run as shown in Figure 22.6 but not less than three set;
6. Take one gauge reading from each side of an opening
7. Take five gauge readings per m^2 but not less than three gauge readings at complex areas (i.e., large brackets of primary support members)
8. Take additional spot checks to verify coating thickness for any area considered necessary by the coating inspector.

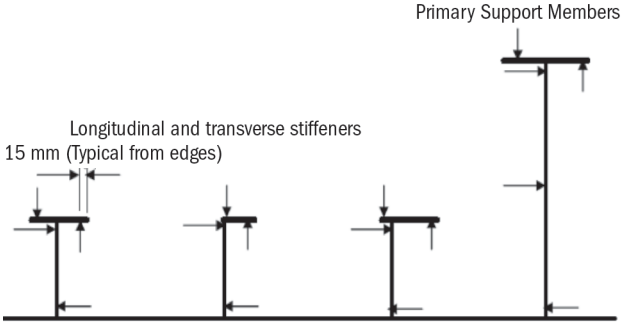


Figure 22.6: Gauge readings needed for longitudinal and transverse stiffener members. Note: Arrows of diagram indicate critical areas and should be understood to mean indication for both sides.

In the past, soft coatings based on lanolin and vegetable oils were used extensively for maintenance of ballast tank linings after they began to exhibit fair to poor corrosion conditions in the periodic surveys required by the classification societies. The reason was simple—they were cheap and required only high-pressure washing prior to application of the soft coatings. Many companies are now banning these soft coatings because it has been found that corrosion has a tendency to hide behind the rust scale that was hidden by the soft coatings until the corrosion became so heavy that structural stability of the bulkheads in the tank was compromised. Besides being soft, these coatings are also quite slippery. Some government agencies and classification societies have banned the use of soft coatings due to safety problems from slipping while surveying the ballast tanks.

One alternative maintenance system that produces good results without the requirement for abrasive blasting is the use of detergents sprayed on the internal tank surfaces followed by high (10,000 to 30,000 psi) or ultra-high (greater than 30,000 psi) water jetting to remove all loose coatings and loose rust scale, followed by application of surface-tolerant epoxy coating systems (Tables 22.7 through 22.9). In severe cases, dry abrasive blasting or slurry blasting in order to establish a proper profile for the new epoxy coating systems follows the water jetting.

TABLE 22.7: Ballast Tank 100% Volume Solids Edge Retentive Epoxy System-Newbuild System

Remove all fabrication defects, remove all weld spatter, double pass grind all edges, sweep blast entire shop-primed surface to expose a surface profile of 50-75 µm. Vacuum before spraying.

Coat No.	Product Description	DFT Range (µm)	Recoat Min. @ 25 °C	Recoat Max @ 25 °C
Stripe coat	Edge retentive epoxy green	75-125	12 h	18 h
1	Edge retentive epoxy white	300-600	N.A.	N.A.

TABLE 22.8: Alternate Ballast Tank Epoxy System

Remove all fabrication defects, Remove all weld spatter, grind edges to minimum 2-mm radius, sweep blast entire shop primed surface to expose a surface profile of 50-75 µm. Vacuum before spraying.

Coat No.	Product Description	DFT Range (µm)	Recoat Min. @ 25 °C	Recoat Max @ 25 °C
1	High solids epoxy green	150-200	4 h	5 days
Stripe coat	High solids epoxy blue	25-75	4 h	5 days
2	High solids epoxy white	150-200	4 h	5 days

TABLE 22.9: IMO 215 (82) PSPC Compliant Ballast Tank System

Remove all fabrication defects, remove all weld spatter, grind edges to minimum 2 mm radius, Sa 2.5 abrasive blast all welds. Sweep blast and power wash to clean intact shop primer,

Coat No.	Product Description	DFT Range (µm)	Recoat Min. @ 25 °C	Recoat Max @ 25 °C
1	Pure universal epoxy bronze	150-175	7 h	14 days
2	Pure universal epoxy aluminum	150-175	N.A.	N.A.

Cofferdam and Void Coatings

While these service areas have traditionally been considered non-critical dry service areas that were protected with inexpensive oil base, hydrocarbon, or bitumen coating systems, that thinking has changed because of the fact that while these areas are normally seal welded after fabrication, they rarely remain watertight in service, leading to general corrosion that is difficult to repair because of the constricted working space in these areas. For that reason and the requirements for a 20-25 year service life on marine vessels, it is now more typical to find these areas protected with one coat of either universal primer or multi-purpose epoxy at a dry film thickness (DFT) of 100-150 µm. The steel used to fabricate these areas are typically abrasive blasted in a centrifugal blast line and coated immediately

with a 12-18 µm thickness of IOZ shop primer and receive only power tool cleaning or light brush-off blasting immediately prior to application of the epoxy coating.

Cosmetic Finishes—Topside Area and Interior Living and Working Spaces

The title "cosmetic finishes" may sound a little odd for products such as acrylics, alkyds, and polyurethanes but it simply means a finish coat of a coating system that is applied mainly for its aesthetic properties such as color and gloss retention. Some of these also have very good protective properties but their main use is to upgrade the finished look on a portion of the ship such as the wheelhouse, living quarter interiors, funnel exteriors, logos, etc.

Prior to the development of high-performance water-based acrylic coatings and polyurethane coatings, oil-based alkyds and silicone alkyds were commonly used in these areas. Alkyds are still used in some interior spaces where the service is not critical but on exterior surfaces the predominant coating used for color and gloss retention is high-gloss aliphatic polyurethane. Silicone alkyds are often used on equipment where both heat resistance and color retention are important. For areas such as logos on funnels and helipads, high gloss polysiloxanes are a very good choice although they are more expensive than polyurethanes. Cruise lines are moving toward using high-gloss polysiloxanes for exterior topsides and freeboard areas on their ships to attract more cruise passengers (Tables 22.10 and 22.11).

TABLE 22.10: Frequently Used Combination of Corrosion Resistance and Aesthetic Finish

Remove all fabrication defects, remove all weld spatter. Power tool clean damaged shop primer, power wash before spraying.				
Coat No.	Product Description	DFT Range (µm)	Recoat Min. @ 25 °C	Recoat Max @ 25 °C
1	High solids zinc rich epoxy	75-125	4 h	5 days
2	High solids epoxy intermediate	100-150	4 h	5 days
3	Acrylic polyurethane finish	50-75	N.A.	N.A.
Note: Finish coat must be contrast color to intermediate coat.				

TABLE 22.11: Alternate Combination of Corrosion Resistance and Aesthetic Finish

Remove all fabrication defects, remove all weld spatter, power tool clean damaged shop primer, power wash before spraying.				
Coat No.	Product Description	DFT Range (µm)	Recoat Min. @ 25 °C	Recoat Max @ 25 °C
1	Universal epoxy primer	100-150	4 h	28 days
2	Acrylic polyurethane finish	50-75	N.A.	N.A.
Note: Finish coat must be contrast color to intermediate coat.				

Deck Coatings—Including Heli-Deck Surfaces

As can be seen from the Table 22.12, deck coatings are mainly high-volume solid epoxies modified with hard pigments such as glass flakes, aluminum oxide (AlO), and flint where non-skid performance is required. High-volume solid polyester/vinyl ester coatings are sometimes used where a hard chemical-resistant coating system is required. Some manufacturers recommend universal epoxies with non-skid pigments broadcast over the first coat prior to application of the second coat. This is better than using sand or garnet as a non-skid media over the first coat, but it will not yield the same long-term performance as when the hard pigments are incorporated in the epoxy resin during the manufacturing process. The marine newbuild manager would be wise to compare the abrasion resistance (in accordance with ASTM D4060 using a CS17 wheel with a 1-kg load, or ISO 7784[8]) of the coatings being selected for working decks and helipad landing decks. The lower the weight loss in this test, the longer the coating will last. Helicopter landing pads are one area where polyester coatings have been used frequently to resist the abrasion damage from twisting of tires during landing and takeoff operations. Some owners use semi-gloss polyurethanes on the main area of the deck to reduce the glare for helicopter pilots landing during bright sunlight.

TABLE 22.12: Premium Performance Deck Coating Systems, Including Heli-Deck Surfaces

Remove all fabrication defects, remove all weld spatter, abrasive blast to Sa 2.5 to expose a surface profile of 50-75 µm.				
Coat No.	Product Description	DFT Range (µm)	Recoat Min. @ 25 °C	Recoat Max @ 25 °C
1	Ethyl silicate IOZ	75-125 µm	18 h	Unlimited
2	High solids abrasion resistant epoxy	150-175 µm	6 h	3 days
3	High solids abrasion resistant epoxy	150-175 µm	N.A.	N.A.
Note: Hard grit broadcast over 3rd coat while it is still tacky.				

TABLE 22.13: Frequently Used Combination of Corrosion Resistance and Abrasion Resistance

Remove all fabrication defects, remove all weld spatter, sweep blast entire surface to expose a surface profile of 50-75 µm.				
Coat No.	Product Description	DFT Range (µm)	Recoat Min. @ 25 °C	Recoat Max @ 25 °C
1	High solids abrasion-resistant epoxy	150-175µm	6 hrs.	3 days
2	High solids abrasion-resistant epoxy	150-175µm	N.A.	N.A.
Note: Hard grit broadcast over second coat while it is still tacky.				

Hull Coatings—Freeboard Area

Most hull coating systems for the hull area below the operating draft line begin with one or two coats of anti-corrosive epoxy coatings followed by either the anti-fouling coatings or the foul release coatings below the operating draft line on the hull. Areas on the hull that will absorb both impact and abrasion damage from fenders during docking operations may have a third coat of high volume solid abrasion-resistant epoxy. Since all epoxies chalk on exposure to ultraviolet rays of the sun, a cosmetic coat such as aliphatic polyurethane or polysiloxane may be called for above the operating draft line on the hull.

The coating systems shown in the following table are for areas above the operating draft line only. Coating systems for areas below the operating draft of the ship can be seen in Chapter 3, "Fouling Control Coating Systems."

Potable Water Tank Linings

Government agencies around the world now require that coatings applied to the internal surfaces of potable water tanks have an approval certificate that proves there will not be any health hazard from materials that might leach out of the cured coating film during immersion in potable water. In the United States most of the certifications are obtained after testing in accordance with the ANSI/NSF 61 standard.[9] In the United Kingdom, this might be in accordance with BS 6920, Part 1.[10] In Norway, this might be the Norwegian Institute of Public Health. In Southeast Asia this might be in accordance with Australia Water Quality Centre Standard AS/NZS 4020:2025.[11] Most of these approvals are for two or more coats of immersion grade epoxies, although some solvent-free polyurethanes and/or polyureas meet these standards.

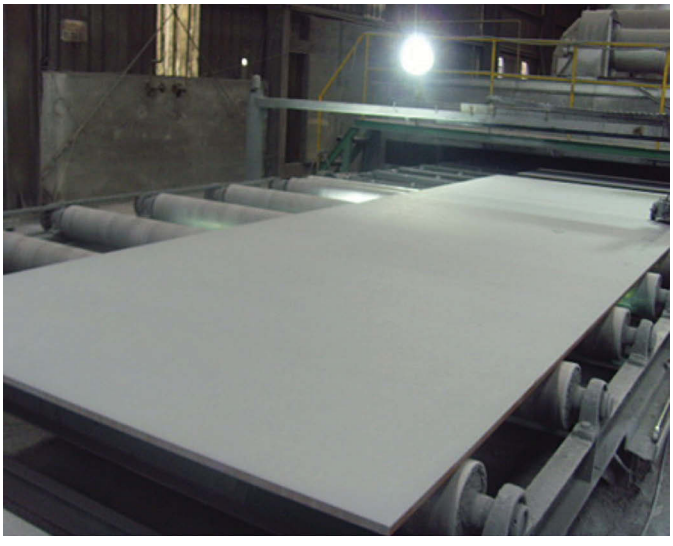


Figure 22.7: Shop-primed plate exiting centrifugal blast booth. Photo courtesy of Hempel Coatings.

Shop Primers

Shipyards love shop primers; so much so that most of the major yards negotiate preferred vendor status with the manufacturer of their choice for an IOZ shop primer that they will apply to all the steel plate and most of the steel beams and angle iron that enter their yard (Figure 22.7). Historically shop primers have been predominantly based on low weight solids ethyl silicate IOZs. With the advent of more restrictive emission requirements by governments around the world, there has been greater use of water-based potassium or potassium/lithium blend IOZ shop primers. These shop primers will normally be applied at a DFT between 15 and 18 µm, which is enough to prevent corrosion for six to 12 months during the fabrication of the modules for the ship. While these are normally compatible with a broad range of organic coating systems, the marine project engineer must obtain a certificate of compatibility from the manufacturer of the topcoat systems that have been specified in the coatings specification for that ship.

There are some issues with IOZ shop primers applied to parts of the ship that will serve in an immersion situation. IOZ does not perform well in immersion in water and the traditional way to solve this is to require a brush-off or sweep blast to be performed immediately before the application of the permanent organic anti-corrosive coating primer for that area of the ship. Shipyards would much rather use secondary preparation methods involving grinders and other tools that mechanically clean the rusty spots on the shop primer and the areas along the welds where the welding process has created burn back damage to zinc.

It is not normally too difficult to get the shipyard to remove the shop primer by sweep blasting or brush-off blasting inside liquid cargo tanks, but there is great resistance to do the same on other areas such as the underwater hull. The issue is compounded by the shipyards' use of universal primers (usually epoxies) wherever they can in order to save time in their production schedules. These universal primers are normally very compatible with shop primers, but not all universal primers are suitable for immersion in seawater, particularly over a shop primer that has only received secondary cleaning with grinders or other mechanical tools.

Universal Primers

If there is any coating that the shipyard loves more than shop primers, it is universal primers. Production schedules are the most critical cost containment items and/or cost creating items in a shipyard. Universal primer/topcoats (also known as multi-purpose epoxies) allow greater flexibility when schedules slip during a newbuilding process. The problem is with the term "universal." They are not universal—they are applicable over a wide range of areas on a ship, but they do not have the same abrasion resistance, chemical resistance, seawater resistance, etc. as coatings that are formulated specifically for a given service. Two examples of potential problems with the use of universal primers are in mud tanks on drillships and on working decks of ships that carry heavy deck loads. Working decks are areas where either IOZ or zinc-rich epoxies have often been used in order to have better corrosion resistance when damage occurs to the topcoats in the system due to abrasion or impact damage. Once the topcoat system is penetrated, universal epoxies do not provide the same level of sacrificial protection or resistance to undercreep corrosion that zinc primers can provide.

Universal epoxies work quite well in dry voids and cofferdams as well as in storage rooms and tool rooms. They are a good choice on topside structures, engine room bulkheads, and overheads, but not in bilges that become very oily and chemically active from spills and leaks of fluids from engines and compressors. Pure epoxy universal primers work best over a broader range of service areas than modified epoxy universal primers simply because they are not modified with light-colored hydrocarbon resins, non-reactive diluents, or plasticizers. A major international marine manufacturer offers a 15-year guaranty on its pure epoxy universal primer that is fortified with aluminum flakes meeting the requirements of IMO MSC.215 (82) PSPC ballast tank linings.

Zinc-Rich Coatings

There is no doubt that IOZ provides the best cathodic protection to steel surfaces. Numerous studies over the years have proven that fact. There is also no doubt that it takes more skill to properly apply IOZ primers than either zinc-rich epoxy primers or universal primers. The decision that the marine project manager and the owners for which he works must make is a financial one. On a typical ship of 250,000 deadweight tons or more, it is not unusual for the shipyard to attempt to extract a premium in excess of $500,000 U.S. for the use of either IOZ or zinc-rich epoxy over its price for applying universal epoxy despite the fact that they signed a contract to build the ship knowing full well that the owner specification called for zinc rather than universal epoxy.

There is also a potential issue with the choice of zinc-rich primers. A well-written coating specification will normally include zinc-rich primers with high levels of zinc in the dried film. The best performing (longest lasting) zinc-rich primers normally have in excess of 80% zinc by weight. Some manufacturers will submit a zinc-rich primer with as little as 50% zinc by weight in order to reduce the price of their quotation to the yard.

The shipyards traditionally offer a warranty on newbuildings of one to two years. For a large order or a preferred client, they might even extend that to five years. The problem is that coating systems normally don't fail dramatically during the first one to two years so there is very little risk on their part. The risk is transferred to the owners when the failure occurs after the expiration of the warranty and the cost of correcting failures after the ship is in service is a minimum of four times more than the initial cost of the application of the coating systems in the shipyard.

Organic Primers and Tie-Coats

Traditionally, organic primers have been considered as a fundamentally necessary base upon which entire coating systems had to be applied (Figure 22.8). Most of these primers had inhibitive pigments in them to slow down the rate of corrosion where the coating system was damaged or degraded to the point that bare metal was exposed. As the technology improved and new resins and curing agents became available and many of the properties of primers were incorporated into self-priming coating systems, this distinction began to be less important. For example, many solvent-free epoxy coatings actually have better adhesion to blasted substrates than to holding primers that are commonly used to prevent the blasted surface from flash rusting prior to application of the solvent-free high-build epoxies. In the building of ships, primers are often included in a specification as an alternate first coat in a coating system to maximize the productivity of the shipyard process by allowing complete blasting and priming of modules prior to joining them into the body of the ship. At that point the entire coating system is applied over the primer, which was chosen for its long re-coat windows without the necessity of brush-blasting prior to application of the final coating system.



Figure 22.8: Secondary surface preparation organic primer. Courtesy of Hempel Coatings.

Tie-coats have always been intended to do exactly what their name implies; to tie one coat of a coating system to a previous coat of a coating system. This is still necessary during maintenance activities when the generic properties of the previous coatings are unknown. The main purpose of these traditional tie-coats has been to allow the tie-coat to wet into the existing coating without lifting or wrinkling the existing coating while at the same time provide a layer of sound coating to which the new coating system would be compatible. Generically, the traditional tie-coats have often been modified epoxies, modified vinyls, modified alkyds, modified phenolics, and combinations of these generic types. However, the use of specialty tie-coats has become a necessity in both newbuilding and maintenance activities where anti-fouling and foul-release systems are applied. Getting proper adhesion of both anti-fouling and foul release coatings to the primer coat or intermediate coat layers is far more critical due to the hybrid resin systems used in the anti-fouling and foul release coatings.

The following tables illustrate the wide variety of primers and tie-coats, some of which are interchangeable in a coating system; most of which are not. The user should always consult with the technical department of the manufacturer prior to applying any of these products.

Heat-Resistant Coatings

While heat-resistant coatings are not used on extensive surfaces of a ship, the area in which they are used is a critical service area. Heat-resistant coatings are very specialized coatings with critical surface preparation and DFT requirements. It should also be noted that the typical temperature resistance limits given in the table are for dry heat. Any requirement for heat resistance in liquid immersion must be clarified with the manufacturer of the coatings being considered. It is not unusual for the wet heat resistance to be 50% greater or less than the dry heat resistance. Typical heat-resistant coating systems are one-component thin-film (13-37 µm) that may be applied directly to Sa 2.5 abrasive blasted steel or over a thin film (37-64 µm) IOZ primer. Excessive thickness of either the zinc or the heat-resistant coating can cause cracking during ship operations.

Spray Metallizing Process (Thermal Spray)

Thermal spray zinc (TSZ) and thermal spray aluminum (TSA) metallizing are simply a different method of applying corrosion-resistant material to a metal structure. All three methods require sharp anchor profiles between 1.2 to 4 mils (30 to 100 µm) along with a blasted surface meeting the requirement of NACE No. 1/SSPC-SP 5/ISO 3.0,[12] "White Metal Blast Cleaning." Thermal spray metallizing can be accomplished by one of three methods:

1. Flame spray—Zinc and aluminum wires are fed through a gun simultaneously with an oxygen/propane-generated flame and low-pressure compressed air. As soon as the molten material hits the work piece, it cools and bonds tenaciously to the base metal.
2. Arc spray—Zinc and aluminum wires are fed through a gun simultaneously with high-voltage current used to melt the wires and low-pressure compressed air. As soon as the molten material hits the work piece, it cools and bonds tenaciously to the base metal.
3. Plasma arc spray—Zinc, aluminum, and other high-density anti-corrosive metal wires are melted by a supersonic plasma jet formed by a transferred arch between a non-consumable cathode and the wire. Atomization is instant and forced air transports the stream of molten droplets onto the piece being coated. The molten droplets flatten when impinged on the metal surface due to the high kinetic energy. The result is a high wear-resistant coating that has been used very effectively to prolong the life of engine and propeller shafts.

Thermal sprayed coatings are finding increased use on ships hulls and tanker interiors. The choice of wire is contingent upon the intended service environment. The most common wire used for atmospheric service is a blend of 85% zinc/15% aluminum. Aluminum wire is a better choice for immersion conditions. A very thin sealer coat of vinyl, silicone, or epoxy is normally applied immediately to seal the normal porosities of thermal spray in order to extend the life of the coating once it goes into immersion.

NACE No. 12/AWS C2.23M/SSPC-CS 23.00,[13] "Specification for the Application of Thermal Spray Coatings (Metallizing) of Aluminum, Zinc, and Their Alloys and Composites for the Corrosion Protection of Steel," covers the requirements for thermal-sprayed metallic coatings, with and without sealers and topcoats. MIL-STD-2138A (SH),[14] "Metal Sprayed Coatings for Corrosion Protection Aboard Naval Ships," may be used to guide the preparation of specifications.

Maintenance Painting Programs

Maintenance painting programs are typically decided based upon the size of the ship, the service environment of the ship, and the complexity of the structures aboard the ship.

Small to medium-sized offshore service vessels such as workboats, self-elevating barges, etc. can be brought into drydocks, slipways, or tied up to piers and docks for coatings maintenance. As a result, the maintenance painting program is not likely to be on a set schedule. Whenever a structural or equipment problem requires servicing, painting crews are mobilized to repair or refurbish the areas that need attention at that time. The result is a propensity for spot repairs, rather than complete painting programs.

By contrast, large ocean-going vessels such as crude oil carriers will normally have a painting program that is largely based on the classification society requirement that these vessels be surveyed a minimum of twice during each five-year service period. These class-mandated surveys are focused on both corrosion conditions and coating conditions (particularly fouling conditions). The surveys may be conducted during an interim drydocking for equipment repairs, or by divers while a ship is tied up at a berth for loading or unloading cargo, or during a lack of trading activity by that ship. The surveys then establish the areas that need repairs or refurbishing and become the foundation of a specific painting program at the next mandated drydocking.

Easily painted areas such as interior rooms or compartments are normally touched up by the ship's crew, but more complex areas such as ballast tanks, cargo tanks, and chemical tanks are rarely normally painted by third-party contractors during a dry docking. In 2011 Sigma introduced a unique single-pack urethane polyester finish coat suitable for decks, deck fittings, and superstructures that allows greater utilization of ship crews for maintenance painting. Some companies have used what are called "riding crews" of professional contractors to repair tank linings aboard ship during a voyage, but these are relatively few.

Shipboard Corrosion Assessment Training (S-CAT)

NACE International has introduced course intended to provide a foundation of coatings, corrosion, and corrosion control knowledge for assessing the condition of tanks and other structures, and determining the required actions necessary to effectively maintain fully operational status. The course equips the assessor with practical guidelines for surveying and evaluating the condition of the protective coating system on specific areas of a marine vessel. The desired end result is that assessors utilize a consistent, orderly, and repeatable process of evaluation that has the confidence of all those involved in the maintenance cycle.

References

1 ISO Sa 2.5, "Very Thorough Blast-Cleaning" (Geneva, Switzerland: ISO).
2 NACE WJ-3/SSPC-SP WJ-3, "Waterjet Cleaning of Metals—Thorough Cleaning" (Houston, TX: NACE International).
3 ISO St 3, "Power Tool Cleaning" (Geneva, Switzerland: ISO).
4 ISO Sa 2, "Thorough Blast-Cleaning" (Geneva, Switzerland: ISO).
5 ASTM D4060, "Standard Test Method for Abrasion Resistance of Organic Coatings by the Taber Abraser" (West Conshohocken, PA: ASTM).
6 IMO PSPC MSC.215(82), "Performance Standard for Protective Coatings" (London, U.K.: IMO).
7 NACE Publication 38457, "Guidelines for Ballast Tank Coating Systems and Surface Preparation" (Houston, TX: NACE).
8 ISO 7784, "Paints and varnishes—Determination of resistance to abrasion" (Geneva, Switzerland: ISO).
9 NSF/ANSI 61, "Drinking Water System Components—Health Effects" (Ann Arbor, MI: NSF).
10 BS 6920, "Suitability of non-metallic products for use in contact with water intended for human consumption with regard to their effect on the quality of the water" (London: U.K.: BSI Group).
11 AS/NZS 4020:2025, "Testing of products for use in contact with drinking water" (Adelaide, Australia: Australian Water Quality Centre).
12 NACE No. 1/SSPC-SP 5/ISO 3.0, "White Metal Blast Cleaning: (Houston, TX: NACE).
13 NACE No. 12/AWS C2.23M/SSPC-CS 23.00, "Specification for the Application of Thermal Spray Coatings (Metallizing) of Aluminum, Zinc, and Their Alloys and Composites for the Corrosion Protection of Steel" (Houston, TX: NACE).
14 MIL-STD-2138A, "Military Standards, Metal Sprayed Coatings for Corrosion Protection Aboard Naval Ships"

23 Pipeline Coatings and Linings

Introduction

The integrity of pipelines or piping must be maintained to serve the line throughout its service life without any breakdown. The most common method to protect these pipes is isolating them from the corrosive atmosphere with suitable protective coatings. For buried lines, a combination of coating and cathodic protection (CP) service is utilized and proven to be the most effective method. The coatings are selected according to the area or environment to which the pipes are going to be exposed. A short history of the development of pipeline coatings is shown in Table 23.1.

While piping is defined as the tubular arrangement used to convey liquids and/or gases from one location to another within a plant facility (ASME B31.3[1]), pipelines are defined as the tubular arrangement for the transmission of crude oil, refined products, and natural gas from the wellhead, refinery, and storage facility to other facilities. (ASME B31.4[2]).

The effective protection of external surfaces of buried pipelines (Figure 23.1) is ideal when a perfect combination of coating system and effective CP work in harmony. CP design and calculations are made based on the type of coating system that is selected for the pipeline. The coating should be capable of providing high electrical resistance throughout its service life without any shielding (disbondment) whenever a failure occurs (Figures 23.2 and 23.3). Due to degradation and mechanical damage of the coating, the electrical current requirement to protect the pipeline cathodically may increase with time.

TABLE 23.1: Modern History of Pipeline Coatings

First Use	Coating Type
1920	Coal tar enamel (un-plasticized)
1923	Asphalt mastic
1927	Fabric-reinforced petrolatum tape
1941	Coal tar enamel (plasticized)
1943	Fabric-reinforced coal tar pitch tape
1948	Epoxy
1960	Single-layer FBE
1960	Extruded polyethylene (PE)
1970	Coal tar polyurethane
1973	Side-extruded PE
1979	Co-extruded PE tape
1980	Three-layer FBE-polyolefin systems
1990s	Dual-layer FBE
1993	Polyureas (pipeline version)

Underground piping systems should be installed so that they are physically separated from all foreign underground metallic structures at crossings and parallel installations and in such a way that electrical isolation could be maintained if desired. Cathodically protected pipelines need to be provided with isolation devices such as flange assemblies, prefabricated joint unions, or couplings installed within the piping systems in which electrical isolation of portions of the system is required to facilitate the application of external corrosion control. These devices should be properly selected for temperature, pressure, chemical resistance, dielectric resistance, and mechanical strength. Installation of isolation devices should be avoided or safeguarded in areas in which combustible atmospheres are likely to be present.[3]

Desirable Characteristics of External Pipeline Coatings

External coatings must be properly selected and applied and the coated piping shall be carefully handled and installed to fulfill the requirements. Various types of external coatings can accomplish the desired functions. Desirable characteristics of external coatings



Figure 23.1: Stringing 3 LPE coated pipeline.



Figure 23.2: External corrosion on pipeline.



Figure 23.3: Disbonded coal tar enamel.

include the following.[3]

a. Effective electrical insulator;
b. Effective moisture barrier;
c. Application to pipe by a method that does not adversely affect the properties of the pipe;
d. Application to pipe with a minimum of defects;
e. Good adhesion to pipe surface;
f. Ability to resist development of holidays with time;
g. Ability to resist damage during handling, storage, and installation;
h. Ability to maintain substantially constant electrical resistivity with time;
i. Resistance to disbonding;
j. Resistance to chemical degradation;
k. Ease of repair;
l. Retention of physical characteristics;
m. Nontoxic to the environment; and
n. Resistance to changes and deterioration during aboveground storage and long-distance transportation.

Typical Factors to Consider When Selecting an External Pipeline Coating[3]

a. Type of environment;
b. Accessibility of piping system;
c. Operating temperature of piping system;
d. Ambient temperatures during application, shipping, storage, construction, installation, and pressure testing;
e. Geographical and physical location;
f. Type of external coating on existing pipe in the system;
g. Handling and storage;
h. Pipeline installation methods; and
i. Cost impact.

Coating Systems for Buried Pipes

A wide variety of tapes and coatings have been utilized in the industry to meet various environmental conditions. While the various tape systems are reasonably cost-effective and easy to install, their service life is not comparable to modern day pipeline coatings. For that reason, only the following coatings with a long service life are included in this chapter:

1. Single-layer fusion-bonded epoxy (FBE)
2. Dual-layer FBE
3. Three-layer high-density PE (3LPE)
4. High-build polyurethane
5. High-build epoxies
6. Field joint coatings
7. Insulated lines



Figure 23.4: Electrostatic FBE spray guns.

FBE

FBE is an epoxy-based powder that is widely used for corrosion protection of steel pipes. FBE coatings are thermoset polymer coatings. The resin and hardener components in the dry powder remain unreacted at normal storage conditions. The powder is sprayed to the heated pipes (Figure 23.4), usually in the range of 180 to 250 °C (356 to 482 °F), by which the contents of the powder melt and transform to a liquid form. The liquid FBE film wets and flows onto the steel surface on which it is applied, and soon becomes a solid coating by chemical cross-linking, assisted by heat. This process is known as "fusion bonding." The chemical cross-linking reaction in this case is irreversible. Once the curing takes place, the coating cannot be returned to its original form by any means. Application of further heating will not "melt" the coating and thus it is known as a "thermoset" coating.

Single-Layer FBE Coating

Surface Preparation

Surface preparation is one of the key aspects for service life of a coating. Each manufacturer recommends the requirement of surface cleanliness and profile. Complying with this recommendation is the key to success. Typically, the following sequence is recommended by most of the coating manufacturers.

- Preheat the pipe to remove the residues/moisture from the pipe.
- Abrasive blast the area to NACE No. 2/ SSPC-SP 10 (near white blast cleaning)[4]/ ISO Sa 2.5[5](near white metal).
- Verify that the surface profile meets the coating manufacturer recommendations.
- Chemical treatment (e.g., phosphoric acid [H_3PO_4]) can be carried out at this stage as an optional surface cleaning to get rid of

various contaminants such as chlorides to enhance the adhesion properties (e.g., chromating).
- Strict care must be taken to remove surface moisture with appropriate equipment immediately prior to coating.

FBE Application (Single Layer)

A detailed coating application procedure should be prepared prior to the application. The procedure will identify the inspection criteria to verify the progress and quality of application. The coating shall be applied prior to the oxidation of the metal surface.

The application of FBE is carried out in the following sequence:

- Heat the pipe to the specified temperature. Heating can be by induction coil, direct flame impingement, or heat-soaking ovens.
- Apply the FBE powder. Electrostatic spray is highly recommended for external surfaces (Figures 23.4 and 23.5).
- Curing of the FBE coating should be as recommended by the coating manufacturer. Maintaining of the temperature throughout the curing period per the manufacturer's recommended level is critical.
- Quench the coating in a fresh water bath or allow natural cooling, depending on the requirement. Quenching is usually carried out for the plant inline process, which allows handling the pipe immediately after cooling.



Figure 23.5: Manual FBE application.

Inspection

- Check the calibration of all instruments.
- Check pipes for mill damage (gouges, burrs, delaminations) and ensure they are ground down or repaired.
- Check that all oil, grease, dirt, or other contaminants are removed.
- Ensure acid bath, if any, is a proper inhibited mixture.
- Check shot/grit mix for centrifugal blasting.
- Check to ensure anchor profile matches the specification.
- Check pre-heated oven (flame should completely surround the pipe).
- Check the temperature of the pipe before it enters the spray booth (ensure it is in the specified temperature range).
- Ensure the speed and distance within the quenching area is sufficient to cure the coating.
- Check dry film thickness (DFT) with calibrated thickness gauges.
- Inspect for holidays using required voltage as recommended by the coating manufacturer. If the there is no recommendation from the manufacturer, the voltage shall be set according to the DFT as recommended in NACE RP0188.[6]
- Conduct an adhesion test, typically at a minimum of 15 MPa (2,175 psi). Use an instrument approved in the specification.
- Curing of the coating shall be ensured by differential scanning calorimetry (DSC) testing per NACE RP0394[7]/CSA Z245.20.[8]
- Mark and carry out necessary repairs, if any.
- Document and report all processes and observations.

Advantages of Single Layer Fusion Bonded Epoxy

- Excellent adhesion
- Low permeability
- It allows the passage of current in case of bond failure; non-shielding to CP current
- Good flexibility

Dual-Layer FBE Coating

Single-layer FBE coating has a successful record for protection against corrosion. Nevertheless, the biggest challenge is to keep the coating free from mechanical damage during the handling and lay down process. A consistent and major drawback is the coating's mechanical resistance. Even though the single-layer FBE offers a high abrasion resistance, it is highly prone to mechanical damage during handling (Figure 23.6). To handle this "weakness" effectively, a secondary layer of FBE coating with better mechanical property is applied during the pre-gel stage of the primary layer. Thus a chemical bond between the two layers is ensured, resulting in excellent bonding between the two layers and creating a thicker single layer with corrosion, abrasion, and impact resistance. The high impact strength of the coating partially compromises the level of flexibility offered by the cured coating system.



Figure 23.6: Handling damage.

Surface Preparation

The surface preparation for a dual-layer FBE coating is the same as for a single-layer FBE coating.

Inspection

- The IR gauge thermometer shall be calibrated and variation with the contact thermometer shall be verified and documented.
- Check pipes for mill damage (gouges, burrs, delaminations) and ensure they are ground down or repaired.
  - Check that all oil, grease, dirt, or other contaminants are removed.
  - Ensure the acid bath, if any, is a proper inhibited mixture.
  - Check shot/grit mix for centrifugal blasting.
  - Check to ensure that the anchor profile matches the specification.
  - Check pre-heated oven (flame should completely surround the pipe).
  - Check the temperature of the pipe before it enters the spray booth (ensure it is in the specified temperature range).
  - Ensure the speed and distance within the quenching area is sufficient to cure the coating.
- Check DFT with calibrated thickness gauges; document the calibration results.
- Inspect for holidays using required voltage as recommended by the coating manufacturer. If there is no recommendation from the manufacturer, the voltage shall be set according to the DFT as recommended in NACE SP0490.[9]
- Adhesion test, typically at a minimum of 15 MPa (2,175 psi). Use an instrument approved in the specification.
- Curing of the coating shall be ensured by DSC testing as per NACE RP0394/CSA Z245.20.
- Mark and carry out necessary repairs, if any.
- Document and report all processes and observations.

Advantages of Dual Layer FBE

- Exhibits excellent corrosion-resistant properties from the primary layer
- Excellent impact resistance
- Good abrasion and gouge resistance
- Greater friction and tough anti-slip coating

Repair of FBE Coating—Single Layer

The damages on the coatings need to be repaired successfully to ensure the coating will withstand the desired service life. The most common method of repairing FBE coating is by using two-pack epoxy compounds. The size of damage that can be repaired shall be restricted within 4 by 4 in (102 by 102 mm). The damaged area needs to be widened enough to apply the sufficient epoxy to wet the metal surface properly. The damaged area needs to be surface prepared by spot abrasive blast cleaning. The prepared surface needs to be feathered prior to applying the well-mixed two-pack epoxy. The epoxy shall have at least 2 in (51 mm) overlap onto the sound coatings.

Patch sticks can also be used to repair small pinholes or damages. The prepared surface shall be spot heated using torches or hot air guns and patch sticks are pressed onto the hot metal surfaces. The heat from the metal and torch will sufficiently melt the stick and a proper film is made. Care shall be taken to not over-heat the area, damaging the existing sound coating. Nevertheless, a slight browning of the parent coating is possible, provided it does not create any blisters or undercutting of the sound parent coating.

Three-Layer High-Density Polyethylene/Polypropylene

Three-layer high-density PE/polypropylene (3LPE/3LPP) is an underground external coating system consisting of three layers with exceptional properties that exhibit high levels of protection. The three layers consist of the following:

1. An FBE primer
2. An adhesive copolymer
3. Extruded high-density PE/PP (HDPE/HDPP)

The merged coating exhibits excellent anti-corrosion properties of epoxy resin (FBE) and excellent mechanical properties of PE/PP. These properties provide long-lasting corrosion resistance for the pipes. Because 3LPE/3LPP is factory coated, field joints create the highest challenge to get protected from failures.

Typically, a three-layer HDPE will withstand a service temperature of 80 °C (176 °F) and a three-layer HDPP will withstand up to 110 °C (230 °F). The main differences between PE and PP are as follows.

- The monomer of PE is ethylene and the monomer of PP is propylene.
- PE has a lower melting point compared to the higher melting point of PP.
- PP is not as sturdy as PE.
- PP is stiffer and resistant to chemicals and organic solvents compared to PE.
- PP is pure, non-stretching, and generally more rigid than PE.

The application method for both HDPE and HDPP are the same. The selection of coating shall depend on the operating temperature variations. Each layer in the system extends its own level of protection. An FBE layer is provided for corrosion resistance. The adhesive layer holds the HDPE/HDPP together and the outer layer HDPE/HDPP gives excellent water resistance and mechanical strength. The factory application of 3LPE/3LPP is discussed briefly below.

Surface Preparation

The surface preparation shall start from the pipe-receiving stage itself. The pipes shall be segregated after confirming the pipe surface is free from mechanical damages, oil, grease, or any other contaminants that may affect the coating application and its integrity. The following process is recommended for the surface preparation.

- Preheat the pipe to remove the residues/moisture from the pipe (Figure 23.7).
- Abrasive blast the area to NACE No. 2/SSPC-SP 10 (near white blast)/ISO Sa 2.5 (very thorough blast cleaning). Abrasive can be



Figure 23.7: Preheating bare pipe with flame.



Figure 23.8: Centrifugal blasting of pipe.



Figure 23.9: Surface profile gauge (Rz).



Figure 23.10: Chloride testing with a bresle patch.

steel grit or an appropriate mix of grit /shot or any other media that can produce the required surface cleanliness and profile. (Figure 23.8).

- Acid cleaning is carried out just after the blast-cleaning process. The pH of the acid shall be verified prior to the cleaning process. Pipes are rinsed with deionized water and pH shall be checked to ensure it is in the range of 6 to 7. The excess water needs to be removed by "air knife" and the pipe is placed in the inspection rack.
- Check the blast-cleaned surface to see if there are any slivers or damages that need to be ground prior to the pipe's release for coating. Ensure that the surface profile meets the coating manufacturer recommendations (Figure 23.9).
- Chlorides shall be checked per ISO 8502-6[10] and 9,[11] which shall be less than 5 micrograms per cm^2 (Figure 23.10).
- To enhance the adhesion property of the FBE primer, chromating may be applied. While the water gets evaporated due to the radiant heat, the chromating gives a slight golden color to the metal surface. After chromating, the pipe is ready to be coated and will be forwarded to the inline induction coil where the pipe surface temperature will be raised to the relevant temperature to apply FBE powder. The temperature shall be maintained at the manufacturer's recommended limits.

Application

Because all three layers are applied simultaneously, the importance of a sample pipe coating is very high. The first couple of pipes will be utilized for setting and verifying all the parameters according to the client requirements. The sample pipe will have partial coating of each layer for at least 1.5 m (5 ft) to verify the quality and integrity of the each layer. This will be the only chance to see each layer without destructing the top layer. The speed of the pipe feeding, FBE spray gun alignments, and bleeding of PE/PP extruder all will be carried out prior to the preparation of the sample pipe coating (Figure 23.11).

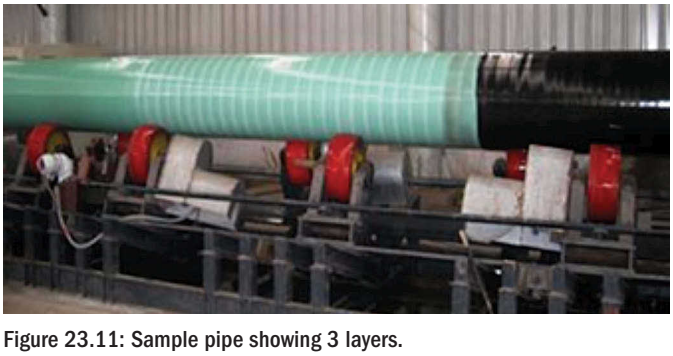


Figure 23.11: Sample pipe showing 3 layers.

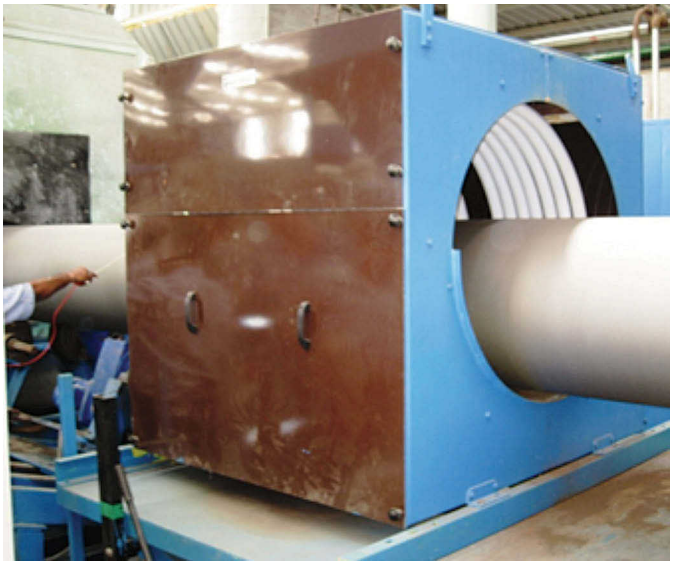


Figure 23.12 Induction coil heating pipe.



Figure 23.13: Temperature check before FBE application.

Pre-Heating

The pipes are passed through an induction coil where the surface temperature is raised to a range of 180 to 220 °C (356 to 428 °F) (Figure 23.12). Because the process is inline (i.e., FBE powder will be sprayed just after the coil within 0.5 m), induction heating shall be quick enough get the uniform temperature throughout the pipe as it passes the induction coil. The temperature shall be monitored continuously with a contact type thermometer and an infrared thermometer to verify the pipe surface is heated enough to melt the FBE powder sprayed on to it. Plotting the temperature graph continuously is very common and the inspector will have the leisure in a later stage to verify whether there was any chance for FBE to under cure due to insufficient metal surface temperature (Figure 23.13).

FBE Application

The major role of an FBE coating in a 3LPE/3LPP is to provide corrosion protection, flexibility, and to have excellent adhesion to the metal surface. The selected FBE powder shall be specially formulated to apply under the 3LPE/3LPP layers. The process of FBE powder application is as follows:

- The dry and moisture-free FBE powder is poured into the hopper. The hopper must have strainers and magnetic separators to remove all the impurities.
- FBE powder is fed to the fluidized bed by means of a screw conveyor. The fluidized bed will be fed with moisture-free air mixed with FBE powder.
- Air-mixed FBE powder will be fed through respective lines to the electrostatic spray guns. The lines will have independent controls for air flow, powder flow, and electrostatic charges.
- The spray guns will be arranged in such a way that the sprayed powder will be melted and provide a uniform epoxy film circumferentially. (Figure 23.4)
- The temperature just after the FBE powder melts will be monitored periodically to ensure the temperature gradients.
- The thickness of the film is controlled either by the speed of pipe feeding or by controlling the volume of powder sprayed through each spray gun.
- The properly formed FBE film shall not have any discontinuities, holidays, lumps, or any other impurities that may hinder the performance of the subsequent layers.
- All the above operations can be monitored within the operator's cabin in the plant.
- A cyclotron is used to collect and separate reusable, uncured FBE powder and send it back to the fluidized bed to spray again to the hot metal surface.

Adhesive Copolymer Application

The purpose of an adhesive layer is to bridge or bond between the FBE primer and the PE or PP top layer. They are usually copolymers or polyolefin modified with polar end groups grafted into the polymer backbone, usually in granule form. The polar groups within the adhesive react and chemically bond to the FBE. Simultaneously, the adhesive fuses with the PE/PP topcoat. Thus, the adhesive layer gives both mechanical and chemical bonding between the layers to provide higher peel strength to the entire coating system. The process of adhesive application is as follows:

- Adhesive copolymer granules are fed into the hopper.
- The granules are taken to the oven by vacuum pressure to pre heat and remove moisture. The temperature of granules at this stage will be around 45 to 50 °C (113 to 122 °F).
- Heated and dried granules will be fed to the heating chamber by vacuum.
- The heating chamber will stage wise heat (typically three stages) and melt the granules. The final temperature will be around 230 to 240 °C (446 to 464 °F).
- Melted granules are fed to the dye where they will be converted as sheet in the desired thickness.
- The adhesive layer will be applied circumferentially as a sheet over the FBE coating within the gel time of FBE (typically 35 to 40 s at 180 to 210 °C (356 to 464 °F).



Figure 23.14: Extruder applying melted copolymer adhesive.

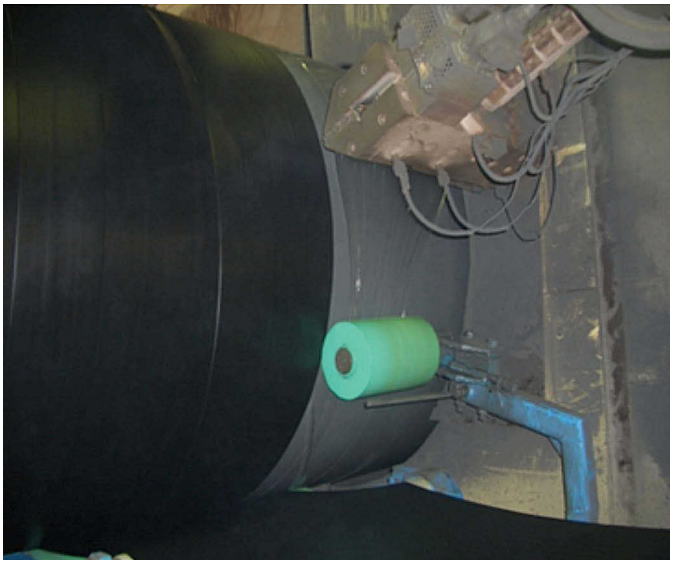


Figure 23.15: Roller smoothing of copolymer adhesive.



Figure 23.16: Virgin Polyethylene granules being poured into hopper.



Figure 23.17 Extruded polyethylene being applied.

- The adhesive layer is rolled to the FBE coating using a Teflon† roller. This process will ensure removal of any entrapped air (Figures 23.14 and 23.15).

PE or PP Top Layer

Normally HDPE is used for the 3LPE coating. Nevertheless, there are other versions of PE, such as:

- LDPE
- LLDPE
- MDPE

Higher hardness of the PE/PP material provides excellent abrasion and impact resistance to the coating system. This helps in avoiding mechanical damages while in the construction stage. Other advantages of these coatings are:

- Slows the ingress of water to the FBE layer and the substrate below.
- Extended ultraviolet (UV) resistance by adding carbon blacks.
- A higher softening point provides the system better suited for higher operating temperature.

Because of its high rigidity, repair work on the damages shall be carried out with good care. Small damages can extend in the course of time due to the high internal strain of these materials. The damages can be repaired by PE/PP melt sticks or by filling the damaged area with mastic fillers followed by PE heat shrinking patches. The process of PE/PP application is as follows:

- The virgin PE/PP granules are fed into the hopper (Figure 23.16).
- The granules are taken to the oven by vacuum pressure to pre-heat and remove moisture. The temperature of the granules at this stage will be around 45 to 50 °C.
- Heated and dried granules are fed into the heating chamber by vacuum.
- The heating chamber will stage wise heat (typically three stages) and melt the granules. (Final temperature will be around 230 to 245 °C (446 to 473 °F).
- Melted granules are fed to the dye where they will be converted as sheet in the desired thickness.
- The molten PE/PP is applied circumferentially as a sheet over the adhesive layer with at least 50 to 60% overlap to achieve the proper thickness as per the client requirements.

†Trade name

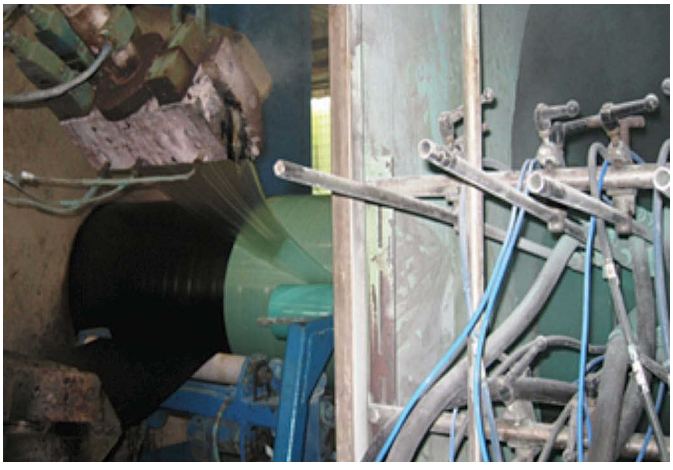


Figure 23.18 Application booth showing FBE, adhesive, and polyethylene layers.



Figure 23.19: Free-fall water quench.



Figure 23.20: Temperature after quench.



Figure 23.21: Cut-back lathe.



Figure 23.22: Measuring cut-back/chamfer.

- The PE/PP is spirally applied as quickly as possible, before the molten adhesive tends to solidify.
- The PE/PP layer is also rolled similar to the adhesive layer using a Teflon roller to have proper adhesion and to avoid any pop ups or air pockets. This process will remove any entrapped air (Figures 23.17 and 23.18).
- In case of SAW pipe or longitudinal weld pipes, maintaining the DFT on the weld is a challenge and care shall be given to have proper overlap on the weld to get adequate thickness.

Quenching

Quenching is the rapid cooling of a work piece to obtain certain material properties. It prevents low-temperature processes, such as phase transformations, from occurring by only providing a narrow window of time in which the reaction is both thermodynamically favorable and kinetically accessible. For instance, it can reduce crystallinity and thereby increase toughness of both alloys and plastics.

Soon after the outer layer application, the hot external coating is quenched in a free-falling water bath. The sudden cooling contracts the coating and provides excellent adhesion to the underneath layers. The cooling will bring down the temperature to a range of 80 to 90 °C (176 to 194 °F). A holiday test will be carried out typically at 25 kV just after the pipe comes out of the water bath (Figures 23.19 and 23.20).

Cut Back

Cut back is the area from which a coating is removed at ends of the pipe/spool to avoid damage to the coating during the welding process. Typically, a 125 to 150 mm (5 to 6 in) coating is removed with a lathe placed in line with the production. These areas will be coated with an anti-corrosion primer to provide temporary protection to the cut back area as well as to prevent creeping corrosion (Figures 23.21 and 23.22).

Full-fledged laboratory support is deemed necessary in the factory to have proper quality control of the production process. A general look into the inspection process is made below.

Abrasive Inspection

In factories, the most common abrasive used will be a mix of steel shot and grit. This can be recycled 25 to 30 times with proper topping up with fresh steel grits. While blast cleaning, steel grits will break down and the effectiveness of cleanliness as well the angular profile produced will gradually decrease. Hence, the abrasive mix needs to be verified prior to the start of each day's production. The abrasive mix shall be capable of producing at least a surface cleanliness of Sa 2.5 and a surface profile of 50 to 100 µm (2 to 4 mils). The abrasive mix needs to be checked for the presence of hydrocarbons by a blotter test and the chloride level must be less than 100 ppm.

Acid Wash

Typically, H_3PO_4 is used for the cleaning as it has the capacity to prepare the surface and remove the chlorides effectively. Concentration of the acid should be around 20 to 25%, which shall be verified by a titration method. A higher concentration can cause pitting of the metal surface. Acid is mixed with deionized water in a plastic container and supplied to the booth as a batch for the acid wash. The wash water must be effectively reclaimed and disposed without any effect to the environment.

Surface Preparation

Close monitoring of surface preparation is very necessary for all types of coatings. After acid washing, the pipes are left on the inspection racks for inspection, which will be carried out in the following sequence:

1. Visual inspection for mechanical damages, slivers, or laminations that can cause discontinuities or holidays in the coating. Such items need to be ground prior to the clearance for FBE application. This grinding shall not be more than 25 cm^2.
2. Surface cleanliness as per NACE No. 2 /SSPC SP10/ISO Sa 2.5
3. Surface profile typically in the range of 50 to 100 µm
4. Surface chlorides as per ISO 8502-6 and 9 shall be no greater than 5 micrograms/cm^2.
5. Dust level shall be less than Level 2 as per ISO 8502-3.[12]

Chromating

Chromating is carried out to enhance the adhesive property of FBE. The chromate powder is mixed in deionized water and poured onto the pipe surface. The water will evaporate from the radiant heat of the induction coil. These pipes will have a golden brown color. Prolonged exposure to the presence of chromate has been reported as the cause of cancer. Some countries have restrictions on the usage of chromates.

Temperature Monitoring

The speed of the pipe needs to be adjusted in such a way that the combination of heating and coating becomes synchronized. The temperature of the pipe at the induction coil shall be maintained in the range of 180 to 220 °C. This has to be monitored and recorded through a graph.

FBE Application

To evaluate the condition of the FBE application, a sample pipe is the only option as the process of coating is continuous. FBE will be applied on the pipe without any topcoating for at least 2 m (6.5 ft). The following will be verified from this sample section.

1. Visual appearance—without any run, sag, or wrinkling
2. DFT measurement—typically 200 to 300 µm (8 to 12 mils)
3. Sample for cure test—DSC testing per NACE RP0394/CSA Z245.20.
4. Adhesion strength—X Cut method as per ASTM D3359[13]

Adhesive Application

The adhesive application is the same as for the FBE layer. The adhesive layer also can be inspected only on the sample pipe. The adhesive layer will be applied over the FBE for at least 2 m without the topcoat. This area will be inspected for its appearance and the DFT, which will be around 150 to 250 µm (6 to 10 mils).

PE/PP Top Layer Application

The top layer has to be applied without any air voids or dimples and with a proper overlap throughout the pipe. The thickness of the top layer is achieved by adjusting the overlap. Typically, an overlap of 70 to 75% is maintained to achieve the specified thickness. The properly applied topcoat needs to be inspected for the following:

- Visual appearance—without any blisters or wrinkling
- DFT measurement—depends on the pipe diameter, 2.5 mm to 4 mm (98 to 157 mils) total thickness of three layers (Figure 23.23)
- Adhesion strength—peel test at 25 °C (70 °F) and maximum operating temperature (Figures 23.24 and 23.25). Typically greater than 15 N/mm at 25 °C and greater than 3 N/mm at 50 °C for HDPE; typically greater than 25 N/mm at 25 °C and greater than 4 N/mm at 90 °C.



Figure 23.23: DFT measurement PE/PP.



Figure 23.24: Constant load peel test.



Figure 23.26: Polyurethane application with a fusion gun.

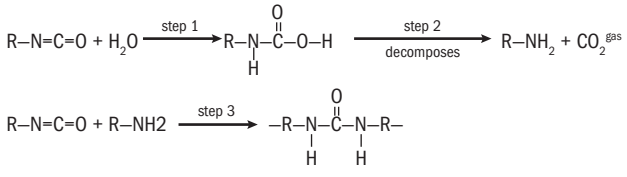


Figure 23.27: Evolution of CO_2 gas in reaction with moisture and polyurethane.



Figure 23.28: Overlap of Shrink sleeve (75mm) over 3LPP/PP mainline coating.

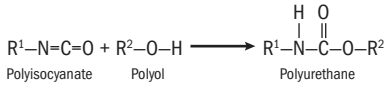


Figure 23.29: Reaction diagram of polyurethane.



Figure 23.25: Peel test results graph.

- Impact test (during prequalification)
  - Elongation (PQT only) (Figure 23.26)
  - Indentation test (PQT only) (Figure 23.27)
  - Cathodic disbondment test (Figure 23.28)
  - Hardness
  - Flexibility
  - Porosity
  - DSC

High-Build Polyurethane Coatings

Polyurethane coatings provide exceptional long-term protection against corrosion, abrasion, or impact problems to the pipelines. Typically, polyurethanes are of two types, aromatic and aliphatic. For the underground services, aromatic polyurethane is being utilized.

Polyurethanes are formed by the reaction between poly-isocyanate and polyol as in the reaction shown in Figure 23.29. When exposed to UV radiation in the presence of oxygen, aromatic polyurethanes suffer UV-initiated auto oxidation degradation. Color deepening may occur of the polyurethane exposed to sunlight (changes to yellow and amber). On extensive exposure it even changes to a brown color, with loss of mechanical properties. Hence these coatings are recommended only for the utilization of the external coating of underground services.

These coating will always possess the following advantages.

- Fast dry, faster backfilling
- Mostly 100% solids—low volatile organic compounds (VOCs)
- High film build up: typically 1 to 2 mm (39 to 78 mils)
- Excellent adhesion to steel
- Very good elongation/flexibility
- Excellent chemical resistance
- Abrasion resistance
- Can be applied in low temperatures (below freezing)

Application Equipment

Polyurethane coatings have a very short pot life, which makes it impossible to apply with a single leg airless spray unit. A plural-component spray machine is required for the application of these coatings. The advantages of these machines are:

- Heats both components separately.
- Mixes resin (part A) and curing agent (part B) components as per pre-set proportion
- Actual mixing can be at the gun tip or a manifold mixer prior to the gun.
- Less material wastage

Plural-component spray equipment parts

- Compartments to deliver unmixed material
- Proportioning device
- Pressure pump
- Mixing device and static mixer or air impingement

- Delivery system (spray gun)
- Flushing system

Surface Preparation

Like all other coatings, surface preparation is the key for the performance of the coating. A higher range of surface profile is required for polyurethane coatings as the DFT will be higher. The prepared surfaces need to be free from all types of contamination. The surface preparation sequence is as follows:

- Remove the surface contamination like grease or oil by solvent wash according to SSPC-SP 1.[14]
- Abrasive blast the area to NACE No. 2/ SSPC-SP 10/ISO Sa 2.5
- Check that the surface profile meets the coating manufacturer recommendations.
- Surface chlorides shall be less than 5 microgram per cm^2.
- Care shall be taken to remove surface moisture immediately prior to coating.



Figure 23.30: Flame heat curing of HSS.

Polyurethane Application

Polyurethane coatings come in two components, which consist of polyol (Part A) and isocyanates (Part B). Polyols are generally viscous and require a minimum temperature of 40 to 50 °C (104 to 122 °F) to have proper agitation. Band-type heaters may be used to heat the drum, which must be monitored with temperature gauges and temperature regulators.

Uneven ratio mixing (i.e., 2:1, 2.6:1 etc.) of two components will be done in a mixing manifold and the product is supplied to the spray gun through a whip hose. The length of the whip hose must be very short so that the low pot life material will be pumped out continuously.

Products with a mix ratio of 1:1 will be mixed right at the tip of the spray gun. The pot life of these products will be less than 10 s. The machines used for spraying will be of fixed ratio type or multiple ratios according to the coating manufacturer's recommendations. A multiple ratio pump can be used for different products with various mix ratios. Calibration of the pump is deemed necessary to confirm the machine is set at the right proportion. Whenever the machine is shut off due to an off ratio mixing, the first pass of application must be discarded in a waste recollection container. The same technique needs to be followed for every stoppage while using a mixing manifold and solvent must be used to bleed out the product from the manifold and/or whip lines. This is to avoid any chance of spraying off-ratio mixed coating onto the surface, which can cause blisters. Maintaining a log for the machine is a recommended practice in which the time of start, stoppage, breakdowns, etc. is recorded and maintained.

If the application is on the field joint of 3LPE-coated pipelines, the overlap area needs to be heated to a temperature of 40 to 50 °C in addition to abrading the surface. This is to enhance the adhesion of polyurethane over the 3LPE coating (Figure 23.30).

The coating applied will be cured in a quick session and can be handled within 2 to 3 h of application. This may require different preparation procedures and must be in accordance with the respective product data sheets.

Polyurethane coatings are very sensitive to moisture/water. The isocyanates react with water to form carbon dioxide (CO2) gas, which will form blisters to the coating. Such areas are found to be under-cured as well (Figure 23.27).

Inspection

The inspection for surface preparation and coating application will be the same as for factory coating as well as for the site works. Preferences of inspection are detailed as below.

Surface Preparation

- Visual inspection for mechanical damages, slivers, or laminations that can cause holidays in the coating. Such items need to be ground prior to the clearance for FBE application. This grinding shall not be more than 25 cm2.
- Surface cleanliness as per NACE No. 2/ SSPC-SP10/ISO Sa 2.5
- Surface profile is typically in the range of 70 to 100 µm (3 to 4 mils)
- Surface chlorides are per ISO 8502-6 and 9, which shall be less than 5 micrograms/cm^2.
- Dust level shall be less than Level 2 as per ISO 8502-3.

Application

Prior to the application, airless spray equipment must be checked for the following:

- Check the heating band for the proper heating of Part A.
- Calibrate the mixing for variable ratio pumps.
- Ensure the solvent line is properly connected and working, if a mix manifold is being used.
- Being a quick curing coating, measurement of wet film thickness (WFT) is almost impossible. Hence, proper practice and understanding must be there for the applicator to achieve proper thickness and to avoid repair or rejection. Cured coatings need to be inspected for the following:
  - Visual appearance—shall be free of sags, voids, blisters, cracks, and dimples
  - DFT—shall be in the range of 750 to 1,500 µm (30 to 60 mils)
  - Hardness—shall meet requirements of the manufacturer
  - Holiday test—free from holidays
  - Adhesion test—typically greater than 12 MPa (1,740 psi)

High-Build Epoxy Coatings

High-build epoxies used on pipelines are two-component coatings where the base polymer contains the epoxide (also called oxirane) group, which reacts usually with an amine to form a protective barrier film. When used as a barrier coating for protecting underground pipelines, it is generally specified between 750 to 1,500 µm in one coat. However, there also exist epoxy coatings that can be applied at up to 3 mm (118 mils) thickness—the thicker the barrier the better, provided the coating maintains its integrity throughout the projected service life. These coatings will always possess the following advantages:

- High-volume solids, low VOCs
- High film build up, typically 1 to 2 mm (39 to 78 mils)
- Excellent adhesion to steel
- Excellent chemical resistance
- Good abrasion resistance
- Excellent cathodic resistance

Surface Preparation

A higher range of surface profile is required for high-build epoxy coatings as well. The prepared surfaces need to be free from all types of surface contaminants. The surface preparation sequence is as follows:

- Remove surface contaminants like grease or oil, if any, by solvent wash according to SSPC-SP 1.
- Abrasive blast the area to NACE No. 2/SSPC-SP10/ISO Sa 2.5
- Check that the surface profile meets the coating manufacturer recommendations.
- Surface chlorides shall be less than 5 microgram per cm^2.
- Care must be taken to remove surface moisture immediately prior to coating.

Coating Application

High-build coatings need to be applied with high-pressure ratio pumps, preferably 64:1 or above. Being highly viscous, lower ratio pumps will get hot and efficiency will be reduced in a short time. Some solvent-free products, with very low pot life, will need a plural pump set up with the appropriate mixing ratio for easy application.

Most of the high-build epoxy coatings are designed as a direct to metal (DTM) coating without a primer. However, some products make use of a blast holding primer where project conditions demand such a primer.

Typical epoxies require greater than 10 °C (41 °F) to start the curing reaction, hence application below such ambient temperature conditions is challenging. Low-temperature cure versions are available nowadays to get around this problem, compromising slightly on the physical properties like flexibility, hardness, and service temperature tolerance.

When application is done through a single leg airless machine, it is a common practice to store the paint in a suitable temperature level until it is ready to mix and spray and get around the short pot life issues.

Inspection

The inspection for surface preparation and coating application will be the same for a factory coating as well as for the site works. Preferences of inspection are detailed as below.

Surface Preparation

- Visual inspection for mechanical damages, slivers, or laminations, which can cause holidays to the coating. Such items need to be ground prior to the clearance for high-build epoxy application. This grinding shall not be more than 35 cm2.
- Surface cleanliness per NACE No. 2/SSPC-SP 10/ISO Sa 2.5
- Check that the surface profile meets the coating manufacturer recommendations
- Surface profile is typically in the range 70-100 µm
- Surface chlorides per ISO 8502-6 and 9, which shall be less than 5 micrograms/cm^2
- Dust level shall be less than Level 2 as per ISO 8502-3

Application

While applying the high-build epoxy coatings, close monitoring of WFT is highly recommended. Because some epoxies take longer to cure, repair work on low or high DFT areas will prolong the delivery time, which may have cost impacts. The cured coating needs to be inspected for the following:

- Visual appearance—shall be free from sags, voids, blisters, cracks, and dimples
- DFT—shall be in the range of 750 to 1,500 µm
- Holiday test—free from holidays
- Adhesion test—typically greater than 12 MPa (1,740 psi)

TABLE 23.2

Pipeline Coating	Girth Weld	Fittings
3LPE	PE heat shrink sleeve or high-build polyurethane	High-build polyurethane
3LPP	PP heat shrink sleeve	PP heat shrink sleeve or FBE
High-build epoxy	High-build epoxy	High-build epoxy
High-build polyurethane	High-build polyurethane	High-build polyurethane
Single or dual FBE	Single FBE	Single FBE

Coating Application—Field Joints

The weld joint coating selection depends on the main pipeline coating. Table 23.2 gives some guidance:

The application method of the most common field joint coating at present in the industry is discussed below.

Heat Shrink Sleeves

The most common method of protecting field joint areas of 3LPP/PP-coated pipelines is by utilizing heat shrinkable sleeves. Overlapping a joint coating over the 3 LPE/PP is the major concern to contemplate (Figure 23.28).

Since PE has a chemically inert and non-polar surface, a surface treatment is required to enhance the bonding to PE. This can be achieved by a flame treatment. This is process is known as "flame corona treatment." With flame treatment, the combustion action of a hydrocarbon gas releases free radicals during formation of the flame. These free radicals penetrate the PE and modify its surface wettability (increase in surface energy).

The surface to be treated must be free of contaminants. PE's surface energy of 30 to 40 dynes/cm prior to treatment can be increased to 60 to 70 dynes/cm after the treatment if measured in accordance with ASTM D2578-94,[15] "Standard Test Method for Wetting Tension of Polyethylene and Polypropylene Films."

All precautions shall be taken to avoid damages while handling 3LPE/PP coated pipes. Unlike any other coating, repairing of damages on 3LPE/PP will be a great challenge.

Surface Preparation

The field joint area must be blast-cleaned along with the 6-in (152-mm) overlap area of 3LPE coating. The overlap area needs only a sweep blast. Flame treating the overlap area of joints is deemed necessary to enhance the adhesion property if any liquid coating is intended to apply on the joints. Care shall be taken from overheating the PE/PP, which could damage the bonding. The following inspection shall be carried out to ensure the quality:

- Remove the residues/moisture from the joint area.
- Weld spatters, sharp edges, and slags shall be removed prior to blast cleaning.
- Abrasive blast the area to NACE No. 2/SSPC-SP 10/ISO Sa 2.5.
- Blast cleaning shall be extended at least 3 to 4 in (75 to 100 mm) over the main line pipe coating to have proper profile for the subsequent coating.
- The blast-cleaned surface shall not be grinded or smoothened in such a way that it will damage the surface profile. Such areas shall not exceed 3 cm^2,
- Loosely adhered main line coating adjacent to cut back shall be carefully removed.
- Flame-heat the overlap area to a maximum temperature of 50 °C (122 °F).
- Feathering shall be properly carried out to ensure a smooth contour.
- Ensure the surface profile (on the metal surface) meets the coating manufacturer recommendations.
- The presence of chlorides shall be checked per ISO 8501 6 and 9, which shall be less than 5 micrograms/cm^2.
- Peel test for heat shrink sleeve PE—typically greater than 4 N/mm at 25 °C
- Peel test for heat shrink sleeve PP—typically greater than 2.5 N/mm at 25 °C

Application

High skill and good temperament are always required for the successful application of heat shrink sleeves. Spreading of flame for uniform heating is the backbone of heat shrink sleeve application. The lesser the heat, the lower the bonding will be (Figure 23.30).

The metal surface may be required to pre-heat to avoid moisture and to provide proper wettability for the primer. Primer is applied to the desired thickness and cured, if necessary, as per the sleeve manufacturer's recommendation. For higher diameters and for the curing of primer for the PP sleeves, induction coil heating is required as it will be almost impossible to achieve high temperatures with normal open flame torches. Soon after the primer application, the heat shrink sleeves need to be installed properly and effectively. The sleeves need to be rolled while in heated condition to get rid of entrapped air.

High-Build Epoxy

The current industrial market is promoting field joint coatings that are meeting performance requirements as well being user-friendly too. High-build epoxies are falling into this category due to the following advantages:

- Can build up to high thickness in one coat
- Easier application
- Good temperature resistance
- Good physical performance over a wide range of environmental conditions
- Economical

The prepared surface needs to be applied with high-build epoxy coating, preferably with airless plural-component spray equipment to the desired thickness. During site conditions, enough ground clearance is deemed necessary to have proper access for the applicator to apply the epoxy uniformly circumferentially. For application in open fields, care needs to be taken to prevent the coating from getting contaminated with dust or other contaminant that could cause premature failure of the coatings. A minimum of 4-in overlap onto the flame-treated PE is made with the epoxy. The cured coating needs to inspected for the following:

- Visual appearance—shall be free from sags, voids, cracks, and dimples
- DFT—can be in the range of 750 to 1,500 μm
- Holiday test—free from holidays
- Adhesion test—typically a minimum of 12 MPa (1,740 psi)

High-Build Polyurethane

Aromatic polyurethanes are being utilized for underground coatings because of their typical advantages:

- Fast Dry—faster back filling
- Mostly 100% solids—low VOCs
- High film build up—typically 1 to 2 mm (39 to 78 mils)
- Excellent adhesion to steel
- Very good elongation/flexibility
- Excellent chemical resistance
- Excellent abrasion resistance
- Can be applied in low temperatures (below freezing)



Figure 23.31: Manual FBE application on field joint.

Being very fast drying, the pipelines will be ready to backfill within hours after the application. This also avoids the chances of embedding with sand or dust that can be a potential risk in open field applications. Most of these coatings have good elongation to match with polyolefin coatings. To get around the very low pot life, a plural-component spray unit is deemed necessary to apply this type of coating. This will give the applicator leisure of easy and sturdy application. But this type of application does demand more space round the pipe, which could sometimes be challenging for rehabilitation works. The cured coating needs to be inspected for:

- Visual appearance—shall be free from sags, voids, cracks, and dimples
- DFT—shall be in the range of 750 to 1,500 µm
- Holiday test—free from holidays
- Adhesion test—typically in the range of 14 to 15 MPa (2,030 to 2,175 psi)

Coating of FBE Joints and Fittings

The preferred field joint coating for FBE-coated pipeline is FBE itself. When FBE is applied on both main line and joints, a homogenous coating is maintained throughout the pipeline, which helps to avoid joint coating failures, an issue that is a very common challenge in the pipeline industry (Figure 23.31).

Surface Preparation

- Remove the residues/moisture from the joint area.
- Weld spatters, sharp edges, and slags shall be removed prior to blast cleaning.
- Abrasive blast the area to NACE No. 2/ SSPC-SP 10/ISO Sa 2.5
- Blast cleaning shall be extended at least 3 in over the main line pipe coating to have proper profile for the subsequent coating.
- The blast-cleaned surface shall not be grinded or smoothened in such a way that it will damage the surface profile. Such areas shall not exceed 3 cm^2.[16]
- Loosely adhered main line coating adjacent to cut back shall be carefully removed.
- Feathering shall be properly carried out to ensure a smooth contour.
- Ensure that the surface profile (on the metal surface) meets the coating manufacturer recommendations.
- The presence of chlorides shall be checked per ISO 8501-6 and 9, which shall be less than 5 micrograms/cm^2. Excess chlorides shall be removed by pressure wash or any other suitable method that doesn't affect the integrity of the coating.

FBE Application

A detailed coating application procedure shall be prepared prior to the application. The procedure shall identify the inspection criteria to verify the progress and quality of application. The coating shall be applied prior to the oxidation of the metal surface that is kept blast cleaned. The application of FBE is made in the following sequence:

- Heat the pipe to the specified temperature as recommended by the coating manufacturer.
- Heating shall be by induction coil. Direct-flame impingement is not recommended, as the temperature may not be controlled efficiently. Offsetting the spacing of the induction coil can be done to consider the temperature variations on joints that are partially exposed to sun. This will ensure uniform heating around the joint. The farther the coil from the metal surface, the lesser the heating rate it will be (Figure 23.32).
- The FBE powder shall be stored within the manufacturer's recommended temperature. Most of the manufacturers recommend storing their powder to below 27 °C. While storing in site conditions, the most care shall be taken to avoid exposing the powder to direct sunlight.
- Application of FBE coating can be either be manual handheld electrostatic spray application or semi-automatic field joint coating. Semi-automated machines will ensure uniform application, lesser dry spray, and uniform consumption of FBE powder. The compressed air for fluidizing the powder shall be free from moisture and other contaminants like oil, dust, or impurities (Figure 23.33).
- Apply the FBE powder to the hot metal surface, which will melt the FBE powder and adhere to metal as well as the main line coating.
- The field joint coating shall be applied to have at least a 2-in overlap on top of the main line coating on either side of the joint.
- Field girth weld joint coating needs to be applied to a slightly high thickness to ensure proper film coverage on the weld capping.
- Cure the FBE coating as recommended by the coating manufacturer.



Figure 23.32: Induction coil heating of FBE field joint.



Figure 23.33: Semi-automatic application of FBE on field joint.

Inspection

- The infrared gauge thermometer shall be calibrated and variation with the contact thermometer shall be verified and documented.
- Check the main pipe coating for any coating defects like lift up, blisters, or any defects that can cause adhesion problems to the joint coatings.
- Check that all oil, grease, dirt, or other contaminants are removed.
- The surface cleanliness need to be verified per NACE No. 2/SSPC-SP 10/ISO Sa 2.5.
- The surface profile need to be verified per NACE RP0287,[17] which shall meet the requirements set by the coating manufacturer.
- Preheating shall be even throughout the pipe joint and variation shall not be more than 20 °C (68 °F).
- The coating shall be uniformly applied and the DFT shall be verified. The maximum and minimum of the thickness shall be within 20% of the manufacture /client specification.
- A holiday test needs to be performed to ensure the coating is free from pinholes or any other defects that allow easy passage of moisture to the metal surface during service. The test needs to be carried out as recommended in NACE SP0490 and the voltage setup shall be as per the coating manufacturer's recommendations. Care shall be taken while selecting the voltage as the high voltage can damage the coating.
- The curing of the applied coating shall be ensured using a DSC test. The test shall be done per NACE RP0394. Delta H, exothermic energy during the curing, and Tg of the cured coating shall be identified.
- A methyl ethyl ketone rub test can be done to verify the under-curing instantly but not as a replacement to the DSC testing as this will not detect slight variations in the curing.
- A porosity test is carried out to quantify the numerical rating of the level of foam bubbles in a coating. The presence of porosity can considerably reduce the structural strength of the coating. Porosities can be of two types, cross sectional and interface. Porosities observed in the areas where there is a break in a coating layer are cross sectional porosities. Porosities observed in the layer where the coating split from the metal surfaces are interface porosities. The sample for a porosity test is normally taken from coated bar used for the bend test, which is chilled sufficiently and bent rapidly to detach the cured FBE coating.
- Document and report all processes, repairs, and observations.

Underground Pipe Hot Polyurethane Foam Insulation

Transportation of products like heavy fuel oil, low sulfur fuel oil, or any product that is highly viscous through a pipeline need to be heated up, but below the flash point, in order to ensure flowability. The temperature of these products needs to be maintained throughout the pipeline to ensure the smooth flow of the fluid. In some countries, pipelines used for water supply also need to be protected to avoid freezing. This is made possible by insulating the lines to protect from heat loss. Such lines need to be protected from corrosion as well as heat loss.

The common method of insulation is the pipe-in-pipe insulation method. The fluid-carrying pipes will be coated with corrosion-resistant coatings followed by insulating material and encapsulated by a PE jacket. Pipe insulation is done per BS EN 253.[18]

In the cross-section view:

1. The carbon steel pipe will be provided with a corrosion-resistant coating like FBE or 3LPP.
2. The second layer is the rigid polyurethane foam (PUF). This provides the required thermal insulation for the pipe. PUF is a spray-applied insulating foam plastic that is installed as a liquid and then expands many times its original size. PUF can be adjusted to have many different physical properties depending on the use desired. For example, the same basic raw materials that can make insulation foam semi-rigid and soft to the touch also creates high-density roofing foam that is resistant to foot traffic and water. PUF insulates and eliminates thermal bridging.
3. The outer layer is a PE jacket that provides protection to the PUF insulation (Figure 23.34).

There are two methods of application of the insulation. The first is carried out by applying the PUF on the main pipeline coating (Figure 23.35) and then by applying the PE layer on the foam (Figure 23.36). The other method is carried out by separately manufacturing a PE casing pipe (Figure 23.37); then the main pipe will be the casing pipe. After insertion, the PUF will be injected between the PE casing and the main pipe.



Figure 23.34: Thermally insulated pipe using PUF and PE outer jacket.



Figure 23.35: PUF applied on mainline pipe.



Figure 23.36: Wrapping PE over sprayed PUF.



Figure 23.37: PE outer jacket extruder.

PE Casing/Layer

The pipe casing/layer may be a separately manufactured pipe or be applied directly onto the insulation by extrusion per BS EN 253.

The casing/layer is made by extruding the HDPE in a extrusion machine. The HDPE pellets are melted in a heating oven and passed on thru a extruder.

The HDPE physical properties (i.e. density, carbon black, melt flow rate, thermal stability, pressure test, tensile strength at yield, elongation at break, constant load tensile test, stress crack resistance, impact resistance, creep behavior, heat reversion etc.); and the minimum wall thickness of the casing/layer shall meet the requirements in BS EN 253.

All extruder parameters as well as the HDPE batch number must be recorded during the extrusion of the HDPE. The minimum wall thickness of the outer casing/layer pipe shall be in accordance with BS EN 253. After extrusion, the HDPE outer casing/layer shall be cooled down using the quenching tunnel. Depending on the manufacturing method, in order to increase bonding between polyurethane and HDPE extruded outer pipe/outer casing, the HDPE pipe shall go through the corona treatment station.

Inspection

The insulated lines are inspected for the following.

- PUF
- Core density control on panel sample
- Closed cell percentage on panel sample
- Cell structure on panel sample
- Water absorption on panel sample
- Compression strength
- Thermal conductivity at 50 °C (122 °F)
- Voids and bubbles

Full Insulation System

- Axial shear strength at ambient temperature
- Axial shear strength at 90 °C (194 °F)

- Tangential shear strength at ambient temperature
- Final inspection
- Center line deviation
- Cut back

Summary

Corrosion engineers and the pioneers in the coatings industry have put forward constant efforts toward the worldwide development of new coating technologies. There are certain inherent limitations in all technologies that must be overcome by exhaustive field case studies within its range.

A broader perspective focus into the field to set the standard for the protection of pipelines with coating and CP is a perpetual process that normally yields incremental improvements, rather than breakthrough advancements.

In this chapter, we have discussed the recommended method of application and inspection for the coatings that are currently being used in the industry. The coating engineer's challenge is to select the proper coating for the right environment. It is abundantly clear that properly selected coatings are good enough to protect the environment for which they have been designed, but the real success of the coating system is how good one has prepared the surface and applied the coating system to that surface. This is particularly true of pipeline coatings in both plant and field applications.

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